Doctoral thesis

Porous silica systems doped with selected transition metals as catalysts for conversion of gaseous nitrogen pollutants

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Mariola and Grzegorz, for faith in me
and unwavering support throughout the whole life

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Abstract (Polish)

Nadmierna emisja zanieczyszczeń gazowych do atmosfery, spowodowana działalnością człowieka, stanowi poważny problem negatywnie oddziałujący na społeczeństwo ze względu na ich bezpośredni wpływ na środowisko naturalne oraz zdrowie i życie człowieka. Związki zawierające azot, w tym tlenki azotu (NO_x) i amoniak (NH_3), należą do jednej z najbardziej niebezpiecznych grup zanieczyszczeń gazowych. W związku z tym, ich uwalnianie do atmosfery ze źródeł antropogenicznych jest ściśle kontrolowane przepisami prawa. Ograniczanie emisji gazowych zanieczyszczeń azotowych opiera się zwykle na ich konwersji w obecności systemów katalitycznych. Zmniejszenie emisji tlenków azotu ze źródeł stacjonarnych jest najczęściej realizowane poprzez zastosowanie technologii selektywnej katalitycznej redukcji NO_x amoniakiem (NH_3-SCR). Niemniej, stosowany komercyjnie katalizator NH_3-SCR jest skuteczny jedynie w stosunkowo wąskim zakresie temperatur, co ogranicza jego zastosowanie poza temperaturowym oknem jego efektywnego działania (300-400°C). Niezbędne są zatem szeroko zakrojone badania w zakresie projektowania nowej generacji układów katalitycznych spełniających wymagania nowoczesnych instalacji NH_3-SCR.

W tym kontekście, celem niniejszej pracy doktorskiej było zaprojektowanie nowatorskich materiałów katalitycznych o rozszerzonym zakresie temperatur efektywnego działania w porównaniu z komercyjnym układem katalitycznym stosowanym w procesie redukcji tlenków azotu za pomocą NH_3. Badania przeprowadzone w ramach prezentowanej rozprawy doktorskiej, koncentrowały się na porowatych materiałach krzemionkowych, modyfikowanych fazą aktywną w postaci metali przejściowych. Badaniami objęto następujące grupy porowatych układów krzemionkowych: zeolity MWW o bimodalnej porowatości modyfikowane żelazem oraz mezoporowate krzemionki typu MCM-41 o zróżnicowanej morfologii domieszkowane metalami takimi, jak miedź, żelazo lub mangan. Pełne badania aktywności dotyczące porowatych układów krzemionkowych modyfikowanych metalami przejściowymi w procesie NH_3-SCR podparto analizą reakcji towarzyszących, wpływających na całkowitą wydajność katalityczną konwersji NO. Ważna część prezentowanych badań poświęcona jest charakterystyce fizykochemicznej próbek pod kątem ich składu chemicznego (ICP-OES, TGA), struktury (P-XRD, DRIFT, RS, UV-vis DRS), morfologii (SEM-EDS), właściwości teksturalnych (niskotemperaturowa sorpcja N_2), kwasowości powierzchniowej (NH_3-TPD, FT-IR z adsorpcją pirydyny) oraz redukowalności fazy aktywnej (H_2-TPR).

Podstawę przedłożonej rozprawy doktorskiej stanowi sześć manuskryptów, z czego pięć artykułów zostało opublikowanych w renomowanych czasopismach naukowych (**P1 – P5**), a jedna z prac jest obecnie w recenzji (**P6**). Artykuły **P1 – P5** zostały opublikowane w czasopismach naukowych indeksowanych przez JCR (średni współczynnik wpływu 2020: 5,43). Każdy z powyższych manuskryptów dotyczy tematyki redukcji emisji tlenków azotu z wykorzystaniem procesu NH_3-SCR. Wszystkie próbki otrzymane w ramach realizacji badań i opisane w pracach **P1** – **P6** okazały się być aktywnymi i selektywnymi katalizatorami procesu redukcji NO amoniakiem w zakresie temperatur zależnym od rodzaju i formy osadzonej fazy aktywnej oraz użytego nośnika. Realizacja założonego celu pracy doktorskiej została osiągnięta poprzez rozszerzenie zakresu temperaturowego efektywnego działania porowatych układów krzemionkowych, modyfikowanych metalami przejściowymi w reakcji NH_3-SCR w porównaniu do katalizatorów komercyjnych.

W pierwszej części podjętych badań (**P1**) zeolity z rodziny MWW charakteryzujące się bimodalną porowatością (mikroporowaty MCM-22 oraz mikro-mezoporowate materiały interkalowane podpórkami krzemionkowymi i krzemionkowo-tytanowymi) zostały zmodyfikowane żelazem, a następnie przetestowane w roli katalizatorów konwersji NO. Rezultaty badań procesu NH_3-SCR wskazują na efektywną pracę zeolitów domieszkowanych żelazem, działających wydajnie do temperatury około 475°C (wraz z rosnącą aktywnością próbek przy wzrastającej zawartości tytanu w podpórkach). Selektywność do pożądanego produktu reakcji, czyli N_2, była bardzo wysoka - powyżej 99% w pełnym zakresie temperaturowym testu katalitycznego. Prezentowana publikacja przedstawia również kompleksowe badania, dotyczące szczegółowej charakterystyki fizykochemicznej otrzymanych próbek, a także analizy reakcji towarzyszących redukcji NO amoniakiem. Reakcje te mogą wpływać na przebieg procesu poprzez zmniejszenie lub zwiększenie jego wydajności. Biorąc to pod uwagę, jako szczególnie istotny proces wskazano utlenianie NO do NO_2. Rezultaty badań uzyskiwania tlenku azotu(IV) w obecności zeolitów zawierających małe zagregowane formy tlenku żelaza wskazują, że proces ten jest odpowiedzialny za aktywację konwersji NO w niskich temperaturach.

Publikacja **P2** przedstawia syntezę i charakterystykę sferycznego materiału krzemionkowego typu MCM-41 o różnej zawartości miedzi lub żelaza, wprowadzonych do ścianek krzemionki przy użyciu metody współkondensacji. Ta stosunkowo prosta metoda syntezy katalizatorów prowadzi do otrzymania materiałów aktywnych i selektywnych (w stosunku do N_2) w procesie NH_3-SCR. Otrzymane próbki z serii zawierających miedź i żelazo okazują się być aktywne i selektywne (powyżej 98% do azotu) w procesie NH_3-SCR, odpowiednio w temperaturach do 300°C i w przedziale temperatur 375–450°C. Dla materiałów zawierających żelazo w roli fazy aktywnej, zaobserwowano wyraźną korelację pomiędzy zawartością fazy aktywnej a konwersją NO. W przypadku próbek zawierających miedź w roli formy aktywnej, zaobserwowano jedynie niewielki związek pomiędzy zawartością tego metalu a ich aktywnością katalityczną. Na podstawie przeprowadzonych badań, można stwierdzić, że jednym z najistotniejszych czynników, wpływających na właściwości katalityczne omawianych próbek, jest dostępność miejsc aktywnych dla reagentów podczas procesu katalitycznego. Warto nadmienić, że spadek wydajności reakcji NH_3-SCR w wyższych temperaturach można przypisać procesowi ubocznemu, to jest bezpośredniemu utlenianiu amoniaku.

W publikacjach **P3** i **P4**, czysto krzemionkowy, sferyczny materiał MCM-41 oraz jego analog zawierający glin, zostały sfunkcjonalizowane za pomocą metody jonowej wymiany templatu (*template ion-exchange,* TIE) oraz jej zmodyfikowanej wersji (TIE-NH_3) pozwalającej na kontrolę stopnia agregacji osadzanej miedzi. W ramach tych publikacji, analizowano właściwości fizykochemiczne otrzymanych próbek oraz badano ich aktywność w procesie NH_3-SCR. Metoda TIE-NH_3 opiera się na traktowaniu próbek roztworem amoniaku tuż po jonowej wymianie organicznej matrycy. Próbki uzyskane w wyniku zastosowania metody TIE charakteryzowały się obecnością miedzi występującej w formach różniących się stopniem agregacji - od kationów monomerycznych aż po agregaty tlenku miedzi. Zastosowanie podejścia opartego na kompleksowaniu amoniakiem, umożliwiło osadzanie fazy aktywnej głównie w postaci monomerycznych kationów miedzi. Efekt ten uzyskano w obydwu przypadkach, zarówno dla Si-MCM-41, jak i jego analogu zawierającego glin. Rodzaj i stopień agregacji fazy aktywnej stanowiły kluczowe czynniki wpływające na aktywność materiałów w procesie NH_3-SCR. Katalizatory zawierające fazę aktywną głównie w postaci monomerycznych okazały się zdecydowanie bardziej aktywne w badanej reakcji w porównaniu z materiałami charakteryzującymi się obecnością bardziej zagregowanych form fazy aktywnej. Temperaturowe okna efektywnej pracy dla najbardziej aktywnych katalizatorów z serii otrzymanej w wyniku zastosowania procedury TIE-NH_3 mieściły się w zakresach około 200–325°C i 225–375°C, odpowiednio dla Si-MCM-41 i Si-Al-MCM-41 modyfikowanych miedzią. Dla powyższych próbek odnotowano wysoką selektywność w stosunku do N_2, wynoszącą odpowiednio powyżej 98% i 95% w zakresie temperatur poniżej 350°C. Otrzymane rezultaty wskazują na możliwość zastosowania tak otrzymanych materiałów w niskotemperaturowym procesie NH_3-SCR, w którym niezbędna jest obecność katalizatorów pracujących w temperaturze około 250°C.

Publikacja **P5** przedstawia rezultaty badań katalitycznych procesu NH_3-SCR w obecności materiału MCM-41 o różnej morfologii (cylindrycznej lub sferycznej), modyfikowanego z użyciem kationów lub oligokationów żelaza metodą TIE. Zastosowanie prekursora żelaza różniącego się złożonością cząsteczki (różna liczba jonów żelaza), spowodowało osadzanie się odpowiednio - monomerycznych kationów żelaza lub bardziej zagregowanego Fe_xO_y w formie nanoprętów. Otrzymane próbki wykazują aktywność w zakresie temperaturowym 350–475°C i stanowią potencjalne katalizatory do zastosowania w wysokotemperaturowym procesie NH_3-SCR. Na uwagę zasługuje wysoka selektywność do azotu, ponad 98%, utrzymana w pełnym zakresie temperaturowym testu. Wydajność katalityczna konwersji NO zależała głównie od ilości wprowadzonego żelaza, na ogół wzrastając wraz ze wzrostem zawartości tego metalu (z wyjątkiem próbek o największej zawartości żelaza). Dla lepszego zrozumienia procesu NH_3-SCR, przebiegającego w obecności otrzymanych próbek, przeprowadzono reakcje utleniania NO do NO_2 oraz bezpośredniego utleniania NH_3. Analiza drugiego z wymienionych procesów (NH_3-SCO) wskazuje, że nieznaczny spadek konwersji NO w wyższych temperaturach jest związany z konkurencyjnym bezpośrednim utlenianiem czynnika redukującego, czyli amoniaku. Niska wydajność procesu NH_3-SCR w obecności badanych próbek w zakresie niskotemperaturowym wynika prawdopodobnie z niedostatecznej ilości powstającego NO_2, kluczowego w postulowanym mechanizmie fast-SCR.

Wyniki badań skoncentrowanych na redukcji NO amoniakiem w obecności sferycznego MCM-41 modyfikowanego miedzią, żelazem lub manganem oraz ich mieszanych bimetalicznych układów z wykorzystaniem metody TIE, przedstawiono w manuskrypcie **P6**. Materiały monometaliczne charakteryzowały się niższą aktywnością w porównaniu do bimetalicznych układów (CuFe, CuMn, FeMn). Spośród prezentowanych serii próbek najbardziej obiecujące wyniki katalitycznej konwersji NO otrzymano dla układów miedziano-manganowych, z temperaturowym oknem efektywnej pracy mieszczącym się w zakresie 275–350°C, z blisko 100% selektywnością do N_2. Efektywność bimetalicznych materiałów okazała się także lepsza w porównaniu z mechanicznie zmieszanymi próbkami zawierającymi pojedynczo miedź lub mangan osadzone na sferycznej krzemionce. Zwiększona aktywność bimetalicznego katalizatora CuMn w redukcji NO amoniakiem jest prawdopodobnie związana z synergicznym współdziałaniem tych metali, poprzez relokacje elektronów pomiędzy nimi, a przez to ułatwione powstawanie NO_2 w wyniku utleniania tlenku azotu(II) oraz aktywację procesu fast-SCR.

Podsumowując, wyniki uzyskane w ramach prezentowanej pracy doktorskiej stanowią istotny wkład w rozwój wiedzy dotyczącej katalizatorów opartych na porowatych układach krzemionkowych nadających się do zastosowania w procesie NH_3-SCR. Otrzymane materiały wykazują obiecujące aktywności w zakresie niskotemperaturowym (prace **P2**, **P3**, **P4**, **P6**), jak i wysokotemperaturowym (publikacje **P1**, **P5**) procesie NH_3-SCR. Prezentowane wyniki wskazują na to, że temperaturowe okno efektywnej pracy otrzymanych katalizatorów zostało rozszerzone lub przesunięte w porównaniu z zakresem temperaturowym wydajnej pracy komercyjnie stosowanego układu katalitycznego procesu NH_3-SCR.

Abstract (English)

The excessive emission of gaseous pollutants into the atmosphere caused by man-made activities constitutes a serious issue that has a negative impact on society due to their direct influence on the natural environment and human health and life. The nitrogen-containing compounds, including nitrogen oxides (NO_x) and ammonia (NH_3), are considered as one of the most hazardous groups of gaseous pollutants. Thus, their production by anthropogenic sources is strictly controlled by legal regulations. Nowadays, gaseous nitrogen pollutants emission abatement is usually based on their conversion in the presence of catalytic systems. The decrease in nitrogen oxides emission from stationary sources is the most commonly realized by selective catalytic reduction of NO_x with ammonia (NH_3-SCR) technology. The commercially used NH_3-SCR catalysts are effective in the relatively narrow temperature range of 300-400°C, which limits their application outside of this operation window. Therefore, extensive studies focused on designing of a new generation of catalytic systems, fulfiling the requirements of the modern NH_3-SCR installations are necessary.

The main goal of the PhD thesis was to design novel NH_3-SCR catalysts with an extended temperature range of effective operation in comparison to the commercial catalytic systems. The research was focused on porous silica materials modified with the selected transition metals. The studies included the following groups of porous silica systems: MWW zeolites with bimodal porosity modified with iron, as well as mesoporous silicas of MCM-41 type with different morphologies doped with copper, iron or manganese (using various precursors of the active phase, methods of synthesis and post-synthesis modifications). The complete investigations of the NH_3-SCR activity over transition metal loaded porous silica systems are supported by an analysis of associated reactions influencing the overall catalytic performance of the NO conversion. The important part of the presented studies is the physicochemical characterisation of the samples including their chemical composition (ICP-OES, TGA), structure (P-XRD, DRIFT, RS, UV-vis DRS), morphology (SEM-EDS), textural properties (low-temperature N_2-sorption), surface acidity (NH_3-TPD, FT-IR with Py-adsorption) and reducibility of deposited transition metal species (H_2-TPR).

The presented PhD thesis consists of six manuscripts, five of which (**P1 - P5**) have been published in high impact scientific journals indexed by JCR (average impact factor 2020: 5.43) and one of the papers is currently under review (**P6**). All the manuscripts are focused on the reduction of nitrogen oxides emissions with the use of the NH_3-SCR process over porous silica

materials modified with transition metals. The catalysts presented in papers **P1** – **P6** were found to be active and selective in the process of NO reduction with ammonia in the temperature range depending on the type and form of the deposited active phase, as well as on the type of catalytic support. The main goal of the doctoral dissertation was achieved by the effective catalytic operation of porous silicas modified with transition metals in the temperature window extended or shifted in comparison to the commercial catalysts of the NH_3-SCR process.

In the first part of the research (**P1**) zeolites of the MWW family with bimodal porosity (microporous MCM-22 and micro-mesoporous silica and silica-titania intercalated materials) were modified with iron and then tested in the role of the NH_3-SCR catalysts. The results of the catalytic studies showed the effective operation of Fe-doped zeolites to about 475°C, along with the higher activity of the catalysts with an increasing titanium content in the pillars. The selectivity to the desired reaction product, N_2, was very high (above 99%) throughout the process. This publication presents also comprehensive studies on the detailed physicochemical characterisation of the catalysts, as well as an analysis of the reactions associated with the NH_3-SCR process. These reactions can affect the NH_3-SCR process by reducing or increasing its efficiency. In this case, the NO to NO_2 oxidation seems to be of particular importance. The results of nitrogen(IV) oxide formation in the presence of zeolites containing small aggregated iron oxide species, indicate NO to NO_2 oxidation as responsible for the activation of NO conversion at low temperatures.

Publication **P2** presents the synthesis and characterisation of spherical MCM-41 with various loadings of copper or iron incorporated into silica walls by the co-condensation method. This relatively easy method of catalyst synthesis results in active and N_2-selective catalysts of the NH_3-SCR process. The obtained samples of Cu- and Fe-series, were active and selective (above 98%) in the NH_3-SCR process up to 300°C and in the range of 375–450°C, respectively. A slight correlation between the metal content and the catalytic activity was observed for the samples containing copper, while for the iron-containing catalysts a strong dependence between metal content and NO conversion was found. The accessibility of active sites for the reagents during the catalytic process was identified as an important factor influencing the catalytic activity of the obtained materials. It is worth mentioning that the decrease in the efficiency of the NH_3-SCR reaction at higher temperatures was attributed to the side process of direct oxidation of ammonia by oxygen present in the reaction mixture.

As it was presented in publications **P3** and **P4**, pure silica MCM-41 and its Al-containing analogue with the spherical morphology, functionalised by the template ion-exchange (TIE) and its modified version (TIE-NH_3) allowing deposition of copper with the improved control of this metal species aggregation. In the presented publications, the physicochemical properties of the obtained samples were analysed and the Cu-doped materials were tested in the role of the NH_3-SCR catalysts. The TIE-NH_3 method, enabling the adjustment of the form and degree of copper aggregation, is based on treating the samples with ammonia solution immediately after metal deposition by template ion-exchange. The samples obtained by using the TIE method were characterised with respect to the presence of copper in the forms varying in the degree of aggregation, from monomeric cations to bulky copper oxide aggregates. The use of the combination of the TIE method with ammonia treatment, TIE-NH_3, allowed deposition of the active phase in highly dispersed forms - mainly as monomeric copper cations. Such forms of copper dominated in both Si-MCM-41 and its aluminium-containing analogue. Aggregation of deposited copper species seems to be a crucial factor influencing the catalytic performance of the studied catalysts in the NH_3-SCR process. The catalysts containing homogeneously dispersed monomeric copper cations were more active in the studied reaction in comparison to the samples containing more aggregated copper species. The temperature window of effective catalysts operation for the most active samples of the TIE-NH_3 series was in the ranges of 200–325°C and 225–375°C, for the Cu-modified Si-MCM-41 and Si-Al-MCM-41, respectively. High selectivity to N_2 was noted in the same series of the catalysts, above 98% and 95%, respectively, in the temperature range below 350°C. Thus, the catalysts obtained by the TIE-NH_3 method can be considered as promising for the low-temperature NH_3-SCR process.

Publication **P5** presents the results of catalytic studies of the NH_3-SCR process over MCM-41 with various morphologies, cylindrical and spherical, modified with iron in the form of monomeric cations and multinuclear iron oligocations by the TIE approach. The application of Fe-precursor differing in the complexity of the cations (various number of metal cations), resulted in the deposition of monomeric or more aggregated iron oxide nanorods, respectively in the case of using $FeCl_2$ and $[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$. The Fe-containing catalysts were tested in the high-temperature NH_3-SCR process. It is important to mention that the high selectivity to dinitrogen, over 98%, is maintained throughout the whole temperature range of the catalytic test. The performance of the catalysts in the NO conversion depended mainly on the loading of Fe-species. In general, the NO conversion increased with an increase in metal loading (except the samples with the highest iron content). To better recognise the mechanism of the NH_3-SCR process carried out in the presence of the studied catalysts, the reactions of NO to NO_2 oxidation and direct ammonia oxidation were studied. The analysis of the latter reaction suggests that the decrease of the NO conversion observed at higher temperatures is related to the competitive oxidation of the reducing agent, NH_3, by oxygen present in the reaction mixture. In turn, rather limited formation of NO_2 at lower temperatures is possibly correlated with the relatively low efficiency of the low-temperature NH_3-SCR process and therefore the conversion of nitrogen oxides according to the fast-SCR process is limited in the case of the studied Fe-containing catalysts.

The studies of the NO reduction with ammonia in the presence of spherical MCM-41 modified by the TIE method with copper, iron or manganese and pairs of these metals are presented in manuscript **P6**. The monometallic catalysts presented lower activity compared to bimetallic catalysts (CuFe, CuMn, FeMn). Among the studied samples, the most promising catalytic results were obtained for the copper-manganese system with the temperature window of effective operation in the range of 275–325°C, with almost 100% selectivity to N_2. The catalytic activity of this system was significantly better in comparison to the mechanically mixed spherical MCM-41 samples containing separately copper and manganese. The increased activity of the CuMn catalyst in the NO reduction with ammonia is possibly assigned to the synergistic effect between the copper and manganese species, thus facilitating the formation of NO_2 by oxidizing nitrogen(II) oxide and activating the fast-SCR mechanism.

In conclusion, the results obtained within the framework of the doctoral dissertation are important contributions to the development of knowledge related to the NH_3-SCR catalysts based on porous silica systems. The obtained catalysts show promising activities in the low-temperature (manuscripts **P2**, **P3**, **P4**, **P6**), as well as high-temperature (publications **P1**, **P5**) NH_3-SCR process. The presented results indicate that the temperature window of effective catalyst operation can be tailored to the specific needs of the NH_3-SCR process.

Foreword

The dynamic economic and industrial progress brings an improvement in the quality of life of the modern society in many aspects including *i.a.* agriculture, new technologies, medicine or energy and transport sectors. However, uncontrolled civilisation advancement driven by human needs without a doubt affects the environment and people's health. The negative phenomena observed over the past decades include air pollution and their harmful influence. Nowadays, air pollution is considered as one of the major health hazards for the world’s population. Pollutants present in the air, such as nitrogen compounds, carbon and sulfur oxides, ozone, volatile organic compounds (VOCs) as well as particulate matter lead to severe cardiovascular, cerebrovascular and respiratory diseases observed in the society.[1,2] The development of technology can therefore be treated as a double-edged sword. On the one hand, it is a source of environmental problems, while on the other hand, it can be used to find solutions that reduce or potentially stop the negative effects of environmental contamination. New technologies have made it possible to better control man-made emissions, *e.g.*, by designing devices for comprehensive monitoring of the type and amount of pollutants emitted into the atmosphere. The development of wet scrubbers enabled the removal of gaseous pollutants from industrial exhaust streams.[3] One can observe constant innovation in residential household heating techniques. Alternative stove designs effectively limited the amount of hazardous matter produced and emitted by our households. The problem of environmental contamination is taken into consideration very seriously by producers of commonly used products such as cleaning agents or building materials, leading to the development of new recyclable materials or to the modification of their production processes to minimalize the emission of harmful chemical compounds into the atmosphere. To sum up, the protection of our environment is one of the most crucial problems of contemporary science.

In response to this important problem, catalytic technologies focused on depollution of the environment have been developed. Methods based on the catalytic conversion of the air pollutants have the potential to meet the requirements of the industry progress and environmental restrictions and therefore are the most often used for this purpose. A decrease in the excessive emission of toxic waste gases, including gaseous nitrogen pollutants, can be achieved by reactions of their catalytic combustion (oxidation), catalytic reduction or catalytic decomposition.[4,5] Nitrogen-containing gaseous contaminants, such as ammonia (NH_3) and nitrogen oxides (NO and NO_2, referred as NO_x) belong to the most dangerous pollutants and therefore their emission has to be strictly controlled.[6,7]

Taking the above into consideration, it is not surprising that the modernisation of installations designed to reduce their emissions is a vital topic of scientific discussion. An indispensable element of the research focused on removing excessive pollutants emissions by catalytic methods is the development of effective catalysts for such processes. The most commonly used technology of NO_x abatement from flue gases is the process of selective catalytic reduction of nitrogen oxides with ammonia (NH_3-SCR). Porous silica materials (zeolites and mesoporous silica materials with an ordered porous structure) modified with transition metals belong to the one of the most promising catalysts of the NH_3-SCR process.[8,9]

This doctoral thesis, entitled: *Porous silica systems doped with selected transition metals as catalysts for conversion of gaseous nitrogen pollutants* is set on the border of chemistry and material engineering, combining new routes of advanced catalytic materials synthesis and catalytic studies. The main emphasis of the doctoral thesis is focused on the design and synthesis of novel series of silica porous materials modified with transition metals as well as systematic studies of the correlation between their properties and catalytic performance in environmental processes.

1. Introduction

1.1 Gaseous nitrogen pollutants

The presence of substances in the air, interfering with the welfare of humans and the natural environment of which the type and quantity exceed the natural capacity of the environment to disperse, dilute or absorb them, is defined as its pollution.[10] Depending on the nature of the contamination, solid, liquid and gaseous pollutants can be distinguished. On the other hand, taking into account the source of air pollutants, it can be specified as natural origin, as well as those related to the human activity. Nevertheless, regardless of the kind and source of emission, their excessive production has a negative impact on both, the environment and human health. Especially, gaseous air pollutants are a particularly dangerous group of contaminations, due to their ease spreading.

In order to control air quality, the European Union has established legal regulations concerning the emission of pollutants by the Member States. Legal regulations concerning atmospheric pollutants are included in the following European Union documents: The Green Deal/Clean air for all (COM(2018) 330)[11] framework strategy, the Ambient Air Quality (AAQ) Directives (2008/50/EC[12] and 2004/107/EC[13]) and the National Emissions reduction Commitments (NEC) Directive (2016/2284/EU)[14].[15] The NEC Directive emission reduction obligations apply for the period of 2020-2029 (earlier limits were in force in the period of 2010-2019), while the more rigorous commitments will be implemented from 2030.[16] According to the NEC Directive, the key air pollutants in Europe encompass anthropogenic emissions of non-methane volatile organic compounds (NMVOCs), nitrogen oxides (NO_x, $NO+NO_2$), ammonia (NH_3), fine particulate matter ($PM_{2.5}$) and sulphur oxides (SO_x).[14,16] Among them, contaminations containing nitrogen, NO_x, constitute an important group, being the main topic of this doctoral dissertation. The European Union also defines the relevant legal regulations with a distinction between the sources of air pollutant emissions. They include, *i.a.*, the industrial emissions Directive[17], the medium combustion plant Directive[18], the fuel standards (Fuel Quality Directive, 2009/30/EC)[19] and the vehicle emission (Euro) standards[20].[15]

Among the cycles of the element's circulation in nature, one of the greatest importance is that of nitrogen. The majority of Earth's atmosphere is composed of nitrogen, which undergoes many various transformations in the ecosystem as a result of bacteria nitrification and denitrification processes (Figure 1.1).[21,22] The forms of its occurrence in the environment are diverse, including both organic and inorganic compounds. Among them, reactive nitrates, nitrites, oxides (*i.a.* NO, NO_2, N_2O), reduced nitrogen (NH_x = NH_3/NH_4^-) and unreactive dinitrogen (N_2) are present.[23] In the last century, due to the intensified human activity, the natural nitrogen cycle has doubled, acting on nitrogen pollution of air, water and soils.[23] Thus, the supersaturation of our close surroundings with such compounds has resulted in an increasing attention of scientists due to the potential environmental risk.

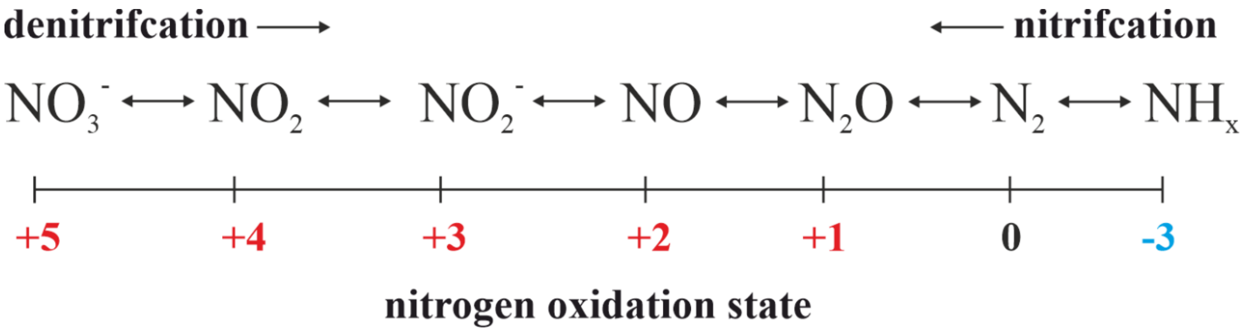

Figure 1.1 Scheme of the natural nitrogen cycle on the Earth (scheme inspired by the illustration from the reference[22]).

Nitrogen oxides

In the topic related to nitrogen oxides, their discoverer should be mentioned. For this purpose, one has to go back about 250 years and recall the figure of the English clergyman, theorist of politics, chemist and philosopher Joseph Priestley (1733–1804). Priestley described his discoveries in the six-volume work '*Experiments and Observations on Different Kinds of Air*'. In 1772, one of the first gases found by him was nitrogen(II) oxide. He referred to it as 'nitrous air'. He is also considered to be the discoverer of other gases, such as NO_2, N_2O, N_2, NH_3, HCl, O_2 and SO_2. The importance of his finding is proved by the fact that a topic that fascinated Priestley a hundred years ago, is still interesting for scientists.[24] The group of gaseous nitrogen compounds, occurring naturally in the environment, includes various oxides (N_xO_y), among which the following can be distinguished: N_2O, NO, NO_2, N_2O_3, N_2O_4, NO_3 and N_2O_5. It is important to note that the abbreviation NO_x denotes nitrogen(II) oxide and nitrogen(IV) oxide (NO and NO_2).

Nitrogen(II) oxide is a compound with a chemical formula of NO. It is a colourless gas (melting point at -163.6°C; boiling point at -151.8°C) with a sweet odour.[25] NO is a relatively unstable, very reactive molecule because it has an electron structure of a free radical (NO has one unpaired electron, Figure 1.2).[25,26]

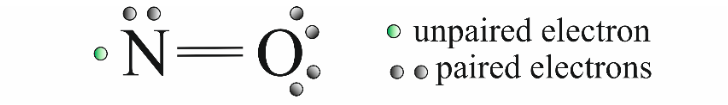

Figure 1.2 Lewis structure of nitrogen(II) oxide molecule.

The second compound belonging to a group of nitrogen oxides is nitrogen(IV) oxide (NO_2) (melting point at –9.3°C; boiling point at 21.2°C). In ambient conditions is a reddish-brown gas with a characteristic pungent, acid smell.[27,28] Nitrogen(IV) oxide, similarly to NO possesses an unpaired electron. Hence, it is also considered as a strong oxidizing agent that causes corrosion. Figure 1.3 presents the Lewis structure of nitrogen(IV) oxide.

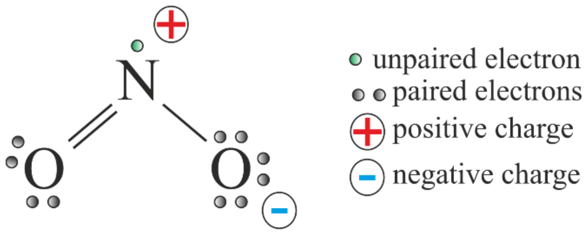

Figure 1.3 Lewis structure of nitrogen(IV) oxide molecule.

Another substance, from the group of nitrogen oxides, is nitrogen(I) oxide - N_2O (Figure 1.4). N_2O is a colourless gas (melting point at -90.8°C; boiling point at -89.5°C), with a faint smell and a sweetish taste. It is also known as 'laughing gas'. It is a non-flammable substance, but it accelerates the burning processes. N_2O dissolves in water, but it is also soluble in fats.[29]

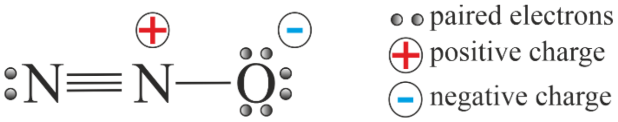

Figure 1.4 Lewis structure of nitrogen(I) oxide molecule.

From an industrial point of view, the nitrogen oxides constitute a key intermediate in the production of nitric acid, varnishes, colourants and nitration of organic substances.[30] NO_x are especially important in the Ostwald process of HNO_3 production from ammonia. The synthesis of nitric acid is based on the oxidation of NH_3 to NO in the presence of a Pt-Rh catalyst (Eq. *1.1*) in the temperature range of 800-930°C, under pressure determined by the used method (from atmospheric to 15 bar). Subsequently, the obtained nitrogen(II) oxide reacts with oxygen giving a rise to NO_2 (Eq. *1.2*), which is then introduced into water to obtain nitric acid as a product (Eq. *1.3*).[31] HNO_3 may be subjected to many industrial processes to obtain nitrogen fertilizers, explosives and other N-derived chemicals.[32]

(*Eq. 1.1*) $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$
(*Eq. 1.2*) $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$
(*Eq. 1.3*) $3NO_{2(g)} + H_2O_{(aq)} \rightarrow 2HNO_{3(aq)} + NO_{(g)}$

Nitrogen(I) oxide is used in medicine as an anaesthetic (especially in stomatology). N_2O is also used in the food industry *e.g.*, in the role of propellant in whipping cream. In the automotive sector, nitrogen(I) oxide is well known as an accelerating factor for racing cars - as a result of the N_2O decomposition, oxygen formed in this process is supplied to the engine, which results in increased fuel incineration and therefore provides additional energy to increase the speed of car.[29]

Despite the significant role played by nitrogen compounds in the industrial sector, these compounds are air pollutants of great concern. As was already mentioned, nitrogen oxides have a negative impact on health, potentially causing various systemic diseases. The human respiratory system is the most vulnerable to the harmful effects of NO_x. It is manifested in respiratory infections, damage to the laryngeal mucosa, bronchitis, pneumonia and asthma. NO_x can lead to irritations of the eyes and skin, dizziness, or contribute to the weakening of the immune system.[33,34] The damaging impact of NO_x on the environment manifests itself in the form of acid rain. The formation of acid rainfall, based on the interaction of NO and NO_2 with SO_2, is responsible for deforestation and acidification of the ground and reservoirs of water. Other, far-reaching effects of acid rain can also be related to the destruction of man-made architecture and crop damage. Moreover, the influence of sunlight radiation on NO_x and volatile organic compounds (VOCs) in the air contributes to the phenomenon of photochemical smog.[35]

Nitrogen oxides can be released into the atmosphere because of emission from both, natural and anthropogenic sources. NO_x are formed in the environment as a result of lightning discharges and microbial processes arising in soils. However, the excessive production of nitrogen oxides is mainly attributed to human activities related to the energy production sectors as well as to the chemical industry.[36] Overproduction of nitrogen oxides is particularly visible in urban areas with high traffic.[37] Agricultural production can be indicated as another significant source of nitrogen pollution, especially in regions with heavy N-type fertilizer exploitation.[38]

Nitrogen(II) oxide (NO) is the major side-product of the fossil-fuel combustion processes in the transportation and electricity generation sectors. Taking into account the types of nitrogen oxides (NO_x) in post-process gases resulting from an incineration reaction it was reported that they contain about 95% of NO and 5% of NO_2.[39] The formation of nitrogen(II) oxide (NO) takes place as a result of (i) oxidation of gaseous nitrogen in the boiler zone with the highest temperature - above 1300°C (thermal mechanism); (ii) high-temperature oxidation of organic nitrogen compounds present in fuels or biomass (fuel mechanism); (iii) oxidation of HCN derivatives obtained from the reaction of atmospheric nitrogen with organic fuel radicals (prompt mechanism).[40] Nitrogen(IV) oxide (NO_2) is also formed as a result of the reaction of NO with oxidants present in the atmosphere (such as oxygen, ozone and volatile organic compounds).[27,39]

In accordance to the European Environmental Agency report on *Air quality in Europe 2021*, (EU27, 27 European Union countries after the UK left the European Union) the NO_x emission in Europe decreased by 36% from 2005 to 2019.[41] There is no doubt that the decrease in nitrogen oxides emissions is related to the legal regulations, which the Member States have committed to comply with.[15] The EEA reported the most recent data, for 2019. The presented report clearly confirms that the main source of nitrogen oxides pollution is road transport (39%). What is more, it was reported that agriculture (17%), manufacturing and extractive industry (14%), as well as energy supply (14%) also make a significant contribution to total NO_x production (Figure 1.5).[41]

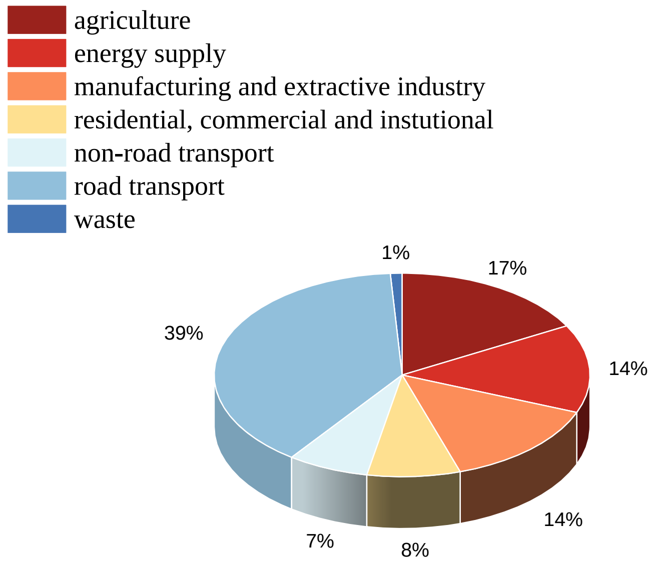

Figure 1.5 Sectors contributing to the NO_x total emissions in Europe, 2019 (prepared according to data from the reference[41]).

In 2019, the overall production of nitrogen oxides in EU27 and Poland was about 6126 Gg and 682 Gg, respectively. In both cases, the emission level was below the limit set by the NEC Directive.[16]

Another serious pollution, the impact of which has been neglected over the years, mainly due to the relatively low level of its emissions, is N_2O. In contrast to NO and NO_2, nitrogen(I) oxide is considered as a greenhouse gas (GHG), which absorbs infrared radiation and increases the greenhouse effect. N_2O also participates in the depletion of the ozone layer through photochemical reactions in the upper layers of the stratosphere.[33,34] Nitrogen(I) oxide is recognised as one of the main greenhouse gas and represents about 6% of GHG emissions in 2019 in the EU27.[42] N_2O is characterised by 310 times greater global warming potential than CO_2 and its remaining time in the atmosphere is estimated to be about 150 years.[43] The formation of nitrogen(I) oxide is related to biological processes of nitrification and denitrification occurring in soils and oceans. Nevertheless, the important contribution of nitrogen(I) oxide production can be assigned to the human activities related to land cultivation and fertilizers in agriculture (74%).[43,44] The sources of emissions with a lower but not negligible input include the transport sector (side-product of fossil fuels combustion) and chemical industry (adipic acid, nitric acid and fertilizers production).[43] Figure 1.6 presents the percentage contribution of N_2O emission in the European Union (EU27) in 2019 distinguished on the source sector.[44]

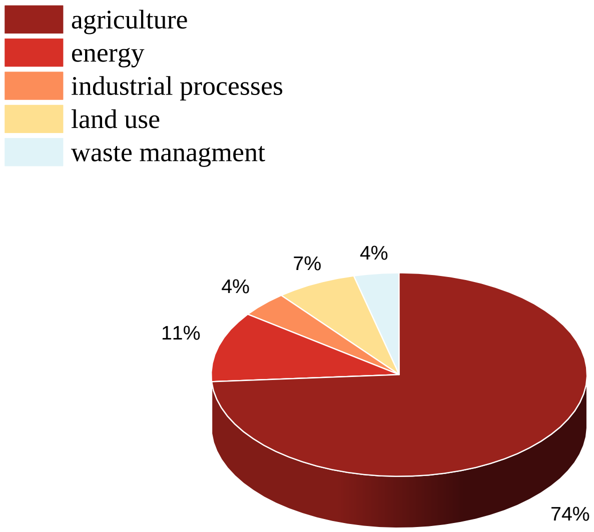

Figure 1.6 Sectors contributing to the N_2O total emissions in Europe, 2019 (prepared according to data from the reference[44]).

Ammonia

In 1773, Priestley synthesized ammonia, by treating salammoniac (the natural mineral composed of NH_4Cl) with HCl. The obtained product was named by him as ‘alkaline air’.[24] Ammonia (NH_3) is an inorganic molecule composed of 3 hydrogen atoms covalently bonded to the central N atom (Figure 1.7). Under normal conditions, ammonia is a colourless gas (melting point at -77.7°C; boiling point at -33.4°C), characterised by a suffocating and pungent odour. Ammonia is soluble in water giving a rise to an aqueous ammonia solution.[45]

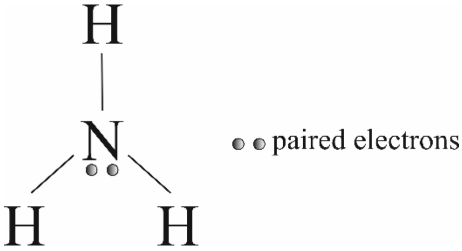

Figure 1.7 Lewis structure of ammonia molecule.

Ammonia is a substance of great importance in many branches of industry. The main ammonia application is related to the production of fertilisers because of the high nitrogen content. In this context, NH_3 can be used directly or indirectly as a substrate for manufacturing other soil conditioners (*e.g.*, urea - $(NH_2)_2CO$, ammonium nitrate - NH_4NO_3, ammonium sulfate - $(NH_4)_2SO_4$, ammonium phosphate - $(NH_4)_3PO_4$). Therefore, ammonia allows to meet the high demand for food production of the growing population. No less important application of ammonia relates to the chemical industry, including nitrogen-derivatives such as nitric acid (HNO_3), sodium bicarbonate ($NaHCO_3$) or hydrazine (N_2H_4). The other industrial sectors in which ammonia is involved, include the production of explosives, plastics and pharmaceuticals.[46,47]

Ammonia occurs in the environment through natural processes, including organic matter decomposition and the biological activity of bacteria in land and water ecosystems (Figure 1.1). NH_3 is also released into the atmosphere as a result of anthropogenic emissions covering various sectors of human activity. In recent years (2005-2019), the decrease in ammonia emissions in the Member States of the European Union was only 8%.[41] The contribution of individual ammonia sources released in Europe according to the European Environmental Agency in 2019 is depicted in Figure 1.8.[41] Ammonia is mainly produced in agriculture (94%)[41] as a consequence of livestock breeding and soil fertilisation with nitrogen compounds.[46–49] Other sources of NH_3 emissions encompass fossil fuel combustion in road transport and industrial processes. It is estimated that ammonia emission related to the mentioned factors is rather negligible. However, ammonia production from these sources is projected to increase due to the ever-expanding transport sector.[47] Such prediction can be linked to the increased ammonia formation as a side-product of the reduction of NO_x emitted from exhaust gasses by a three-way catalytic system.[47]

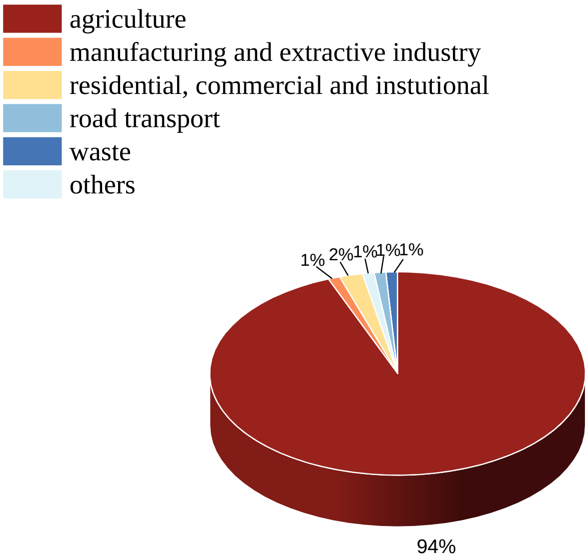

Figure 1.8 Sectors contributing to the NH_3 total emissions in Europe, 2019 (prepared according to data from the reference[41]).

Despite the high industrial importance of ammonia, its excessive emission to the atmosphere contributes to the negative impact on public health and the natural environment. NH_3 causes irritation of the skin and eyes when exposed to small concentrations of this gas. Higher doses of ammonia contribute to more serious health problems, such as bronchiolar, alveolar oedema and damage of the breathing system resulting in serious lung diseases.[47] Concerning the environmental risks caused by excessive ammonia emissions, special attention should be paid to the eutrophication processes of land and water ecosystems.[47,48] It may negatively influence fauna and flora, affecting the danger of biodiversity degradation.[48,49]

1.2 Nitrogen pollutants emission abatement

Due to the noxious effect of NO_x on the environment, studies on its emission control are still conducted. The main topic is related to NO_x removal from exhaust gases produced by vehicular (*e.g.*, processes of fuels combustion in motor vehicles)[50–52] and stationary (*e.g.*, operation of electric power stations, high-temperature industrial installations or chemical production emissions)[52–54] sources. Currently, various technologies of the NO_x abatement are being used to comply with the restrictions imposed by legislation. Among the approaches to the NO_x conversion, one can distinguish combustion methods and also methods dealing with processes of tail-gasses removal.[34,55,56] The last of the mentioned methods has gained a huge significance because of the high effectiveness in NO_x removal. In particular, the following methods of NO_x emissions control can be specified: (i) selective noncatalytic reduction (SNCR), (ii) selective catalytic reduction (SCR), (iii) non-thermal plasma (NTP) and (iv) electron beam treatment.[34,55,56]

The methods based on the selective catalytic reduction of NO_x are the most commonly applied to limit their emission.[34,55–57] Among various technologies of NO_x removal, the direct decomposition of NO to N_2 and O_2 seems to be an appropriate method. Unfortunately, the efficiency of this way of NO conversion is not satisfactory. Therefore, a reducing agent is indispensable to convert NO into N_2.[55] For this purpose, various reducing agents, such as hydrocarbons (HC)[58], carbon(II) oxide (CO)[59] hydrogen (H_2)[60] or ammonia (NH_3)[61], are used. It is worth mentioning that the approach using ammonia for the selective catalytic reduction of NO_x (NH_3-SCR) emitted from stationary sources is considered the most widespread in the world.[34,55–57,61] The first commercial NH_3-SCR installation was mounted by the IHI Corporation in 1978[62], although the beginnings of this technique date back to 1957, when it was patented by the Engelhard Corporation in the USA[63].

From the chemical point of view, selective reduction of NO_x (NO+NO_2) in the presence of a catalyst (SCR) can be described by the equations (*Eq. 1.4* and *Eq. 1.5*) shown below.[64] The following reactions of the SCR proceed in the temperature range of 250-450°C, when oxygen excess is present in the system.[65]

(*Eq. 1.4*) $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
(*Eq. 1.5*) $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

The acceleration of the SCR of nitrogen oxides and its shift towards lower temperature is postulated as a result of the interaction of NO, NO_2 and ammonia.[66] The reaction is called fast-

SCR and can be detailed by the following equation (Eq. 1.6). Due to the fact that the composition of the post-process NO_x gases mainly consists of nitrogen(II) oxide, the presence of NO_2 is ensured by its introduction into the gas stream, or is obtained by the partial oxidation of NO by oxygen present in the reaction mixture.[66,67]

(*Eq. 1.6*) $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$

The desirable products of the NH_3-SCR are dinitrogen and water vapour (*Eq. 1.4* and *Eq. 1.5*). However, the reaction may otherwise lead to the side compounds, reducing the selectivity of the process to N_2.[64] The mentioned selectivity of the considered process is assigned to the reaction of NH_3 with NO_x instead of direct oxidation of the reducing agent to N_2, NO or N_2O (*Eq. 1.7 - Eq. 1.9*). The side products of ammonia oxidation can be nitrogen(II) oxide and nitrogen(I) oxide, which are considered as components of air pollutants.

(*Eq. 1.7*) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
(*Eq. 1.8*) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
(*Eq. 1.9*) $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

In NH_3-SCR technology, the recommended catalyst applied in industrial processes (power plants and stations as well as industrial boilers) is based on the V_2O_5 deposited on titanium dioxide and supported by promoters (WO_3 or MoO_3).[64] The same catalyst type can be used for heavy-duty diesel cars.[68] However, in such cases, the commercialised technology is based on the urea-SCR process. In this case, the reducing agent, NH_3, necessary for the SCR reaction, is produced from ‘AdBlue’ solution – 32.5 wt.% aqueous solution of urea. Ammonia is formed by hydrolysis of $(NH_2)_2CO$ (Eq. 1.10) and then injected into the exhaust gas to reduce NO_x in the presence of the catalyst.[68,69] After introducing ammonia into the system, the SCR reaction proceeds according to the equations described above (*Eq. 1.4* and *Eq. 1.5*).

(*Eq. 1.10*) $(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$

The V_2O_5-TiO_2 catalytic system promoted with WO_3 or MoO_3, used for conversion of NO_x in flue gases emitted by stationary sources (*e.g.*, electric power stations, industrial boilers) operates with a good selectivity to dinitrogen at moderate temperatures of 300-400ºC. At temperatures below 300°C, the NO_x conversion is insufficient, whereas above 400ºC the side process of direct ammonia oxidation plays an important role (*Eqs. 1.7-1.9*).[64] The relatively narrow window of efficient operation of such catalyst, together with the possibility of the release of toxic vanadium constitute the main weaknesses of such catalytic system.[68,70]

Moreover, in industrial installations, the V_2O_5-TiO_2 catalysts, deposited on a monolithic honeycomb, are located upstream of the electrostatic precipitator (ESP). Thus, the high-dust stream of exhaust gasses is passing through the monolith, which may result in the blockage of monolith channels. Such arrangement of the NH_3-SCR system is called the high-dust configuration (Figure 1.9 A). Nevertheless, the possible reorganisation of the installation, allowing for the placement of the monolith unit downstream of the gas cleaning system would enable the catalyst to work with a pre-treated flue gas stream. The change, from high-dust to low-dust configuration of the NH_3-SCR system (Figure 1.9 B), can eliminate the problem of premature catalyst deactivation. However, the temperature of the gases downstream of the ESP is about 250ºC. Therefore, the use of a commercial V_2O_5-TiO_2 based catalytic system with an effective operating window of 300-400°C would require heating the gases downstream of the ESP unit. In order to avoid additional costs related to the heating of gases, a good solution would be development of a catalyst operating in the low-temperature range (about or lower than 250ºC).[9,71]

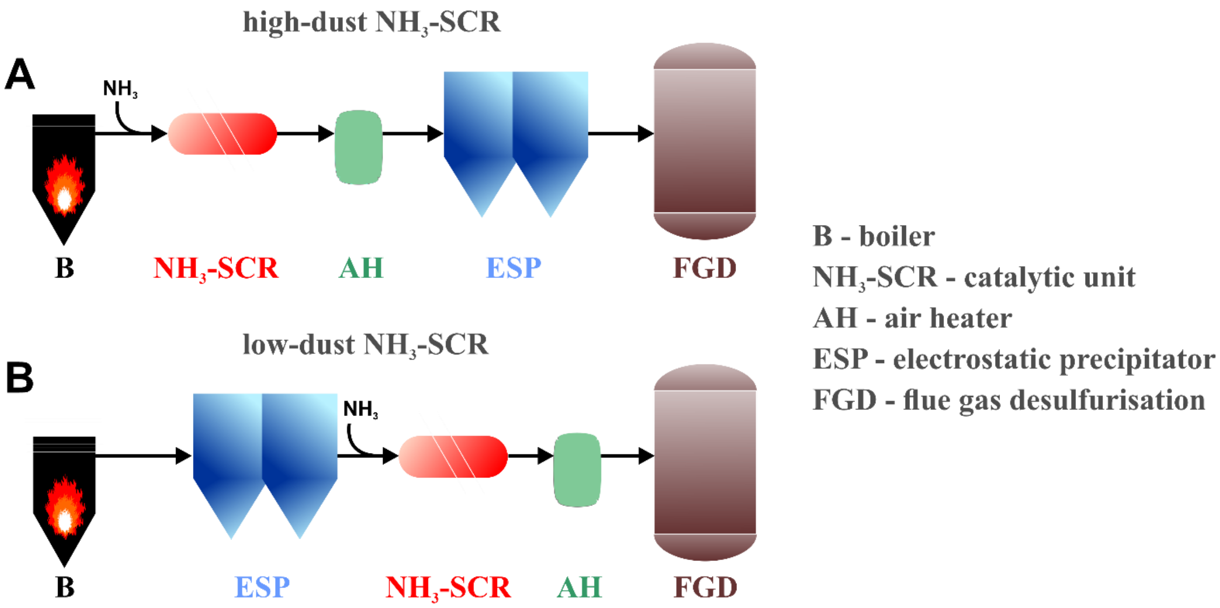

Figure 1.9 High-dust (A) and low-dust (B) NH_3-SCR process configurations (scheme inspired by the illustration from the reference[9]).

In addition to the mentioned above disadvantages of NH_3-SCR, another fundamental problem, which must be highlighted, is related to ammonia. The NH_3-SCR technology involves the storage of large amounts of NH_3, which constitutes health hazards and safety issues. Moreover, special attention must be paid to the possible release of ammonia into the atmosphere due to its incomplete conversion in the NH_3-SCR process (ammonia slip).[55,72] The uncontrolled emission of ammonia from the NH_3-SCR installations may contribute to numerous environmental issues as well as harm human health. Moreover, the released NH_3 can react with acidic components of exhaust gasses (nitrogen oxides, sulfur oxides) resulting in ammonium sulfate and ammonium nitrate, and finally leading to the formation of fine particulate matter ($PM_{2.5}$). In addition, the interaction between ammonia, water and SO_3 (formed as a result of SO_2 oxidation by the SCR catalyst) may lead to the generation of ammonium bisulfate (ABS), which due to its relatively high viscosity and tendency to trap fly ash from the flue gas stream, may damage the SCR installation. The destructive effect of ABS deposition is manifested by clogging the channels of the catalytic monolith. Consequently, the NO_x conversion efficiency may be decreased and the effective operation time of the SCR unit is reduced.[72–74]

The discussed above redesign of the NH_3-SCR installation (low-dust configuration, Figure 1.9 B) of gas purification system should also limit the risk of the ammonia release. However, it is noteworthy that in the industrial NH_3-SCR process, various methods are used to eliminate the problem of ammonia leakage. One can distinguish its catalytic decomposition, liquefaction, thermal oxidation, absorption or separation by biofilters.[47,73] Nevertheless, due to the insufficiency of such methods and high operation costs, their application in coal power plants is rather restricted. A better solution to the problem of ammonia slip is based on its selective catalytic oxidation (NH_3-SCO). In the NH_3-SCO process, the escaping ammonia reacts with oxygen to form N_2 and H_2O over the so-called 'guard catalyst' (*Eq. 1.7*).[73,74] The advantage of the NH_3-SCO process, in terms of its use as an additional technology supporting the SCR system, is its operation in the presence of post-process gases. Accordingly, there is no need to introduce any extra component into the gas stream as the reaction passes between ammonia and oxygen. Even though the formation of N_2 is thermodynamically favourable[47], the possible formation of secondary pollutants (NO, N_2O; Eq. 1.8, Eq. 1.9) by the non-selective oxidation of ammonia may take place at higher temperatures. To avoid this adverse phenomenon the selection of the appropriate temperature window of the NH_3-SCO process as well as a suitable catalyst is extremely important. In industrial power plant applications, the optimal temperature range is from 250 to 400°C, whereas SCO catalyst is usually located downstream of the SCR system, typically deposited on the same monolith or as a single separate unit.[47] Of course in retrofitted low-dust installations these catalysts should operate at temperature of 250°C or even lower. As potential 'guard catalysts' the systems based on noble metals, transition metals as well as functionalised zeolites, are considered.[5,47,73,74]

1.3 Development of catalysts for the conversion of gaseous nitrogen pollutants

Due to some disadvantages of currently used commercial catalysts, much effort has been devoted to the development of novel, more effective NH_3–SCR catalysts. In these regards, the synthetic pathways leading to more efficient catalysts are based on the appropriate selection of support of the catalysts as well as the type of the catalytically active phase. Materials such as zeolites[67,75–77], activated carbons[78], modified metal oxides[73], hydrotalcites[79,80], mesoporous silicas[81–83] or modified clays[84,85] have found widespread use as catalyst supports. In this context, porous silica systems including zeolites and mesoporous silica materials of the M41S family (*e.g.*, MCM-41) deserve special attention. However, usually their catalytic activation in the NH_3-SCR process requires suitable active components, typically transition metal species, introduced on their surface. This group of metals includes, in particular, copper, iron and manganese.[67,73,75–84]

1.3.1 Catalytic supports and their functionalisation

As defined by IUPAC, porous materials can be divided in terms of their pore size (d) into microporous ($d < 2$ nm), mesoporous ($d = 2$-50 nm) and macroporous ($d > 50$ nm).[86] Among them, porous silica systems (including zeolites and mesoporous silica sieves) are a group of materials characterised by a very large specific surface area, uniform porous structure in the range of micro- or mesopores and relatively high thermal and hydrothermal stability.[9,87]

Zeolites

Zeolites are very promising catalytic carriers due to their textural properties (high surface area, homogeneous microporosity), surface acidity, ion-exchange properties and exceptional hydrothermal stability. This group of crystalline materials can occur naturally or can be obtained in the synthetic route. Regardless of origin, zeolites are composed of vertex-sharing SiO_4 and $(AlO_4)^-$ primary tetrahedral building blocks (Figure 1.10 A). These building units by sharing oxygen ions with other tetrahedral units form the secondary building blocks (Figure 1.10 B), creating a complex combination of connections in the zeolite structure. Nowadays, there are known more than 240 synthetic zeolites and 67 zeolites of natural origin.[88] The discussed group of microporous aluminosilicates are used on a large scale in many industrial and everyday applications, such as the production of detergents or feed additives, separation and catalytic processes.[89,90] Heterogeneous catalysis using zeolites deserves a special attention concerning its large global utilisation, especially in the chemical industry. Since the 1950s zeolites are commercially applied in the role of catalysts or catalytic supports in numerous processes of the oil refinery industry, *e.g.*, Fluid Catalytic Cracking (FCC) and Hydro-Cracking (HC).[89–91] Among the many zeolite structures, about 20 are used industrially. They include the 'Big Five' - the zeolite families the most commonly used in large-scale processes. It consists of the following network types: BEA, FAU, FER, MFI and MOR.[89,91] Another zeolite of significant industrial importance is MCM-22 belonging to the MWW family. Despite being outside of the 'Big Five', it is used in many chemical processes based on hydrocarbons conversion. MCM-22 is used for the processes for monoalkyl benzenes synthesis *e.g.*, ethylbenzene or isopropylbenzene.[92]

MCM-22, IZA (International Zeolite Association) code MWW, is an example of a nanoporous zeolite prepared on a laboratory scale by hydrothermal synthesis. It is a relatively novel structure, obtained in 1990 by ExxonMobil Oil researchers.[93] MCM-22 zeolite is built of two individual pore systems: the first consists of bidimensional channels with 10-ring pore openings (diameter 0.6 nm), whereas the second one possesses cups with 12-ring openings containing egg-like shaped super-cages (diameter 1.4 nm).[94] Model structure of MCM-22 zeolite is presented in Figure 1.10 C. Due to the unique topology, ensuring high specific surface area, as well as high hydrothermal stability, MCM-22 is an attractive material for possible catalytic applications.

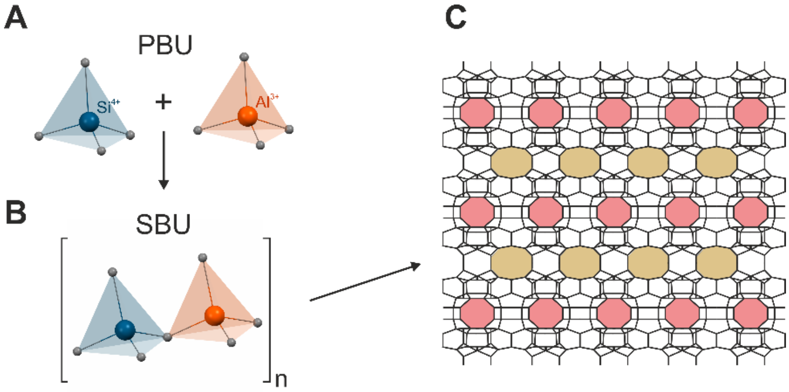

Figure 1.10 Primary (A) and secondary (B) building units of zeolite; model structure of MCM-22 zeolite (C).

MCM-22 is the very first example of zeolite that can be obtained directly in the form of layered precursor (MCM-22(P)) with 2.5 nm thick sheets organised vertically. The topotactic transformation from the 2D to 3D structure, taking place upon calcination, connects the layers by the condensation of the Si-OH groups on neighbouring MWW-sheets.[95–97] Nevertheless, modifications within the precursor layers allow obtaining a variety of MCM-22 derivatives, characterised by different micro-mesoporous structures. The mentioned systems with bi-modal porosity can be obtained from MCM-22(P) by swelling, resulting in MCM-22(S) and its subsequent delamination or pillarization to produce ITQ-2 and MCM-36 structures, respectively (Figure 1.11).[95–97] ITQ-2 is a delaminated material with the house-of-cards layers arrangement, while MCM-36 contains inorganic pillars located between the sheets of zeolite. Typically, MCM-36 material is intercalated with silica pillars. However, depending on the type of the used pillaring agent, the composition of the pillars may be diverse, *e.g.*, silica-titania pillars.[98] Due to the presence of additional mesoporosity and hence a more open porous structure, both MWW-derivatives are characterised by enhanced surface area and reduced internal diffusion limitations. Such kind of structures allows better access to zeolite active centres, which is especially important in the case of bulkier molecules conversion.[97]

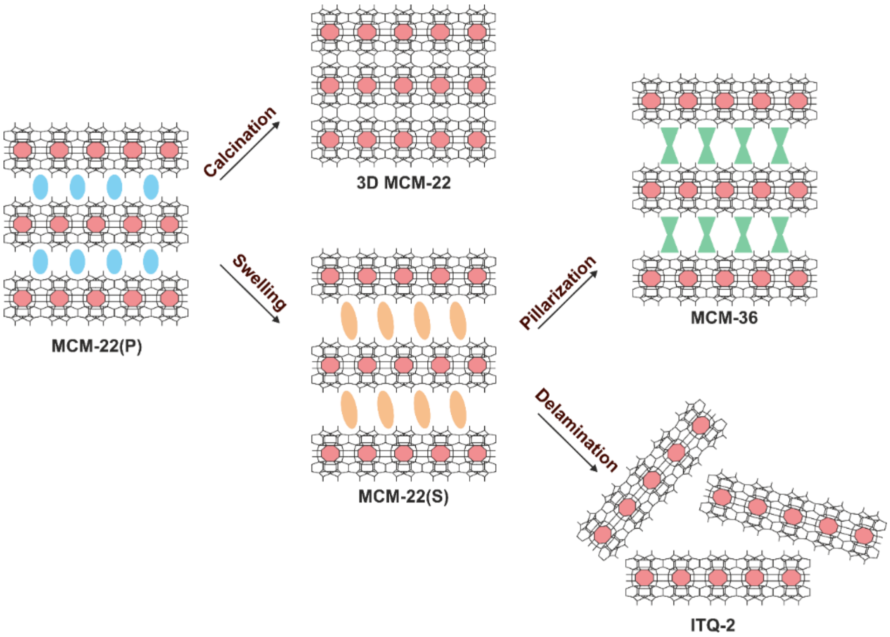

Figure 1.11 Transformations of layered MCM-22 precursor by swelling procedure to form delaminated (ITQ-2) and intercalated (MCM-36) structures (scheme inspired by the illustration from the reference[97]).

The catalytic activation of zeolite precursors for many catalytic processes demands the introduction of transition metal cations, which play a role of catalytically active components. The isomorphous substitution of catalytic components into the zeolite framework is one of their functionalisation methods.[99] The other methods of zeolites modifications, such as: (i) impregnation and (ii) ion-exchange method are related to the deposition of the active components on the surface of the catalytic support. Impregnation is one of the simplest approaches to introduce metal centres into zeolites. The impregnation procedure involves the deposition of the catalytically active components by filling the pores of the catalytic support with a solution containing metal precursor (dry impregnation) followed by solvent evaporation and calcination.[100] The application of the ion-exchange method in the case of zeolites is strictly related to their internal structure. Because each atom of trivalent aluminium introduced into the SiO_4 tetrahedron network is bound to four oxygen anions, the AlO_4 tetrahedron has an overall charge (-1). Therefore, in order to maintain the electroneutrality of the aluminosilicate network, the presence of counter-cations to compensate for the negative charge is necessary. During the ion-exchange procedure, the charge-compensating cations may be replaced by metal cations desired for a given catalytic process (Figure 1.12). It can be achieved by immersing and mixing zeolitic support with a solution of metal precursor of the concentration adjusted to the zeolite ion-exchange capacity.[101]

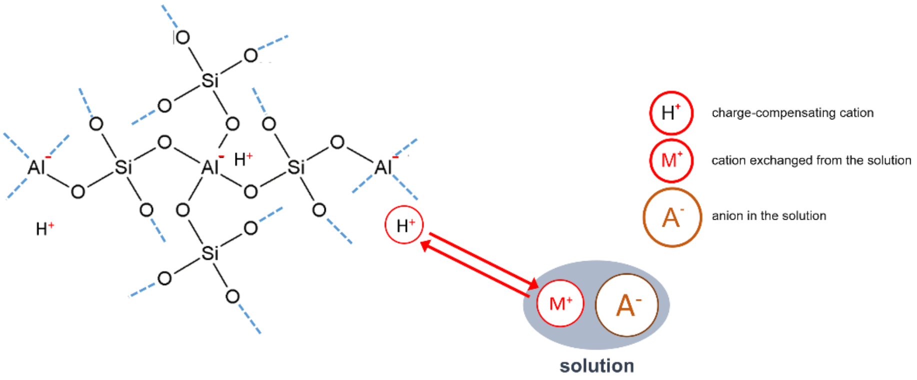

Figure 1.12 Schematic representation of the ion-exchange method conception.

Mesoporous silica sieves

The discovery of ordered mesoporous silica materials was first reported in 1992 by researchers from Mobil Oil Company.[102] The new family of nanostructured silicas, so-called M41S, includes hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 materials. M41S family members present an ordered porous arrangement, with their highly uniform distribution in terms of size within the 2–10 nm range.[103] The milestone in the development of mesoporous sieves appeared together with the synthesis of another silica material, SBA-15, also characterised by a hexagonal array of pores. Its structure is similar to MCM-41, although with a larger pore diameter and thicker silica walls.[104] Discovery of nanoporous silicas initiated a new research pathway towards the development of a novel group of materials for various applications.

One of the most widely studied mesoporous silica sieves of the M41S family is MCM-41. Its synthesis is based on the alkylammonium surfactant directed method.[105] The scheme of the MCM-41 formation is shown in Figure 1.13. The process of MCM-41 forming begins with the creation of micelles from cationic surfactant in an aqueous medium (i) and subsequent self-arranging into cylindrical micellar rods (ii). Afterwards, the cylindrical micelles organise themselves to form a hexagonal array (iii). Silica source hydrolyses and condenses in the spaces not occupied by micellar structures resulting in an ordered silica framework (iv). The removal of the pore-forming templates to form MCM-41 material can be accomplished by calcination (v') or by extraction of an organic matrix with suitable solvents (v'').

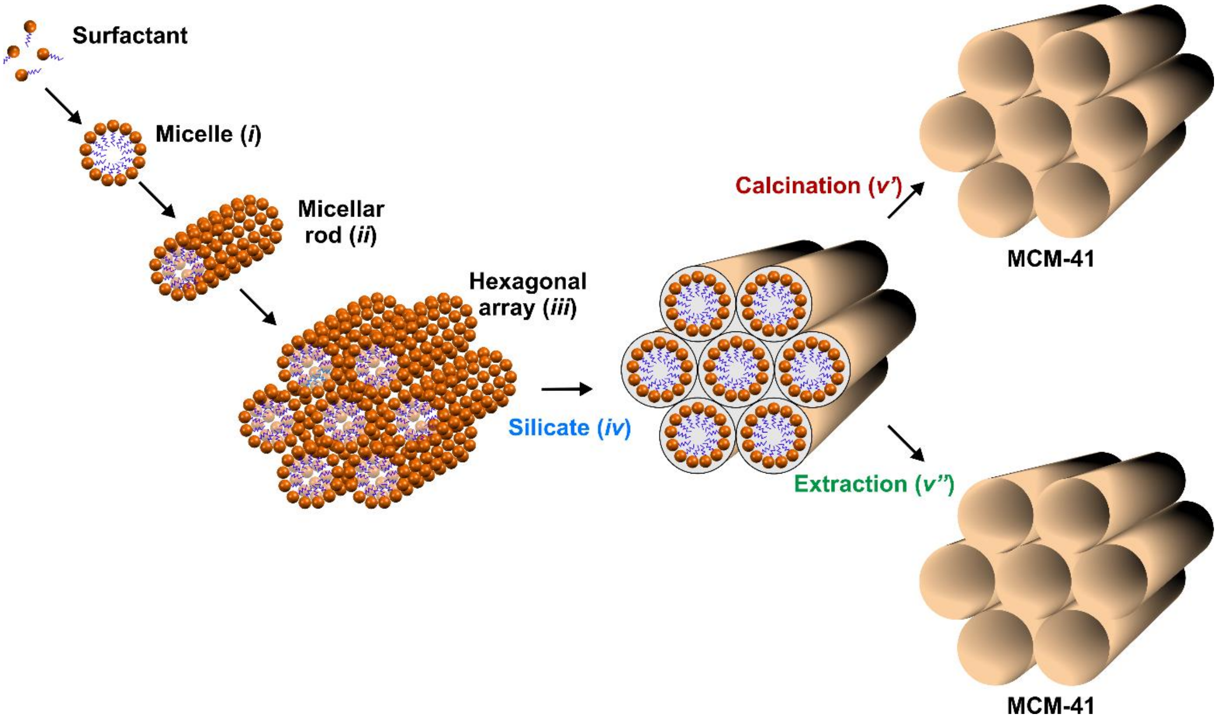

Figure 1.13 Scheme of MCM-41 synthesis performed by surfactant directed method (scheme inspired by the illustration from the reference[9]).

The synthesis gel contains an aqueous solution of cationic surfactant (acting as a pore-forming matrix), silica precursor (*e.g.*, tetraethyl orthosilicate, TEOS) and basic medium accelerating its hydrolysis and condensation. In general, in the synthesis of materials of the M41S family quaternary ammonium ions dispersed in an aqueous solution are used as an organic template of mesopores. The most often as a cationic surfactant - cetyltrimethylammonium ion, $C_{16}H_{33}(CH_3)_3N^+$, is used.[106] However, the size of pores in MCM-41 can be regulated by using surfactants with different lengths of alkyl chain.[107] This enables designing of the silica material tailored for the needs of a given application. Another important factor enabling the possible use of the silica materials is their morphology. By the appropriate selection of the synthesis mixture composition, the formation of nanoporous MCM-41 can be driven to the desired morphological form. Mesoporous silicate of MCM-41 type most often is synthesised in a classical (cylindrical) morphology (Figure 1.14 A). Nevertheless, it can be obtained also in a spherical arrangement (Figure 1.14 B). The synthesis procedure of spherical MCM-41 is based on the modified Stöber method and was firstly implemented by Grün *et al*.[108], while the classical Stöber method was originally intended for the preparation of non-porous sphere-shaped silicas[109]. The modified Stöber synthesis involves hydrolysis and condensation of silica source around organised micelles in the alkaline hydro-alcoholic solution. The obtained template-containing material is subsequently subjected to the organic matrix removal procedure by calcination or extraction to obtain spherical mesoporous silica of MCM-41 type. The mechanism of the spherical MCM-41 formation is most likely related to the addition of low-boiling alcohol (*e.g.*, ethanol) to the synthesis gel, which acts as a co-solvent that favours the formation of sphere-shaped particles.[110] The introduction of ethyl alcohol is responsible for the limitation of silica precursor (TEOS) hydrolysis, but also may initiate the growth of rod-shaped micelles. In the case of the organisation of rod-like micelles of different lengths, the longer rods connect with each other ends, while the shorter tubes slide into the free spaces between them, leading to the formation of silica nanospheres.[111] Apart from sphere-shaped MCM-41, other systems, like silica nanorods, thin films and monoliths that differ in terms of textural parameters, particle shape or morphology can be obtained by modifying the ratio of the reactants or synthesis conditions, *e.g*., reaction temperature.[110]

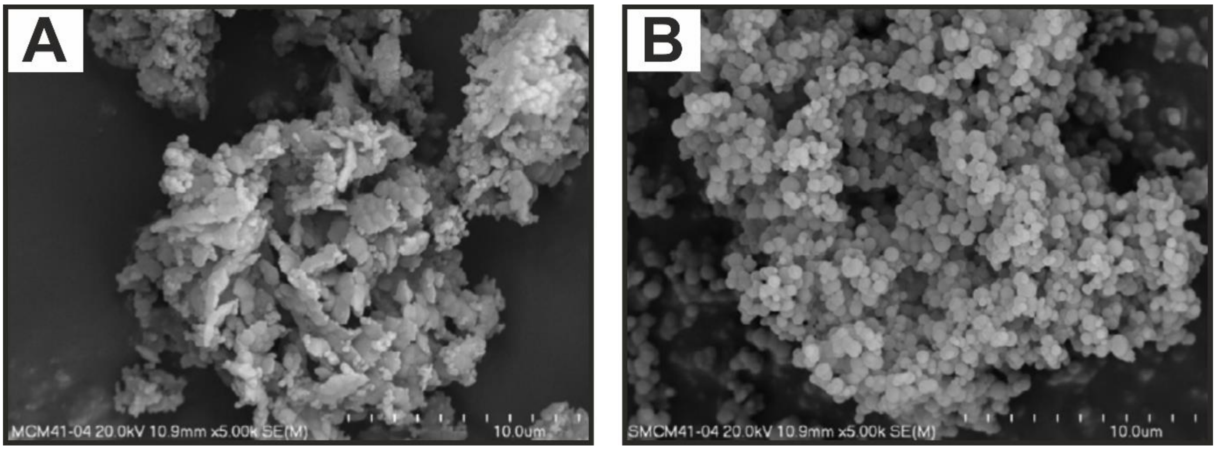

Figure 1.14 SEM images of MCM-41 type in classical (A) and spherical (B) morphologies (reprinted from the reference[9]).

M41S mesoporous silica sieves are characterised by unique properties, such as large specific surface area (above 700 m^2/g), homogeneous mesoporosity, tunable pore dimensions, relatively good thermal stability and large pore volumes, which allow them to be applied in the separation processes, drug release, chromatography, adsorption and catalysis.[112] Due to the physicochemical characteristics of mesoporous silica materials, it was initially believed that they would be in some measure an extension for zeolites in catalytic applications. The aforementioned reasoning was related to larger pore diameters of these materials, which would facilitate mass transfer and therefore, enabling reactions involving bulkier compounds (substrates/products). Although, the porous structures of mesoporous silicas are related to their regular pore's arrangement. However mesoporous silica sieves, in contrast to zeolites, are classified as amorphous materials. The amorphous character and relatively thin channel walls of the mesoporous silica walls have certain consequences, which are manifested in lower chemical, hydrothermal and mechanical stability in contrast to crystalline zeolites. Since the skeleton of the mesoporous sieves is built of pure silica, these materials do not possess active sites and therefore cannot act as catalysts. To overcome these drawbacks, it is possible to generate surface acidity, *e.g.*, by adding aluminium to the silica network. However, the acidity of mesoporous aluminosilicates is substantially weaker than that of zeolites and formed in this way active centres are characterised by a diversified acid strength.[113] These factors restrict the possible application of mesoporous silica sieves substituted with hetero-atoms in the reactions demanding the presence of catalysts with well-defined acid properties. Another important issue is related to the lack of ion-exchange properties in the pure silica mesoporous materials. Nevertheless, their generation by the introduction of Al^{3+} ions into silica walls during synthesis is possible. The aluminosilicates obtained in this way exhibit ion-exchange properties, but the introduction of higher content of aluminium causes the formation of extra-framework of Al-species disturbing mesoporous arrangement and not exhibiting ion-exchange capacity.[114] Nevertheless, physicochemical characteristics of mesoporous silica materials, especially high specific surface area and uniform porosity, are particularly important for catalysis. These factors constitute the driving force staying behind the search for new methods of their activation for use in catalysis.

Functionalisation of ordered mesoporous silicas is usually based on catalytically active phase deposition on their surface. One of the most often used methods of mesoporous silicas modification is based on impregnation. Unfortunately, this method results in the formation of various forms of the active phase, from less to more aggregated species. Despite the fact that mesoporous molecular materials are characterised by a larger pore diameter than zeolites, the introduction of the high content of the catalytically active phase using the impregnation method may result in a partial clogging of the porous system. Another simple method of functionalising mesoporous silica materials is co-condensation, also termed as direct or one-pot synthesis.

Basically, the introduction of the active phase takes place at the stage of silica formation, by the addition of the catalytically active phase precursor into the synthesis gel. As a result, silica material with an active phase built into its walls is formed. In such case, the functionalised silica may be characterised by lower textural parameters in contrast to the pure silica mesoporous material.[111] The mentioned drop depends on the type and content of the active phase, especially in the case of larger metal loadings. Silica materials functionalisation can be also performed using the following procedures: molecular designed dispersion (MDD), deposition of oligomeric metal species (DOMS) and template ion-exchange method (TIE).[9,115] The first method is based on selective grafting of metalorganic compounds on the silica surface. Thermal decomposition of grafted metalorganic complexes leads to the formation of well-dispersed monomeric metal cations.[116] The second method, DOMS, consists in anchoring on the silica surface suitable anionic organic species, which are capable to bind monomeric and oligomeric metal cations. As a result of the calcination of the materials prepared in this manner, it is possible to obtain a highly dispersed active phase deposited on silica surface.[117] The latter procedure, TIE, is based on an exchange of cationic surfactants in freshly prepared mesoporous silica (prior to the calcination) for metal cations.[118] In comparison to MDD and DOMS, the TIE method is much cheaper and faster and therefore the most promising method out of described approaches.[9]

The template ion-exchange (TIE) procedure was originally aimed for recovering surfactants from mesoporous silicas containing organic matrix.[119] However, its potential was quickly noticed and research on this method was directed towards using it to functionalise mesoporous silica materials by depositing various metals on their surface. According to scientific literature, it is possible to introduce selected metal species into MCM-41 type material *i.a.* Cu[118,120,121], Fe[118,122,123], or Mn[118,124,125]. In as-synthesized mesoporous silica sieves, the organic template in the form of cationic (S^+) or neutral (S^0) surfactant is attached to the silica framework electrostatically or via hydrogen bonding, respectively.[126] During the template ion-exchange procedure, the porous matrix is removed by extraction with appropriate solutions. In the case of a system containing neutral surfactant, it is sufficient to use an alcoholic solution, due to the nature of the surfactant-network interactions. Assuming the template is formed by positively charged surfactant molecules, its removal involves replacing the eluted S^+ particles with components allowing to balance of the negative charge of the lattice ($\equiv$Si$-$O$^-$).[122] This is the concept of using the TIE procedure to functionalise the silica materials obtained with the use of cationic surfactants. The basis of the TIE method is the possibility to exchange the organic matrix into metal cations by extraction in polar solutions containing the introduced active phase (Figure 1.15). The TIE method is only applicable for freshly synthesized, non-calcined, silica sieves. In the case of protons attaching to the ≡Si−O$^-$ groups (during calcination or exchange for hydrogen ions), the pore-forming organic template is removed and stable ≡Si−OH silanol groups are formed. The formed surface silanol groups do not exhibit ion-exchange properties.[82,118]

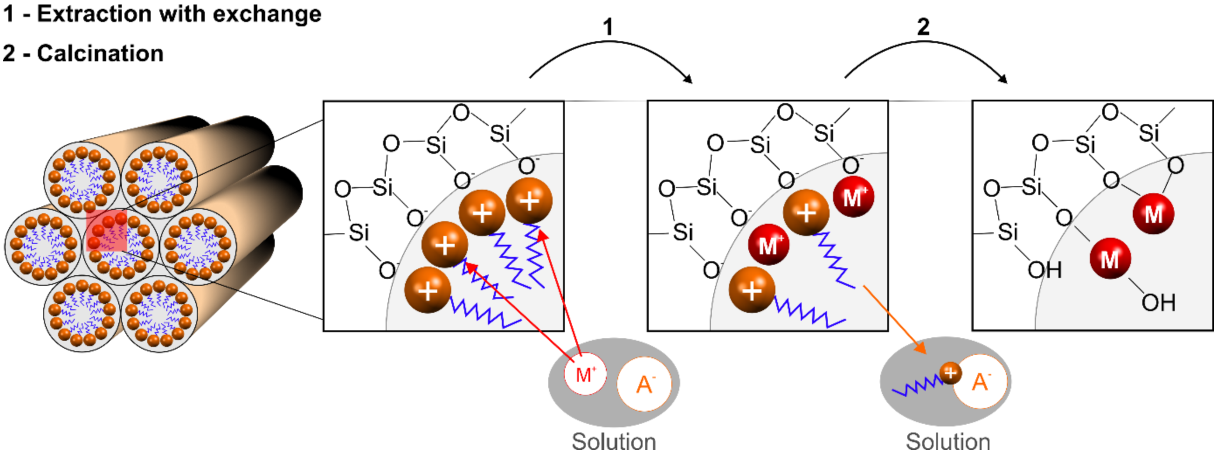

Figure 1.15 Schematic visualisation of the template ion-exchange (TIE) method conception (scheme inspired by the illustration from the reference[118]).

The template ion-exchange method most often leads to the deposition of high metal loadings, usually well dispersed on the surface of the support, in the form of monomeric cations and small metal oxide aggregates.[118,127] Using appropriate modification conditions (paying attention to chosen solvents, metal precursors and post-synthesis treatment), it is possible to control the form and aggregation of the introduced active phase. For instance, optimisation of the TIE procedure based on the replacement of water by methanol as the solvent for the copper salt resulted in improved dispersion of copper species.[82] Adjusting the form of metal introduction is correlated with the use of various types of its precursors (*e.g.*, monomeric or oligomeric cations of iron).[127] In turn, to control the aggregation of deposited species, the post TIE treatment of the samples with ammonia is necessary. Such modification of the TIE method leads to the deposition of copper into MCM-41 nearly exclusively in the form of monomeric cations of this metal.[82]

1.3.2 Catalysts for NH_3-SCR process based on porous silica systems

The effective conversion of nitrogen oxides depends on the form and type of the introduced catalytically active components. The deposition of a large amount of well-dispersed and homogeneous metal species is a crucial factor influencing the high catalytic efficiency of supported catalysts of the NH_3-SCR process. The enhanced NO_x conversion is related to the high availability of a large number of catalytically active species for reaction reagents, whereas their transformation into desired products can be correlated with the regular distribution of metal species. The choice of a particular catalytically active phase is certainly related to the specific temperature range of effective work of the catalytic system in the NH_3-SCR process. Among the various types of catalytically active phases, transition metals are considered to be the most promising in the process of selective catalytic reduction of NO_x with ammonia. Especially copper[67,82,128,129], iron[127,130,131] and manganese[83,132,133] deposited on porous silica carriers (zeolites and mesoporous silica sieves) have attracted considerable attention.

Copper modified porous silica catalysts

In general, copper-containing catalysts are considered to be suitable for the low-temperature NH_3-SCR process.[9,62] The high activity of Cu-modified samples may be correlated with the tendency of well-dispersed copper species to be reduced at relatively low-temperature region. Such copper species are considered to be catalytically active in the oxidation process of NO to NO_2, thus enabling the fast-SCR reaction (Eq. 1.6).[67] Święs *et al.*[67] and Liu *et al.*[134], postulated that Cu-exchanged zeolites promote the NO_2 formation, which could enhance the low-temperature NH_3-SCR process according to the fast-SCR pathway. In the fast-SCR process NO is activated by reactive oxygen molecules on the catalyst surface, to form NO_2. In the next step, NO_2 is transformed into nitrate and nitrite species. The produced reactive surface N-derivatives interact with coordinated NH_3 molecule to form NH_4NO_2 and NH_4NO_3. Subsequently, ammonium nitrite (NH_4NO_2), easily decomposes to generate dinitrogen and water, while NH_4NO_3 upon decomposition may produce N_2O. NH_4NO_3 can be also reduced by nitrogen(II) oxide to NH_4NO_2 and further decomposed into the desired products.[135]

Święs *et al.* studied the modified layered ferrierite (FER) derivatives with various Si/Al molar ratios (Si/Al = 30 or 50) modified with copper by the ion-exchange method.[67] The obtained samples exhibited high catalytic activity in the NH_3-SCR process, depending on the active phase form and loading as well as the porous structure of the used support. In the case of microporous Cu-doped 3D-zeolites, copper was introduced mainly in the form of aggregated species, located on the external surface of the FER framework. In the case of more open FER structures, both silica pillared (ITQ-36) and delaminated (ITQ-6), the diffusion limitations of active phase precursor were decreased, which allowed for the deposition of copper in more dispersed forms, possibly also inside the narrow channels. The catalysts obtained by Święs *et al.*[67] differed also in the content of catalytically active components. These properties, connected with both the porosity of the systems and their elemental composition, were correlated with the catalytic performance of modified zeolites in the NH_3-SCR process. Within one series of the same Si/Al ratio, the samples with copper doped, the micro-mesoporous zeolites were more catalytically active compared to catalysts based on 3D-ferrierite. The selectivity to dinitrogen, considered as the desired NH_3-SCR product, in the case of all tested catalysts was very high (over 97%). The differences in the catalytic activity of the samples can be related to the form of copper that was introduced. In the case of catalysts with bi-modal porosity, ITQ-36 and ITQ-6, copper is present mainly in highly dispersed form while for the microporous ferrierite zeolite significant contribution of more aggregated copper oxide species was found. It was postulated[67] that the enhanced catalytic performance of micro-mesoporous FER-derivatives is attributed to the higher activity of monomeric copper cations in NO to NO_2 oxidation in comparison to copper oxide species, thus facilitating the fast-SCR process.

Rutkowska *et al.*[136] reported the catalytic activity of zeolites of the layered MWW family with the intended Si/Al molar ratio of 15. The samples were modified with copper by the ion-exchange method. The studied copper doped catalysts were obtained by delamination (ITQ-2) and silica intercalation (MCM-36) of the zeolite precursor. Functionalisation of the MWW-derivatives with copper resulted in the introduction of 4.6-7.5 wt% of this metal, deposited mainly in form of monomeric copper cations. The catalytic activity of all studied samples in the NH_3-SCR reaction was comparable. The NO conversion above 90% was achieved in the range of 200-550°C for microporous MCM-22. For pillared MCM-36 and delaminated ITQ-2 forms of zeolite, nearly the same conversion level was reached. The side process of direct ammonia oxidation decreased the efficiency of the NH_3-SCR process at higher temperatures.[136] The high resistance for water vapour is an important advantage of copper-dopped MCM-22 and ITQ-2 zeolites. Their catalytic activity did not change significantly after the hydrothermal treatment.[136] This makes the tested catalysts an interesting alternative to use in industrial conditions. Especially considering their wide range of effective work (200-500°C) compared to the commercial V_2O_5-TiO_2 catalytic system that capably operates at 300-400°C.[64]

Chen *et al.*[129] tested Cu-modified microporous MCM-22 obtained by the incipient wetness impregnation method in the NH_3-SCR process. The intended Si/Al ratio of the studied samples was 15, while the copper content was in the range of 2.1-10.4 wt%. Copper was introduced into the samples in the form of monomeric, but also in the form of more aggregated Cu_xO_y species – their contribution increased with an increase of metal loading (above 4 wt%). The sample with the lowest copper content, 2 wt%, exhibited the lowest activity in the NH_3-SCR process. The NO conversion above the level of 90% was achieved in the range of 230-420°C. The catalytic activity of the samples with copper loadings above 4 wt%, did not differ significantly, despite the differences in the active phase content. The NO conversion above the level of 90% was obtained in the range of about 180-400°C. It was postulated that the limited availability of redox copper centres for the reactants decreased the efficiency of the NH_3-SCR process, especially in the case of the catalysts containing significant amounts of copper in the form of bulky oxide aggregates. Thus, the balance between the content of catalytically active components and their dispersion was found to be extremely important in terms of the effective NH_3-SCR catalyst's design.

Another interesting group of the NH_3-SCR catalysts are silica porous materials loaded with copper. Qiu *et al.*[137] verified the catalytic performance of the Cu-doped MCM-41 samples in the process of selective catalytic reduction of NO with NH_3. The authors prepared two series of the Cu-functionalised MCM-41 supports by (i) hydrothermal and (ii) wet impregnation methods. The obtained samples differed in copper content, which was in the range of 1-16.7 wt% in the case of hydrothermally treated series, while for impregnated catalyst the copper loading was 3.5 and 10.3 wt%. In both series, the contribution of aggregated copper species became dominant with an increase in metal content. The dispersion of the active phase in the catalysts with copper incorporated into silica walls was higher than in the impregnated samples. However, in the case of hydrothermally synthesized samples, the porous silica structure was disturbed and this effect was more distinct for the samples with the increasing copper content. In general, the catalytic activity of the studied samples increased along with the rising content of the active phase. Noteworthy is the better catalytic performance of catalysts obtained by copper incorporation into the framework of MCM-41 in comparison to the impregnated series. It may be explained by a large proportion of copper, most likely present on the catalyst surface in the form of large oxide aggregates (10-20 nm) in the case of impregnated mesoporous silicas.

Liu and Teng[120] reported an interesting comparison of Cu-modified MCM-41 by various functionalisation methods, including template-ion exchange, dry impregnation and ion-exchange. Catalytic tests of the NH_3-SCR process indicated the higher catalytic activity of the samples modified by the ion-exchange method, especially at temperatures lower than 350°C. The higher catalytic performance of the samples modified by the ion-exchange method was correlated with the smaller Cu_xO_y aggregates in this series of the catalysts compared to the more aggregated copper oxide forms introduced by two other approaches. It was shown that copper oxide species contain both Cu^{2+} and Cu^+, whereas in the case of the ion-exchange modified catalysts the presence of Cu^+ is slightly more dominant. Due to the higher activity of Cu^+ cations than Cu^{2+} in catalytic reduction of NO, the higher conversion of nitrogen(II) oxide over the ion-exchanged samples was postulated.[120]

Kowalczyk *et al.*[82] described the modified template ion-exchange method involving the procedure of controlled deposition of copper species on cylindrical MCM-41. The change proposed by authors included the use of methanol in the role of a solvent for the preparation of the active phase solution applied for the TIE procedure. The gradual substitution of methanol in place of water resulted in an increasing contribution of copper in more dispersed forms. The subsequent adaptation of the TIE method consisted in treating of the Cu-modified samples with an aqueous ammonia solution directly after the template ion-exchange process. The use of $NH_3{\cdot}H_2O$ solution was intended to cause complexation of the support-anchored copper ions leading to the limitation of their excessive aggregation. The application of the post-synthesis ammonia treatment resulted in high loading of metal, 12.9 wt%, mainly in the form of monomeric copper cations. The sample with the highest copper content showed the best catalytic activity in a series of MCM-41 catalysts doped with copper. The catalytic reaction started at 125°C and the NO conversion exceeded 90% in the temperature range of 200-300°C with a very high selectivity to dinitrogen - above 98%.

In conclusion, porous silica systems doped with copper have been intensively studied in the role of the catalysts for the NH_3-SCR process. Copper, as a catalytically active phase, can be undoubtedly considered as a component facilitating the low-temperature conversion of nitrogen(II) oxide. However, copper content and its form are crucial factors determining its usefulness for the application in selective catalytic reduction of NO with NH_3. Predominantly, the activity of catalysts is dependent on the copper loading and its increasing content enhances their efficiency in the NO conversion. However, due to the tendency of copper to aggregate, especially at high concentrations, the efficiency of the NH_3-SCR process may be significantly limited. Thus, the careful design of the catalytic systems providing high-loaded and well-dispersed copper active phase, mainly in the form of monomeric cations, is the key strategy to obtain effective catalysts of the low-temperature NH_3-SCR process. Another important issue in the tailoring of copper-based catalysts is the choice of suitable catalytic support, allowing the introduction of the active phase in an appropriate amount and form. Porous silica supports with a more open structure, like micro-mesoporous zeolites and mesoporous silica sieves, are well tailored to this purpose. Therefore, it must be pointed out that the direction of study focused on shifting the temperature window towards the lower temperatures with the use of copper-modified supported catalysts is contemporary in the field of environmental catalysis.

Iron modified porous silica catalysts

Among the new emerging NH_3-SCR catalytic systems many efforts have been focused on the iron promoted silica porous samples. In general, Fe-doped catalysts are considered to work efficiently over a higher temperature range in comparison to the Cu-containing catalysts. Their main activity, observed at high temperatures, is presumably related to the redox properties of Fe-species that need higher temperatures to be reduced compared to Cu-species.[62] The course of the SCR reaction at high temperatures over iron-containing catalysts probably consists in the dissociative adsorption of O_2 molecules on Fe_xO_y species to form reactive oxygen, which supports dehydrogenation of adsorbed ammonia resulting in the surface NH_2 groups. The NH_2 species interacts with nitrogen(II) oxide present in the gas phase to produce NH_2NO. The generated NH_2NO active complex decomposes and results in the reaction products - N_2 and H_2O.[138] However, at lower temperatures, Fe-containing species may direct the NH_3-SCR reaction into a different way. It also requires active monomeric oxygen species for the generation of NO_2 molecules from NO adsorbed on the surface. Subsequently, the fast-SCR reaction (Eq. 1.6) is possible on the surface of the catalyst.[138,139]

Chen *et al.*[130] reported the studies related to the catalytic activity of iron modified zeolites of the MWW family in the NH_3-SCR process. The samples with a similar Fe-content (4.4–4.8 wt %) were obtained using various methods including one-pot synthesis, ion-exchange, dry impregnation and mechanical mixing. Among the studied catalysts, the Fe-containing samples obtained by direct synthesis exhibited enhanced NO conversion in the wide temperature range of 200-500°C, with selectivity to N_2 of above 97%. The other studied catalysts were found to be less catalytically active in the NH_3-SCR process. The one-pot synthesised sample was characterised by the higher concentrations of isolated and dimer iron species than larger Fe_2O_3 nanoparticles in a series of the studied samples.[130] It was postulated that such distribution of iron species forms guarantees the enhanced activity in the NH_3-SCR reaction. Especially the presence of dimer iron sites, which are playing an important role in the formation of NO_2. The generation of NO_2 molecules was analysed over two catalysts of the series, one-pot synthesized and impregnated, indicating the better NO oxidizing properties of material obtained by the direct method. Thus, the facilitated formation of NO_2 on the catalyst with a higher contribution of well-dispersed dimer Fe^{3+} species may enable the fast-SCR pathway and therefore increase the efficiency of the NO reduction at lower temperature.

Rutkowska *et al.*[136], apart from micro-mesoporous derivatives with MWW topology doped with copper, tested iron-modified zeolites, microporous MCM-22 and delaminated ITQ-2 in the role of the NH_3-SCR catalysts. In comparison with the Cu-containing catalysts, iron-modified layered zeolites were less active in the NH_3-SCR process. The dissimilarities in catalytic activity between those two series were correlated with the differences in copper and iron loadings in the samples. The NO conversion on the level of 90% for Fe-MCM-22 and Fe-ITQ-2 catalysts was obtained in the range of 300-550°C and 350-500°C, respectively. What is more, the selectivity to the desired reaction product, dinitrogen, was maintained at a high level in the entire temperature range of the reaction being carried out. The impact of the form of the deposited iron species on the catalytic activity of the studied samples was significant. In the case of the Fe-MCM-22 sample, iron was introduced partly in the form of small iron oxide species, while for the Fe-ITQ-2 nearly exclusively in the form of monomeric iron cations. Thus, possibly due to the presence of the larger amount of oligomeric iron species, Fe-loaded microporous zeolite exhibited the higher NO conversion in the low-temperature range in comparison to its delaminated analogue. These observations stay in line with the Chen *et al.*[130] reports.

Li *et al.*[140] presented studies of iron-loaded MCM-41 materials in the role of the NH_3-SCR catalysts. The samples, differing in the Fe/Si molar ratio from 0.02 to 0.1, were obtained by hydrothermal treatment using coal-series kaolin as the precursor of mesoporous support. The increased NO conversion of Fe-doped MCM-41 was observed for the samples with an increasing content of the active phase until reaching the Fe/Si ratio of 0.05. For the catalysts with higher iron loadings, the distortion of the ordered porous structure and reduction of the concentration of catalytic centres were detected. The decrease in the textural parameters, as well as the acidic properties of the studied samples, were reflected in their catalytic performance in the NH_3-SCR process. The catalytic reaction started at about 200°C, reaching the maximum (about 90%) at 350°C for the most active catalyst (with the Fe/Si of 0.05). The samples with the higher iron content were less active, even in comparison to the catalysts with the lowest iron doping. The decrease of the NO conversion for these iron-rich catalysts was related to the formation of aggregated iron oxide species on the external surface of the catalyst and inside mesopores. Such bulky Fe_xO_y clusters may block the availability of surface acid sites and thereby reducing the catalytic activity.

Kowalczyk *et al.*[127] examined the selective catalytic reduction of NO with ammonia over cylindrical MCM-41 (pure silica and titania-containing) doped with iron. Iron in the form of monomeric cations ($FeCl_2$ used as iron precursor) but also as three-centred oligocations (Fe3 = $[Fe_3(OCOCH_3)_7 \cdot OH \cdot 2H_2O]NO_3$ used as iron precursor) was introduced into MCM-41 supports by the template-ion exchange method. The use of various precursors of the active phase resulted in the formation of iron active species of different aggregation. As a result of $FeCl_2$ use, iron was present mainly in the form of monomeric cations, while in the case of using Fe3 oligocations in addition to well-dispersed cations, also iron oxide-rods located outside of the mesoporous MCM-41 framework were identified. The obtained samples were found to be active catalysts of the NH_3-SCR process. The clear influence of the used support on the catalyst's operation was not found. The studied catalysts were characterised by a very high selectivity to dinitrogen. For the most active catalysts, the NO conversion above 90% was achieved in the temperature range of 350-450°C and 325-375°C for the samples modified with iron cations and oligocations, respectively. The increased catalytic activity of the samples containing well-dispersed iron forms at higher temperatures in comparison to the catalysts containing aggregated bulky iron oxide species was observed. Such Fe_2O_3 crystallites promote direct ammonia oxidation at higher temperatures, thus influencing the observed decrease of the NO conversion in this temperature region.

Li *et al.*[141] tested catalysts based on SBA-15 modified with iron and manganese and their bimetallic system by incipient wetness impregnation method in the NH_3-SCR process. The metal loading in the case of deposition of single metal was equal to 22 wt%, while for the Fe-Mn-SBA-15 sample, the content of each metal was approximately 11 wt%. High-alumina fly ash was used for the preparation of catalyst support. The obtained SBA-15 silica was characterised by an ordered hexagonal pore structure, which was partially disturbed after deposition of the catalytically active components. The transition metal modified silicas were catalytically active in the low-temperature range (100-350°C). The catalytic activity of monometallic catalysts, containing iron or manganese, is lower compared to the Fe-Mn-SBA-15 system. The Mn-SBA-15 sample is more active in the lower temperature range (below 250°C), while in the case of Fe-SBA-15, the NO conversion increased at elevated temperatures (above 250°C), reaching 90% at 350°C. For bimetallic catalyst, the maximum of the NO conversion, at the level of 90%, was achieved in the temperature range of 200-250°C. Therefore, the synergistic effect between Fe and Mn deposited on the SBA-15 was postulated. The increased catalytic activity of the bimetallic Fe-Mn-SBA-15 system in the NH_3-SCR process is observed owing to enhanced dispersion of iron oxide caused by manganese addition and formation of catalytically active β-MnO_2 phase stabilised by deposition of iron.

To summarize, porous silica supports modified with iron were reported to be low- or high-temperature catalysts of the NH_3-SCR process. The temperature range of their effective operation strictly depends on the form of deposited iron species and can be promoted by the addition of other components *e.g.*, manganese. The general trend shows the increase of their catalytic activity with increasing content of the active phase. However, the high amount of iron leads to the formation of iron oxide clusters, which exhibit the enhanced activity of the side reaction of direct ammonia oxidation by oxygen present in the gas mixture. The effect of reducing agent consumption limits the efficiency of the Fe-loaded catalysts in the high-temperature NH_3-SCR process.

Manganese modified porous silica catalysts

As was already mentioned, manganese is reported to be catalytically active in the low-temperature NH_3-SCR process. Manganese may be present in various oxidation states, including Mn^{2+}, Mn^{3+} and Mn^{4+}. According to scientific reports, the low-temperature activity of manganese oxides in the range of 110-300°C increases in the following order: $MnO < Mn_3O_4 < Mn_2O_3 < Mn_5O_8 < MnO_2$.[142] The high activity of Mn^{4+} in the NH_3-SCR process is assigned to its promotional effect influencing NO to NO_2 oxidation. The formation of reactive nitrogen(IV) oxide is necessary for the fast-SCR reaction (Eq. 1.6) postulated as a process responsible for the increased activity of the NO_x conversion at lower temperatures.[66,67,142] In the presence of the manganese species with high valence state (*e.g.*, Mn^{4+}), the oxidation of adsorbed NO is possible by lattice oxygen. Possibly such adsorption is associated with the reduction of Mn^{4+} to the lower valence states, such as Mn^{3+} or Mn^{2+}.[9] On the other hand, such adsorbed NO molecule is oxidised to NO_2 by oxygen from the gas phase. The formed NO_2 is transformed into surface nitrites and nitrates, which reacts with ammonia and then decomposes into the desired NH_3-SCR reaction products (N_2 and H_2O).[142] Moreover, it was reported that other manganese oxides (*e.g.*, Mn_2O_3) can participate in the NH_3-SCR reaction by the formation of coordinated ammonia molecules and adsorbed NO in the form of various nitrite and nitrosyl species on different active sites.[143] Thus, the catalytic activity of manganese doped into porous silica systems should be carefully analysed regarding the manganese valence state playing a different role in the mechanism of the NH_3-SCR process.

Yu *et al.*[144] studied the NO conversion over MnO_x/SAPO-34 (SAPO-34 - microporous molecular sieve with the chabazite structure) catalytic systems. The samples were prepared by two methods: (i) molecularly designed dispersion (MDD) and (ii) impregnation (IM). The manganese content in the samples of each series was about 7 and 13 wt%. The samples modified by the MDD method were catalytically active in the low-temperature NH_3-SCR process. The most active catalyst, containing about 13% of Mn, reached above 90% of the NO conversion at 175°C with high selectivity to dinitrogen, at the level of 95%. The increased NO conversion, as well as high selectivity of the reaction, remained at high levels up to 300°C. Slightly worse results of the catalytic tests were obtained for the sample containing lower manganese loading introduced by the MDD method. In this case, the NO conversion level of 95% was reached at about 230°C. The series of the impregnated samples were characterised by much worse catalytic activity in the NH_3-SCR process. The NO conversion level of 90% for the samples doped with about 7 wt% of manganese was obtained at above 250°C, while for the catalyst loaded with a higher amount of active phase such level of the NO conversion was not reached over the whole studied temperature range. The superior catalytic activity of Mn-MDD modified SAPO-34 support was correlated with its enhanced ability of NO to NO_2 oxidation, thus facilitating the fast-SCR reaction being a dominant mechanism in the low-temperature NH_3-SCR process. The increased catalytic activity of the most active catalysts was assigned to the high contribution of Mn^{4+} and Mn^{3+} cations, which in comparison to Mn^{2+}, are preferable in the promoting of the NH_3-SCR reaction. In the case of impregnated series of the catalysts, the tendency to metal sintering on the surface of the catalyst caused difficult access to the active phase for the reaction reagents, which decreased their catalytic activity.[144]

Baran *et al.*[145] reported the NH_3-SCR catalytic performance of Mn-modified Si- and Al-BEA zeolites. The manganese content differed between 1–4 wt% for the Mn_x-Si-BEA series, while for the Mn-Al-BEA was equal to 1.9 wt%. The catalytic activity of the obtained samples was studied in the temperature range of 150-500°C, indicating the enhanced NO conversion in the low-temperature (90% of NO conversion at 200-300°C), for the sample with the highest manganese loading - Mn_4-Si-BEA. In this sample, polynuclear extra-framework species, responsible for the high NO conversion at low temperatures were identified.[145] A sharp drop in the NO conversion, observed for this catalyst above 300°C, is probably related to the side reaction of ammonia oxidation at elevated temperatures, which was accelerated by bulky manganese oxide clusters.[145] This side process was reflected in the selectivity to N_2, which gradually decreased from the level above 95% at 350°C to below 10% at 500°C. The other samples of the Mn_x-Si-BEA series effectively operated at higher temperatures (above 250°C), although with the improved selectivity to dinitrogen. In the case of these samples, manganese was introduced mainly in the form of Mn^{2+} and Mn^{3+}, indicating a strong effect of manganese oxidation states on the catalytic activity. The Mn-Al-BEA catalyst was found to be the less active in the series of the tested catalysts. The maximum of the NO conversion at the level of about 80% was achieved in the temperature range of 450-500°C. However, this catalyst was characterised by the highest selectivity to dinitrogen, which did not drop below 95%, probably due to the protective function of aluminium preventing direct ammonia oxidation as a side reaction of the NH_3-SCR process.[145]

Li *et al.*[83] tested catalytic activity of MCM-41 obtained by the hydrothermal method and subsequently modified with 7 wt% of Mn by impregnation method in NH_3-SCR. Additionally, mesoporous silica support was impregnated with $Al(NO_3)_3 \cdot 9H_2O$ to obtain the intended 1, 3 and 5 wt% of aluminium content. The Al-containing MCM-41 was also impregnated with manganese salt with the intended 7 wt% of manganese loading. The real metal contents were slightly lower than the planned loadings, both in the case of aluminium and manganese. The XRD analysis proved that deposition of the manganese did not destroy the well-ordered hexagonal mesoporous structure of MCM-41. In the case of Mn-Al-modified silica, the intensity of XRD (100) reflection is reduced, especially for the highest aluminium loading, pointing out that a part of aluminium may be located inside pores. The NO conversion on the level 100% in the low-temperature range of 200-300°C, with the selectivity to dinitrogen above 90% was obtained for the Mn-MCM-41 catalyst. Introduction of aluminium to the catalytic support not only extended the range of effective work of the catalysts to 380°C but also improved their selectivity to N_2. The sample with a medium aluminium content, with an intended loading of 3 wt%, effectively operated with 100% of the NO conversion up to 400°C. The only exception was the sample with the highest aluminium content, characterised by the worst catalytic performance, both in terms of the NO conversion and selectivity to dinitrogen, within the Mn-Al-MCM-41 series. These results are possibly related to the clogging of the MCM-41 channels by alumina deposited during the impregnation step, limiting the access of reactants to the active sites. However, the appropriate amount of aluminium can enhance the redox activity of manganese oxides resulting in the increased catalytic activity of porous silica systems in the NH_3-SCR process.[83]

Concluding, the Mn-modified silica porous systems are promising catalysts for the application in the low-temperature NH_3-SCR process. However, their catalytic performance strictly depends on the form of deposited manganese species. Due to the various oxidation states varying in the ability to efficiently convert NO in the low-temperature range. The efficiency of the Mn-doped catalysts is directly related to the capability of NO to NO_2 oxidation, which is considered as a crucial step of their low-temperature activity. The presence of additional acid sites, due to the presence of aluminium, promotes the catalytic activity of the manganese loaded samples, as well as improves their selectivity to dinitrogen.

2. Aims and scope of the research

The main goal of the studies was the synthesis of active, selective and stable catalysts based on porous silica materials for the process of selective catalytic reduction of NO with ammonia (NH_3-SCR). The obtained catalysts were designed for the application in the temperature range, where the commercial V_2O_5-TiO_2 system is insufficient, below 300°C and above 400°C. The motivation of the studies has been necessity of the catalysts operating in the low-temperature range of the NO conversion needed for retrofitting of the existing stationary NH_3-SCR installations for operation with low-dust flue gases. On the other hand, the catalysts designed for high-temperature NH_3-SCR should be less active in the side reaction of direct ammonia oxidation.

To reach these goals the porous catalytic supports of different morphology were modified with selected transition metals deposited by different methods. The following groups of the catalytic systems were included in the presented studies: (i) microporous MCM-22 zeolite and its silica and silica-titania intercalated derivatives modified with Fe; (ii) spherical MCM-41 loaded with Cu or Fe obtained by the co-condensation approach; (iii) spherical Si-MCM-41 and Si-Al-MCM-41 modified with Cu by the TIE method and its modified version including ammonia treatment; (iv) MCM-41 with the cylindrical or spherical morphology functionalised with iron in the form of monomeric cations and trinuclear-iron-acetate oligocations deposited by the TIE method; (v) spherical MCM-41 doped with Cu, Fe or Mn and their bimetallic systems deposited by the TIE method.

The obtained materials were physicochemically characterised with respect to their chemical composition (ICP-OES), structure (XRD), textural parameters (low-temperature N_2 sorption), morphology (SEM), oxidation state and aggregation of deposited transition metals (UV-vis DR, FT-IR, Raman spectroscopies), reducibility of transition metal species (H_2-TPR), surface acidity (FT-IR with Py-adsorption, NH_3-TPD) and thermal stability (TGA). The obtained samples were tested in the role of catalysts for the NH_3-SCR process in flow microreactor system. Moreover, the reactions associated with the NH_3-SCR process, such as NO to NO_2 oxidation, N_2O decomposition and ammonia oxidation were studied. For the selected, most promising catalysts, the long-term stability NH_3-SCR tests, as well as catalytic study in the presence of water, were done.

3. List of publications constituting the doctoral thesis

The number of manuscripts included in the doctoral thesis: **6**.
Five publications (**P1 – P5**) have been published in high impact scientific journals indexed by JCR, while manuscript (**P6**) is currently under review.
All journals are indexed by JCR, (**P1 – P5**) total impact factor 2020 (IF): **27.16**, the average impact factor 2020 (IF): **5.43**.

PUBLICATION 1 (P1)

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Barbara Gil, Lucjan Chmielarz*
Title: Silica and silica-titania intercalated MCM-36 modified with iron as catalysts for selective reduction of nitrogen oxides – the role of associated reactions
Catalysis Science and Technology, 2020, **10**, 7940-7954 (IF= 6.119)

PUBLICATION 2 (P2)

Authors: Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Shiquan Liu*, Lucjan Chmielarz*
Title: Catalytic performance of spherical MCM-41 modified with copper and iron as catalysts of NH_3-SCR process
Molecules, 2020, **25**, 5651 (IF= 4.412)

PUBLICATION 3 (P3)

Authors: Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Marek Michalik, Shiquan Liu*, Lucjan Chmielarz*
Title: Enhanced catalytic performance in low-temperature NH_3-SCR process of spherical MCM-41 modified with Cu by template ion-exchange and ammonia treatment
Microporous and Mesoporous Materials, 2021, **315**, 110920 (IF= 5.455)

PUBLICATION 4 (P4)

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Lucjan Chmielarz*
Title: Spherical Al-MCM-41 doped with copper by modified TIE method as effective catalyst for low-temperature NH_3-SCR
Molecules, 2021, **26**, 1807 (IF= 4.412)

PUBLICATION 5 (P5)

Authors: Aleksandra Jankowska, Justyna Ciuba, Andrzej Kowalczyk, Małgorzata Rutkowska, Zofia Piwowarska, Marek Michalik, Lucjan Chmielarz*

Title: Mesoporous silicas of MCM-41 type modified with iron species by template ion-exchange method as catalysts for the high-temperature NH_3-SCR process – Role of iron species aggregation, silica morphology and associated reactions

Catalysis Today, 2022, **390-391**, 281-294 (IF= 6.766)

MANUSCRIPT 6 (P6)

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Lucjan Chmielarz*

Title: Catalytic performance of bimetallic systems (Cu-Fe, Cu-Mn, Fe-Mn) based on spherical MCM-41 modified by template ion-exchange in NH_3-SCR process

Journal of Porous Materials, manuscript under review (IF= 2.496)

4. Description of catalytic tests

Catalytic experiments of a selective catalytic reduction of NO with ammonia (NH_3-SCR), as well as accompanied reactions including NO to NO_2 oxidation, N_2O decomposition and ammonia oxidation (NH_3-SCO), were performed in a flow fixed-bed quartz microreactor (Figure 4.1). For each experiment, 100 mg of catalyst, with a particle size in the range of 160-315 μm, was placed on a layer of quartz wool mounted on insets in the middle of the microreactor length. The temperature of the catalyst during reaction was measured with a thermocouple inserted directly into its bed (protected by quartz capillary). The reaction gasses were supplied to the microreactor using mass flow controllers. The composition of outlet gasses was analysed using detection systems - mass spectrometer (with quadrupole analyser, QMS), gas chromatograph (GC equipped with TCD detector) or a FT-IR spectrometer (with a gas cell of 10 cm length) depending on the type of catalytic study. The schematic presentation of the elements of the catalytic system used in the catalytic tests is shown in Figure 4.2.

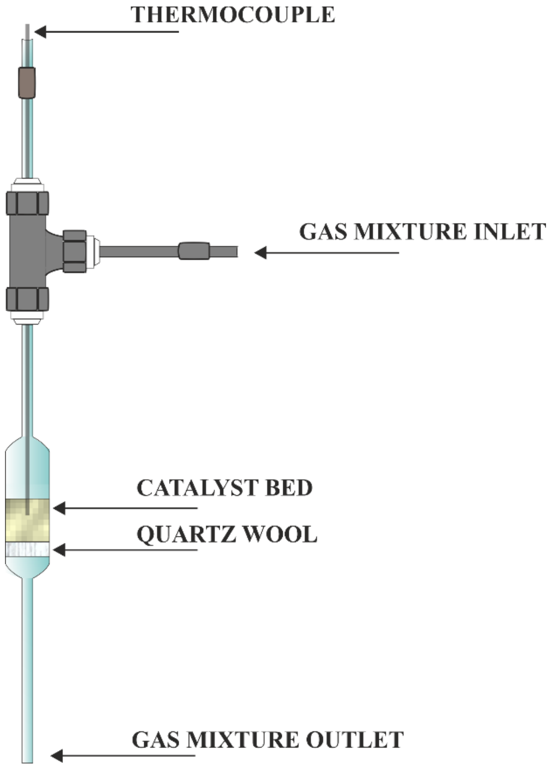

Figure 4.1 Scheme of flow fixed-bed quartz microreactor used for the catalytic tests.

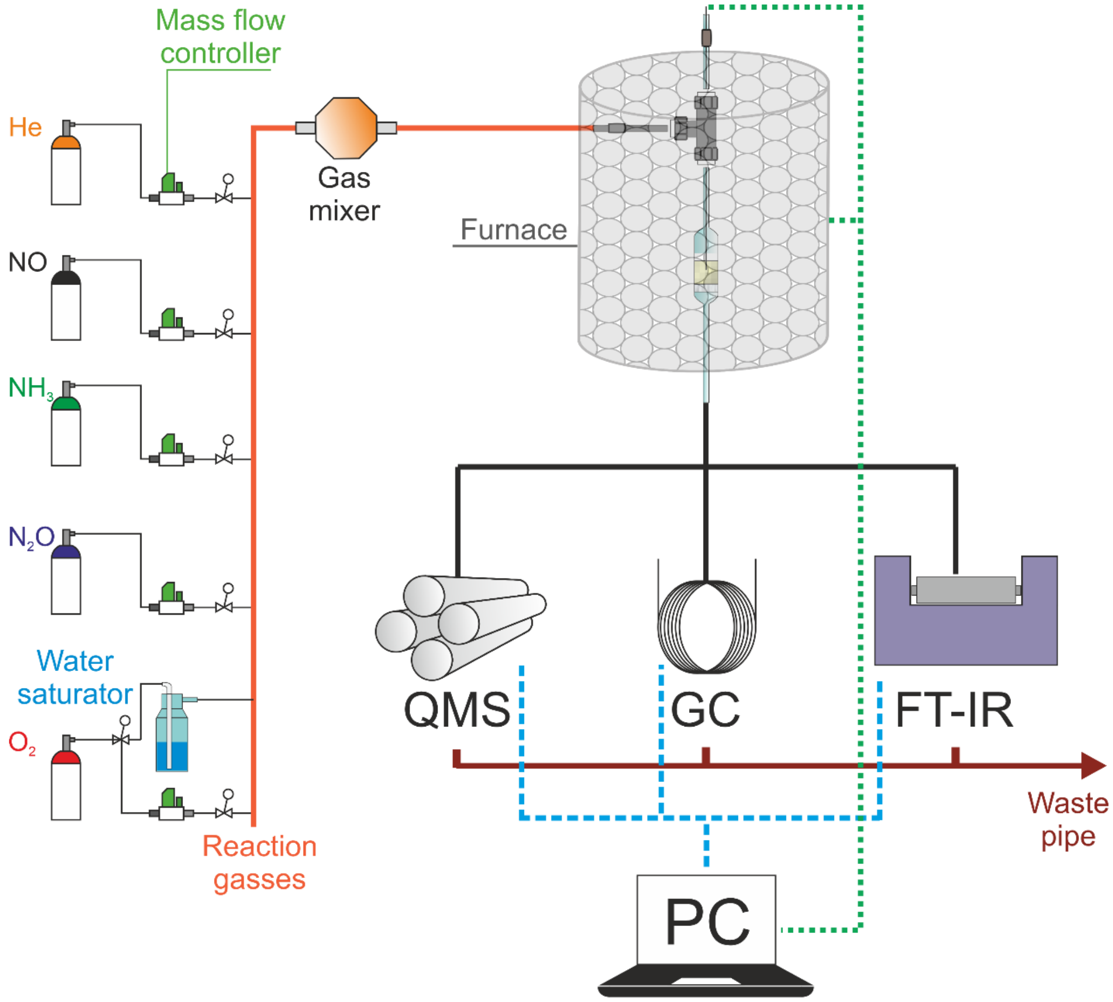

Figure 4.2 Schematic representation of the apparatus for the catalytic tests.

Prior to each catalytic test, catalyst placed in the microreactor was outgassed in a flow of pure helium (purity grade 5.0). The gas mixture, used for the NH_3-SCR reaction, contained: 0.25 vol% NO, 0.25 vol% NH_3 and 2.5 vol% O_2 diluted in helium, with a total flow rate of 40 mL/min. The more detailed description of catalytic parameters, as well as the composition of the gas mixture used for the analysis of associated reactions (NO oxidation, N_2O decomposition and NH_3-SCO), is presented in the manuscripts (**P1-P6**).

The NO conversion (α_{NO}) in the NH_3-SCR process was determined using the following equation (Eq. 4.1):

$$(Eq.\ 4.1)\ \alpha_{NO}[\%] = \frac{C_{NO}^{0} - C_{NO}}{C_{NO}^{0}}\ x\ 100\%,$$

where: C_{NO}^{0} – concentration of NO in inlet gases; C_{NO} – concentration of NO in outlet gases.

The selectivity toward desired NH_3-SCR reaction product (dinitrogen) was calculated including all emerging N-containing components, especially N_2 and N_2O. For this purpose, the following equation (Eq. 4.2) was applied:

(*Eq. 4.2*) $S_{N_2}[\%] = \frac{C_{N_2}}{C_{N_2} + C_{N_2O}} \; x \; 100\%,$

where: C_{N_2} and C_{N_2O} – concentrations of dinitrogen and nitrous oxide in outlet gases, respectively.

5. Summary of results obtained within the frame of publications

5.1 Publication P1

The studies focused on designing novel catalytic systems for the NH_3-SCR process with the extended temperature window of the effective NO conversion should consider various factors influencing their overall catalytic performance. The final efficiency of the NH_3-SCR process is composed of mutually dependent reactions, which may increase or decrease its effectiveness. Therefore, apart from the analysis of the NH_3-SCR process, also the studies of possible accompanying reactions should be considered. One of the most important processes influencing the NH_3-SCR performance, which should be taken into account, is the possible oxidation of NO to NO_2. The formation of nitrogen(IV) oxide is necessary for the fast-SCR reaction, which is one of the low-temperature ways of the NO_x conversion.[66] In turn, at higher temperatures, the efficiency of NO removal may be negatively influenced by the side reaction of direct ammonia oxidation, which results in a decrease of nitrogen(II) oxide reduction but also may cause the formation of N-derived by-products, including N_2O. Thus, the catalyst operating in the high-temperature regime should be inactive in direct ammonia oxidation. What is more, the discussion concerning the overall NH_3-SCR catalytic performance should include the selectivity to the desired product (N_2). The NH_3-SCR process may lead to unfavourable products, *e.g.*, nitrogen(I) oxide. Therefore, in the case of non-selective NH_3-SCR, or when ammonia oxidation to nitrogen oxides becomes dominant, it is extremely important to design catalysts, which could prevent the formation of N_2O. Hence, the idea of the **P1** publication presents a study of the NH_3-SCR process and its associated reactions over Fe-modified layered zeolites of the MWW framework type. The choice of the catalytic support was determined by the possibilities of its post-synthesis modification. The material with a bimodal porous structure, which could be obtained from 2D MWW precursor, facilitates the mass transfer of reagents during the catalytic reaction and increases their accessibility to active sites located in the interlayer voids.[136]

In the frame of the discussed publication **P1**, microporous MCM-22 and its pillared silica and silica-titania MCM-36 derivatives were obtained. In the next step, zeolitic materials were modified with iron by the ion-exchange method. The intention of the presented studies was the verification of the role of the porous structure of zeolitic supports on their performance in the NH_3-SCR process. Moreover, the modification of the composition of pillars, located between

MWW sheets, by introducing Ti-species into silica aggregates, generated additional acid sites. The obtained samples were characterised with respect to their chemical composition, structure, texture, acidic properties and reducibility of deposited iron species. The layered arrangement of the MCM-22 precursor and its intercalated derivatives, containing organic template in the interlayer space, was proved by the presence of (001) reflection in the diffractograms. The shift of this reflection position towards lower ranges of the 2θ angle for the pillared samples indicates an increase in d-spacing between MWW layers. For the Si-Ti intercalated samples, the interlayer distance decreased with an increase in titanium content. Moreover, after calcination process, the reflections corresponding to the layered stacking of the zeolite sheets disappeared, indicating the formation of delaminated structures with a non-parallel arrangement of the MWW layers. For all the studied samples, the (100) reflection remained unchanged, thus the internal structure of the MWW zeolitic layers was not disturbed by the applied post-synthesis treatments. The micro-mesoporous character of the obtained samples was proved by the analysis of the textural properties of the catalysts with bimodal porosity, showing an increased mesopore volume and decreased volume in the micropores range compared to 3D microporous MCM-22 material.

The UV-vis DR, Raman and H_2-TPR analyses indicate the presence of iron in the form of monomeric cations, as well as small aggregates of Fe_xO_y. The results of UV-vis DR and Raman analyses also confirmed the presence of tetrahedrally coordinated Ti^{4+} cations incorporated into silica pillars. In the case of the samples with higher titanium loading, additionally aggregated titanium species were identified. It is worth mentioning that in the case of the Fe-exchanged Ti-containing samples, Raman analysis indicated the presence of small aggregates of anatase. Such Ti-form was not detected for the Si-Ti pillared zeolitic supports. Presumably, as a result of the ion-exchange procedure used to introduce iron species, part of the titanium was extracted from pillars and deposited on the zeolite surface and subsequently transformed to anatase aggregates under calcination conditions.

The obtained Fe-modified samples, both microporous MCM-22 and its micro-mesoporous analogues with silica (MCM-36) and silica-titania (xTi-MCM-36) pillars, were active and selective catalysts of the NH_3-SCR process. The catalysts effectively operated up to about 475°C with the increasing NO conversion in the series: Fe-MCM-22 < Fe-MCM-36 < Fe-x-Ti-MCM-36. For the Ti-containing catalysts, the enhanced catalytic activity was observed with the increasing titanium content in the samples: Fe-1Ti-MCM-36 < Fe-5Ti-MCM-36 < Fe-10Ti-MCM-36. The NO conversion above the level of 90% was obtained for the microporous Fe-MCM-22, micro-mesoporous Fe-MCM-36 and the most active Fe-10Ti-MCM-36 in the ranges of 425-475, 400-475 and 350-475°C, respectively. Therefore, the more open structure of the catalysts with bimodal porosity, as well as the incorporation of titanium into silica pillars, catalytically activated zeolites towards operation at lower temperatures. The higher activity of the Si-Ti-pillared samples modified with iron is possibly correlated with their activity in the process of NO oxidation to NO_2, facilitating the fast-SCR reaction at lower temperatures. The presence of surface $\equiv Ti–O^-$ groups enables the bonding of NO_2 and their subsequent transformation to reactive nitrates, which easily react with NH_3 molecules. Titanium species may play a role of active sites in the NH_3-SCR reaction. When Ti^{4+} cations are reduced to Ti^{3+}, the conversion of surface nitrates by ammonia is possible.[146,147] The activating role of titanium may be also attributed to the improvement of the redox properties of Fe-species, by the formation of Ti–O–Fe groups enabling to oxidation of NO to NO_2.[148] The obtained catalysts effectively operate up to relatively high temperatures (475°C). Therefore, the other associated reactions, which may be dominant in this temperature range should be taken into account, *i.e.*, the formation of reactive surface O-species over Fe_2O_3 promoting the dehydrogenation of adsorbed NH_3 to $-NH_2$, which reacts with NO from gas-phase forming reaction products - N_2 and H_2O.[138]

It is worth to mention that besides NO to NO_2 oxidation, also other associated reactions affect the overall efficiency, in terms of activity and selectivity, of the NH_3-SCR process. The observed decrease of the NO conversion for all the studied Fe-MWW catalysts is most likely related to the competitive ammonia oxidation at higher temperatures, above 475°C. However, the activity of the iron-containing catalysts in the NH_3-SCO reaction is relatively low, therefore, the window of effective catalytic operation of the obtained materials is extended towards higher temperatures. The other important process influencing the catalytic efficiency, related to the selectivity to dinitrogen, is the reaction of N_2O decomposition. N_2O is the side product of NH_3-SCR. The nitrogen(I) oxide formed as a result of the non-selective NH_3-SCR process can be catalytically decomposed in the presence of well-dispersed iron species to N_2, thus improving the N_2-selectivity of the overall NH_3-SCR process. The schematic presentation of the influence of the reactions associated to the overall NH_3-SCR process for the Fe-MWW samples is presented in Figure 5.1. Concerning the possible future application of the Fe-MWW zeolites on a larger scale, the most promising sample, Fe-10Ti-MCM-36, was examined in the long-term NH_3-SCR stability tests in dry and dry-wet conditions. The sample was characterised by high catalytic stability in terms of activity (NO conversion) and selectivity to N_2. Regarding the results of polythermal and stability catalytic studies of the NH_3-SCR reaction, the synthesized materials can be considered as promising catalysts for the high-temperature NH_3-SCR process.

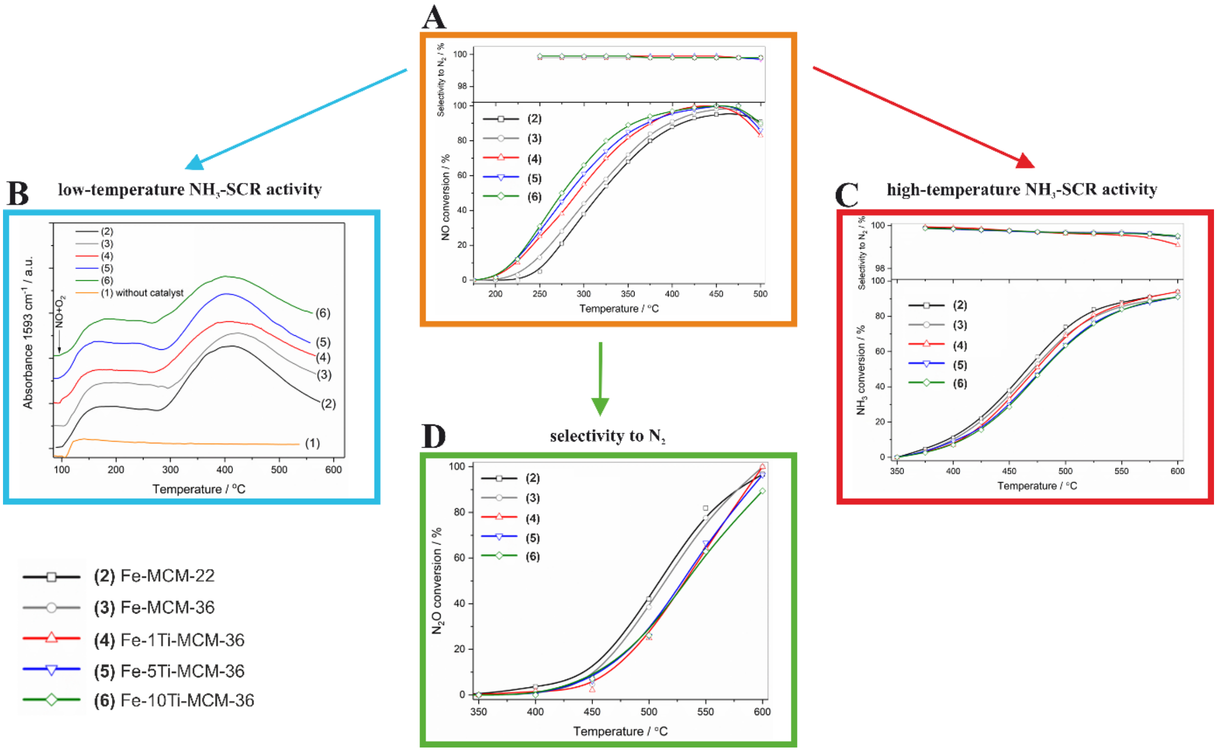

Figure 5.1 Schematic presentation of the influence of associated reactions on the overall NH_3-SCR efficiency of the Fe-MWW samples. (**A**) NH_3-SCR process; (**B**) NO to NO_2 oxidation process; (**C**) NH_3-SCO process; (**D**) N_2O decomposition process. Adapted from illustrations included in the article **P1**.

5.2 Publication P2

Mesoporous silica sieves, due to their porous and morphological characteristics, are very promising materials for various applications, including catalysis and adsorption. However, pure silica materials are catalytically inert, therefore their use in the role of catalysts dedicated for the conversion of nitrogen(II) oxide requires the introduction of catalytically active phase on their surfaces, usually in the form of transition metal species. One of the mesoporous silica materials modifications with metals is the co-condensation method. In this approach, the precursor of desired metal is added to the synthesis silica gel. In general, the distribution of the active phase in the final product is homogeneous, but larger metal loadings may influence the porous structure as well as the morphology of the formed material.[111] In this context, the publication **P2** describes the successful catalytic synthesis of copper and iron modified spherical MCM-41 materials obtained by the one-pot method, as catalysts of the NH_3-SCR process. To verify the efficiency of the synthesized catalysts in the high-temperature NH_3-SCR process, the possible competitive reaction of direct ammonia oxidation was studied. The issues related to the postulated NH_3-SCR and NH_3-SCO mechanisms involving ammonia chemisorption and activation on the surface of the catalysts were discussed in publication **P2**.[47,64]

The catalyst samples contained various loading of metal incorporated into the silica framework, 2.1 and 5.6 wt% for Cu and 1.1-9.8 wt% for Fe. In the case of the studied catalysts, their mesoporous character was maintained, although the higher loadings of transition metals noticeably decreased the textural parameters of the samples. Moreover, the influence of metal content on the spherical morphology of the synthesized MCM-41-based materials was also observed. The analysis of SEM images indicated a decrease in the size of silica spheres, as well as their sticking to form more aggregated, irregular arrangements, with an increase of copper or iron loadings (Figure 5.2).

The physicochemical properties of the obtained samples had a direct impact on their catalytic activity in the NH_3-SCR process. The Cu- and Fe-modified spherical MCM-41 samples presented a very promising NO conversion, dependent mainly on introduced metal. The copper-containing catalysts showed a very comparable catalytic activity, despite the different content of deposited copper and similar distribution of copper species. The NO conversion level of 90% was achieved at about 300°C with the selectivity to N_2 above 98%. Thus, copper active sites, depending on metal species aggregation, may exhibit different catalytic activity as indicated by the determined turn-over frequency (TOF) values at 250°C. For the sample with higher Cu-content (25Cu-MCM-41), the TOF value is lower than for the catalyst with lower copper loading (50Cu-MCM-41). Therefore, the 50Cu-MCM-41 sample is characterised by the higher average activity of a single active site in comparison to the silica sample with higher copper content. The iron-containing spherical MCM-41 catalysts exhibited relatively high NO conversion level in the wider and elevated temperature range in comparison to its copper analogues. For the most active sample of this series, 20Fe-MCM-41, the NO conversion above 90% with nearly 100% selectivity to dinitrogen was obtained in the range of 300-450°C. The samples with lower iron loadings, 50Fe-MCM-41 and 100Fe-MCM-41, exhibited decreased catalytic activity due to the lower content of the active phase. In the case of the 10Fe-MCM-41 sample, despite the higher iron content (9.8 wt%), the NO conversion was lower in comparison to the most active catalyst - 20Fe-MCM-41 (Fe content equal to 4.0 wt%). The results of the NH_3-SCR tests, obtained for the Cu- and Fe-modified silicas are presented in Figure 5.2. The decreased catalytic activity of the 10Fe-MCM-41 sample is probably correlated with the hindered access of the reactants to aggregated iron species located on silica spheres. For both series, Cu- and Fe-modified spherical MCM-41, the efficiency of the NH_3-SCR process decreased above 300°C and 375-450°C, respectively. The observed drop in the NO conversion relates to the secondary process of direct ammonia oxidation by oxygen being a component of the reaction gasses mixture.

The reactivity of ammonia molecules chemisorbed on the catalyst surface in NH_3-SCR and ammonia oxidation was verified by temperature-programmed surface reactions. The surface-adsorbed ammonia molecules were desorbed by increasing reaction temperature in the flow of gas mixture containing $NO+O_2$ diluted in helium or O_2 diluted in helium for the NH_3-SCR process and for ammonia oxidation, respectively. The analyses of the mass to charge line corresponding to NO showed that the NO conversion started at lower temperatures for the Cu-containing sample in comparison to iron-modified silicas. The profiles of the temperature-programmed surface studies of the NH_3-SCR process indicated that the largest amount of chemisorbed ammonia was converted during the performed reactions, giving a raise to N_2 and H_2O for the Fe-modified catalyst. In the case of 25Cu-MCM-41 additionally, small amounts of nitrogen(I) oxide were formed. In the case of the second studied process, ammonia oxidation, the desorption profiles consisted of two steps: (i) direct oxidation of NH_3 to nitrogen(II) oxide; (ii) NO interaction with remaining NH_3 to form N_2 and side product - N_2O. Thus, the application of the temperature-programmed methods in terms of their use for the examination of the NH_3-SCR and ammonia oxidation mechanism over transition metals doped silicas seems to be an interesting research direction.

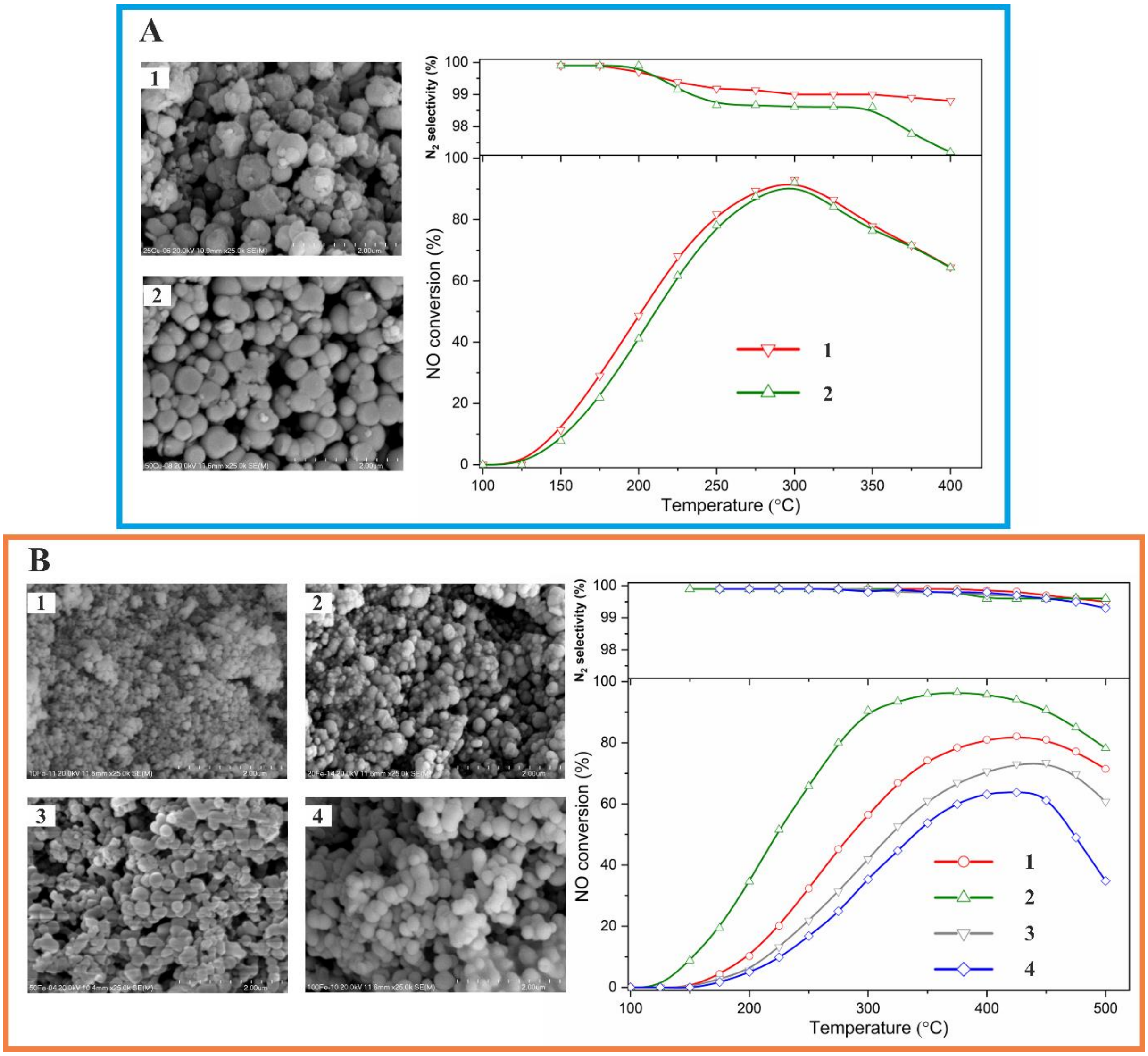

Figure 5.2 SEM images and NH_3-SCR catalytic results for the (**A**) Cu-modified MCM-41 (1: 25Cu-MCM-41, 2: 50Cu-MCM-41); (**B**) Fe-modified MCM-41 (1: 10Fe-MCM-41, 2: 20Fe-MCM-41, 3: 50Fe-MCM-41, 4: 100Fe-MCM-41). Adapted from illustrations included in the article **P2**.

5.3 Publications P3 and P4

Mesoporous silica materials are used in a wide range of various applications owing to their unique properties such as narrow pore size distributions, high pore volumes and high surface area. However, pure silica porous materials are catalytically inert, thus their catalytic activation requires deposition of catalytically active components on their surface.[9] In contrast to zeolites, mesoporous silica sieves do not exhibit ion-exchange properties, while the incorporation of heteroatoms (*e.g.*, Al) into their framework, leads to the generation of limited ion-exchange properties.[149] Therefore, the application of the ion-exchange method for deposition of catalytically active species into mesoporous silicas is low-effective. Homogeneous deposition of the active phase is especially important in the case of copper modified materials used as catalysts of the low-temperature NH_3-SCR process. It was claimed that monomeric copper cations exhibit high low-temperature catalytic activity in the NH_3-SCR process.[150,151] Therefore, controlling copper species aggregation is a crucial issue in designing catalysts for the low-temperature NH_3-SCR process. The development of such catalytic materials operating efficiently in the low-temperature range provides the basis for the modernisation of the existing NH_3-SCR installations operating in the low-dust configuration.[9]

In this context, publications **P3** and **P4** present the results of the successful synthesis of Cu-modified spherical mesoporous MCM-41 materials, their physiochemical characterisation, as well as catalytic study in the NH_3-SCR process. In the role of catalytic supports spherical MCM-41, composed of pure silica (**P3**) and silica-alumina (**P4**), were used. In both cases, spherical MCM-41 was doped with copper using the template ion-exchange method (TIE) and its modified version including treatment of the samples with ammonia solution directly after substitution of an organic matrix with metal ions (TIE-NH_3). The application of both TIE and TIE-NH_3 approaches allows the introduction of high loading of copper, while ammonia post-treatment guaranteed the improved dispersion of the active phase. The application of the TIE-NH_3 procedure, based on the post-synthesis ammonia treatment, influenced the well-ordered mesoporous structure, resulting in partial degradation of the silica framework in an alkaline medium (especially in the case of higher copper loadings). The same effect was observed for both pure silica and aluminium-containing catalytic supports. In the case of the samples modified by the TIE method, apart from highly dispersed copper species, also more aggregate oxide species, were identified (SEM images, Figures 5.3 A and 5.4 A). The possible mechanism of such copper oxide clusters forming is related to the interaction of Cu-precursor with surfactant micellar structures extracted from the silica mesopores, both present in the solution during the TIE procedure. The subsequent calcination process of such copper species leads to their transformation into aggregated copper oxide forms - nanorods and bulky 3D-CuO crystallites. This effect may be eliminated by treatment of the samples directly after the TIE procedure with ammonia (SEM images, Figures 5.3 B and 5.4 B). The protective role of ammonia, preventing the formation of aggregated copper oxide forms is probably related to the complexation of copper species with ammonia, which reduces the sintering effect under calcination conditions. This is only hypothesis that should be proved in the future. Thus, the use of TIE and TIE-NH_3 methods allows for designing catalysts containing highly dispersed forms of deposited copper, mainly monomeric copper cations, which are catalytically active in the low-temperature NH_3-SCR process.

The obtained spherical MCM-41 materials (both silica and silica-alumina), modified with copper were found to be active and selective catalysts of the low-temperature NH_3-SCR process. It should be pointed that deposition of copper in the form of the highly dispersed species by the TIE-NH_3 method leads to more effective NH_3-SCR catalysts in comparison to the samples obtained by the TIE method (without NH_3 post-treatment). The NO conversion started at about 125°C and in the ranges of 200-325°C and 225-375°C was above 90% for the Cu-modified silica and silica-alumina spherical MCM-41, respectively. Thus, the temperature operation window of these catalysts was shifted towards the lower temperature range in comparison to commercial V_2O_5-TiO_2 based catalysts (300-400°C). The decrease in the NH_3-SCR efficiency at elevated temperatures is related to the side process of direct ammonia oxidation. This effect was more significant for Cu-containing pure silica MCM-41. The incorporation of aluminium into the silica MCM-41 framework generated additional acid sites, significantly prolonging an effective operation window of nitrogen(II) oxide reduction with NH_3 towards higher temperatures. The role of Al-sites in the NH_3-SCR process can be correlated with the activation of NH_3 molecules for the performed reaction, but also such sites can play a protective function against ammonia oxidation and the creation of NH_3-reservoir on the catalyst surface. The lower catalytic efficiency of the copper loaded MCM-41 samples, non-modified with ammonia (TIE method), can be related to the higher contribution of aggregated copper oxide species. Their presence is supposed to be responsible for the enhanced activity of the catalyst in direct ammonia oxidation, and hence the reduction of the NO conversion efficiency in the higher temperature range. It is worth to mention that the selectivity to N_2 is above the level of 98% and 95% at temperatures below 350°C, for all series of Cu-modified silica and silica-alumina spherical MCM-41, respectively.

Figures 5.3 and 5.4 present the SEM images (Figures 5.3 A and B and 5.4 A and B), as well as results of NH_3-SCR catalytic studies over the most active catalysts described in publications **P3** and **P4** (Figures 5.3 C and 5.4 C).

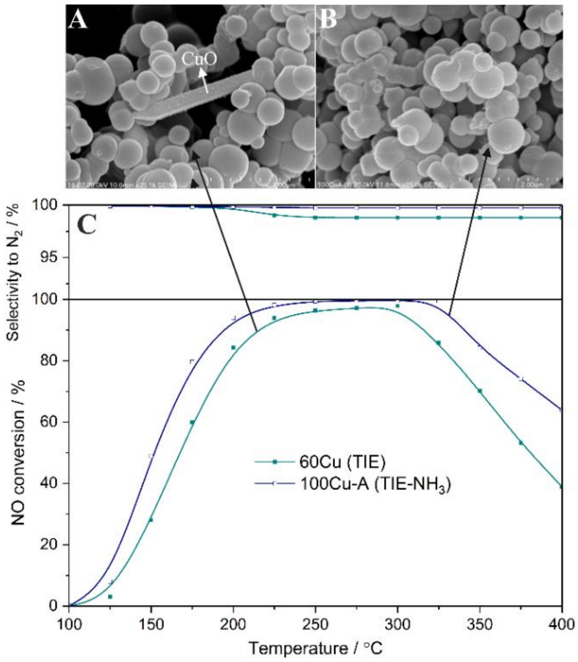

Figure 5.3 SEM images (**A**: 60Cu and **B**: 100Cu-A) and NH_3-SCR catalytic studies (**C**) for the selected most active Cu-modified silica MCM-41 samples. Adapted from illustrations included in the article **P3**.

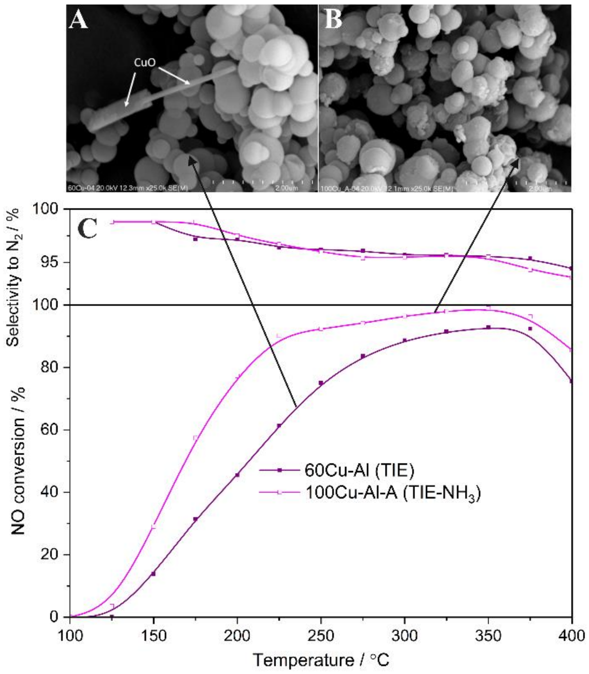

Figure 5.4 SEM images (**A**: 60Cu-Al and **B**: 100Cu-Al-A) and NH_3-SCR catalytic studies (**C**) for the selected most active Cu-modified silica-alumina MCM-41 samples. Adapted from illustrations included in the article **P4**.

The results of the catalytic studies indicate the obtained catalysts as promising catalysts for the low-dust NH_3-SCR installations (requiring an effective catalyst operating at about 250°C). It should be mentioned that the results of stability tests in dry and wet conditions for these catalysts are very promising, due to the only small differences (**P3**) or any significant changes (**P4)** in the NO conversion and N_2 selectivity during such tests.

5.4 Publication P5

The mesoporous silicas of MCM-41 type can be obtained with classical (cylindrical) and spherical morphology.[9] The latter is characterised by shorter interior canals and therefore reduced internal diffusion limitations in comparison to its cylindrical analogue. Hence, the application of nano-spherical MCM-41 in the role of catalytic support should decrease the possible restrictions of internal diffusion of reactants and therefore improve the overall rate of the catalysed reaction.[9] Moreover, the open structure of mesoporous silica materials guarantees the enhanced accessibility of the reaction gasses to the catalytically active components. It is worth mentioning that, apart from the appropriately selected catalytic support, it is also important to use a suitable method of its catalytic functionalisation. It is necessary to ensure homogeneous deposition and high loadings catalytically active species in the desirable form. The modification of mesoporous silica sieves by the template-ion exchange method (TIE) allows to meet these demands. The modification of mesoporous materials with iron by TIE[127] and other techniques[117] resulted in catalysts operating in the high-temperature NH_3-SCR process. However, an unequivocal determination of the role of various iron species in this process is constantly a matter of scientific discussion.[152,153]

The research presented in publication **P5** are focused on the analysis of the influence of the iron aggregation in the Fe-loaded morphologically diverse MCM-41 materials in the NH_3-SCR process. The studies include the role of the accompanying reactions and physicochemical properties of the silica-based catalysts on the NH_3-SCR process efficiency. In this regard, publication **P5** describes the successful TIE catalytic functionalisation of cylindrical and spherical MCM-41, using two iron precursors varying in the number of metal centres. The implemented iron sources, $FeCl_2$ and $[Fe_3(OCOCH_3)_7{\cdot}OH{\cdot}2H_2O]NO_3$, resulted in the deposition of this metal in highly dispersed and aggregated forms, respectively (Figure 5.5 A1, B1, C1, D1). The increased iron aggregation was observed especially for more concentrated solutions of trinuclear-Fe-acetate oligocations. In these cases, the formation of iron oxide nanorods located outside of the mesoporous arrangement was observed. The mechanism of such Fe_2O_3 nanostructures formation is probably similar to this described for copper oxide crystallites that appeared in Cu-loaded silica and silica-alumina spherical MCM-41, discussed in the 5.3 subsection.

The Fe-doped cylindrical and spherical MCM-41 materials exhibited an enhanced catalytic performance at elevated temperatures in the NH_3-SCR process. The effective NO conversion over the studied samples was observed from 350 to 475°C, with a very high selectivity to dinitrogen (above 98%). The noticeable decrease of catalytic activity in the NH_3-SCR process is related to the competitive reaction of ammonia oxidation, examined as one of the associated processes. Nevertheless, the NO reduction with ammonia was more preferable process, than the side reaction of ammonia oxidation. What is more, the analysis of the NO conversion profiles, indicated that the obtained catalysts may be considered as high-temperature NH_3-SCR catalysts. Thus, the process of NO to NO_2 oxidation exhibited low efficiency, pointed to the restricted low-temperature NH_3-SCR process facilitated by the fast-SCR mechanism.

In general, despite the similar contents of the active phase in the samples in each series, silicas modified with iron trinuclear oligocations exhibited slightly higher NO conversion in comparison to their analogues modified with monomeric iron ions. It seems that the morphology of the silica support is not crucial in designing of effective catalysts, however slightly better catalytic results were observed in the case of the catalysts based on spherical MCM-41. Moreover, the efficiency of the NH_3-SCR process increased with an increase in iron content in the samples. The exceptions are materials with the highest amount of deposited active phase, especially those modified with iron cations. In these cases, the accessibility of the reactants to Fe-sites was presumably hindered, because of the formation of bulky iron oxide species and therefore noticeably affecting the NO conversion.

In order to evaluate the catalytic activity of the active sites, the turn-over-frequency (TOF) values for the studied samples in the NH_3-SCR reaction at 300°C were determined. It was assumed that all iron cations exposed in the catalysts surface play a role of catalytically active sites. The TOF values determined for active sites in the silica materials modified with oligomeric cations indicated higher catalytic activity in comparison to their analogous modified with iron monomeric cations (except samples with the highest iron content). Thus, most probably small aggregated oligomeric iron species are responsible for the enhanced activity of the Fe-doped samples in the NH_3-SCR process. Figure 5.5 presents the results of NH_3-SCR catalytic studies over the samples presented in publication **P5** (Figure 5.5 A, B, C, D), together with SEM images of the selected catalysts (Figure 5.5 A1, B1, C1, D1).

The future possible application of the obtained catalysts in the high-temperature NH_3-SCR process was verified for the most promising sample (40Fe3-S). The long-term isothermal stability study at 325°C, as well as test with periodical changes from dry to wet reaction mixture (also at 325°C), were also done. In the case of the first experiment, the reduction of the catalyst activity after 18 hours in the NH_3-SCR reaction was about 5%, while N_2-selectivity was stable. In the second experiment, the NO conversion, as well as the selectivity to N_2 decrease after switching from dry to wet reaction mixture. However, after subsequent switching to dry conditions, the catalytic performance was nearly fully restored. Therefore, the observed decrease in catalytic efficiency in the NH_3-SCR process in the presence of water vapour was not permanent deactivation of the catalytic system.

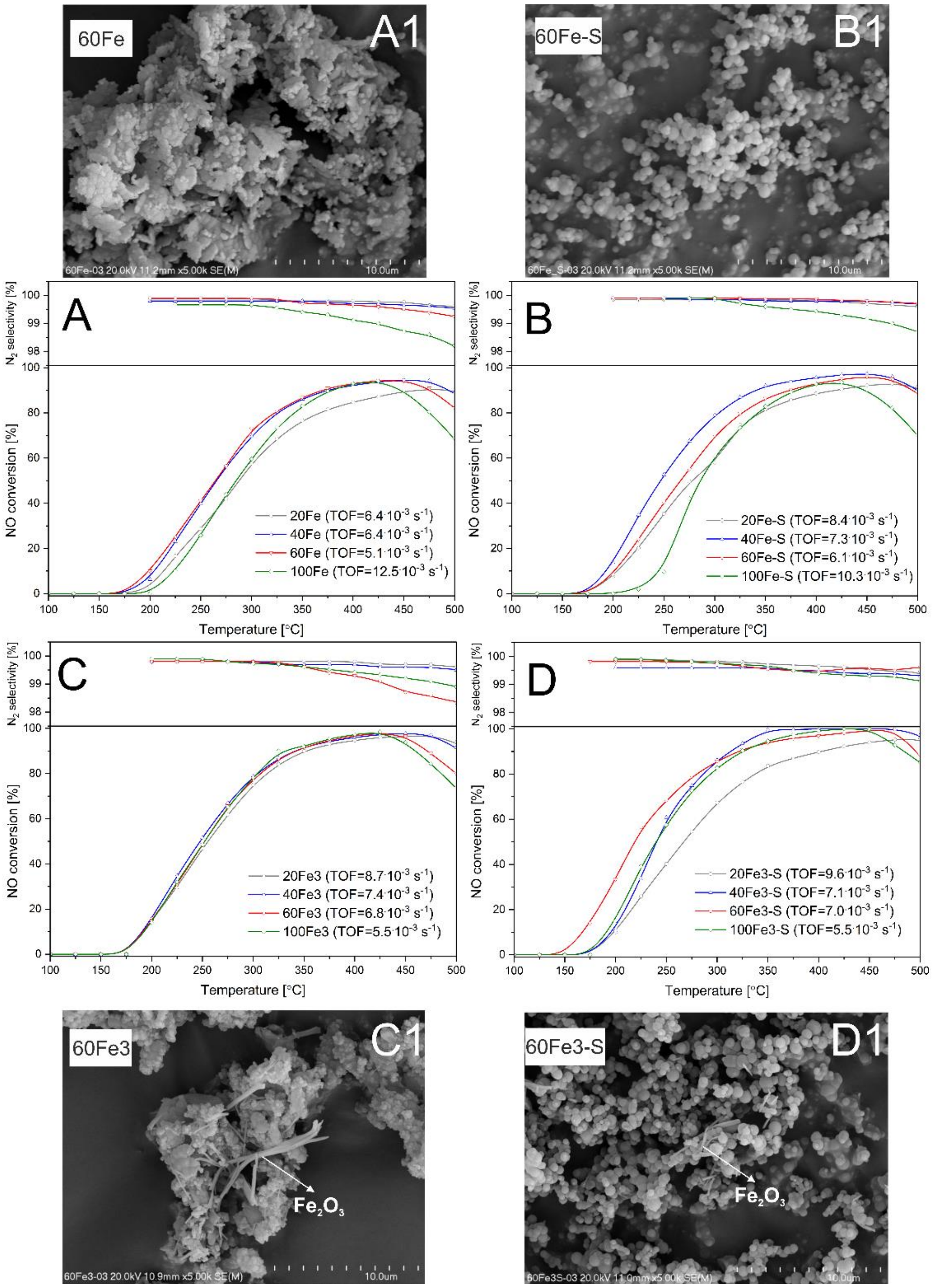

Figure 5.5 Results of NH_3-SCR catalytic tests for cylindrical MCM-41 (**A**) and spherical MCM-41 (**B**) modified with iron cations as well as cylindrical MCM-41 (**C**) and spherical MCM-41 (**D**) modified with iron oligocations together with SEM images (**A1**: 60Fe, **B1**: 60Fe-S, **C1**: 60Fe3, and **D1**: 60Fe3-S). Adapted from illustrations included in the article **P5**.

5.5 Manuscript P6

Nowadays, the development of catalysts effectively operating in the low-temperature NH_3-SCR process constitutes one of the biggest challenges in the field of environmental catalysis.[9,62] Such requirements are connected with the retrofitting of the NH_3-SCR installations to work with the low-dust gas stream. In such case temperature of flue gases leaving the electrostatic precipitator (ESP) is about 250°C. Thus, to avoid the additional heating of de-dusted gasses to above 300°C, before passing them to the NH_3-SCR converter, the solution could be using the efficient catalysts of the NO reduction with ammonia operating at temperatures about 250°C, or even lower. Such reconfiguration of the industrial NH_3-SCR system allows protection of the monolith catalyst against deactivation due to operation with low-dust exhaust gasses (Figure 1.9). It is also a promising solution from an economic point of view, due to the savings related to avoiding gasses re-heating.[9,62,71] An interesting materials with the potential application in the role of catalytic supports for deposition transition metals, such as Cu, Fe and Mn, are mesoporous silica sieves.[82,83,120,127,137,140,141] Among them, the studies of the NO reduction with ammonia over mesoporous silica-based materials loaded with manganese are rather scarce. Therefore, this is an unexplored topic with a high applicative potential in the low-temperature NH_3-SCR process, especially considering the reported high activity of Mn-containing systems in this temperature range.[83]

Regarding the abovementioned dependencies, manuscript **P6** reports the examination of the catalytic activity of Cu, Fe and Mn and their bimetallic pairs (CuFe, CuMn and FeMn) deposited on spherical MCM-41 by the TIE method, along with the study of the possible synergistic relations between these metals in the NH_3-SCR process. Moreover, the physicochemical characterisation of the obtained samples, concerning their structure, metal content, morphology, textural parameters, surface acidity, deposited forms of active phase and reducibility was done.

For the spherical silica loaded with the active phase in the form of single metal, deposition of iron and manganese was possible in the form of well-dispersed metal species. In the case of the Cu-modified sample, a significant contribution of copper in aggregated form was identified. For the bimetallic CuFe sample, the contribution of aggregated copper oxide species was considerably reduced, while for the other samples of this series, CuMn and FeMn, the formation of aggregated metal oxide species was not observed. SEM images of the selected samples, Cu, Mn and CuMn, are presented in Figure 5.6. The obtained materials were found to be active and selective catalysts of the NH_3-SCR process. The catalytic performance of spherical MCM-41 modified with pairs of transition metals, CuFe and CuMn, was considerably improved in comparison to their monometallic analogues. Only in the case of the bimetallic FeMn system, the NO conversion was lower for the catalysts containing pair of metals in comparison to the monometallic sample, Fe-modified spherical MCM-41. The observed decrease in the efficiency of nitrogen(II) oxide conversion at elevated temperatures is correlated to the side reaction of direct ammonia oxidation.

The synergistic effect was especially significant in the case of copper and manganese species simultaneously deposited on the surface of the silica support. It should be pointed out that the amount of loaded active phase, copper and manganese, is the same in the case of bimetallic CuMn and a mechanical mixture of these species. Despite the above fact, in the studied temperature range, the catalytic activity of this sample in the NH_3-SCR process was noticeably increased comparing to the mechanical mixture of single metal-containing samples (Cu+Mn). Thus, the CuMn sample can be considered as catalysts dedicated for the application in the low-temperature NH_3-SCR process with almost 100% selectivity to dinitrogen. Moreover, the possible synergistic effect between the components of the active phase, copper and manganese, present in the bimetallic sample was also proved by analysis of the turn-over-frequency (TOF) values determined for the bimetallic CuMn and single metal, Cu or Mn, deposited on mesoporous silica spheres. In the case of simultaneous introduction of the transition metals phase, the estimated TOF value ($10.0 \cdot 10^{-3}$ s^{-1}) is higher than its cumulative Cu and Mn value ($7.8 \cdot 10^{-3}$ s^{-1}), which indicates the improvement of the catalytic efficiency of the bimetallic system in the NH_3-SCR process (Figure 5.6 B). The increased catalytic performance of the bimetallic copper-manganese sample is probably related to the coexistence of redox systems of Cu^+ and Mn^{4+}, $Cu^{2+} + Mn^{3+} \rightarrow Cu^+ + Mn^{4+}$ and $Cu^{2+} + Mn^{2+} \rightarrow Cu^0 + Mn^{4+}$, promoting the formation of reactive intermediates necessary for the low-temperature NO conversion by the fast-SCR reaction. The postulated fast-SCR mechanism requires the presence of NO_2, thus the experiments concerning its formation in the reaction of NO to NO_2 oxidation are essential in the verification of the proposed low-temperature reaction pathway (Figure 5.6 A). The obtained catalysts from the copper-manganese series, both mono- and bimetallic samples, are active in the formation of nitrogen(IV) oxide, while the NO oxidation over the CuMn sample is more effective. Thus, the CuMn catalyst operates in the lower-temperature range as a result of the accelerating of the fast-SCR pathway. The stability of the catalyst was verified by the long-term stability NH_3-SCR test, performed at 275°C for 17 hours. The obtained results revealed the high stability of the CuMn catalyst.

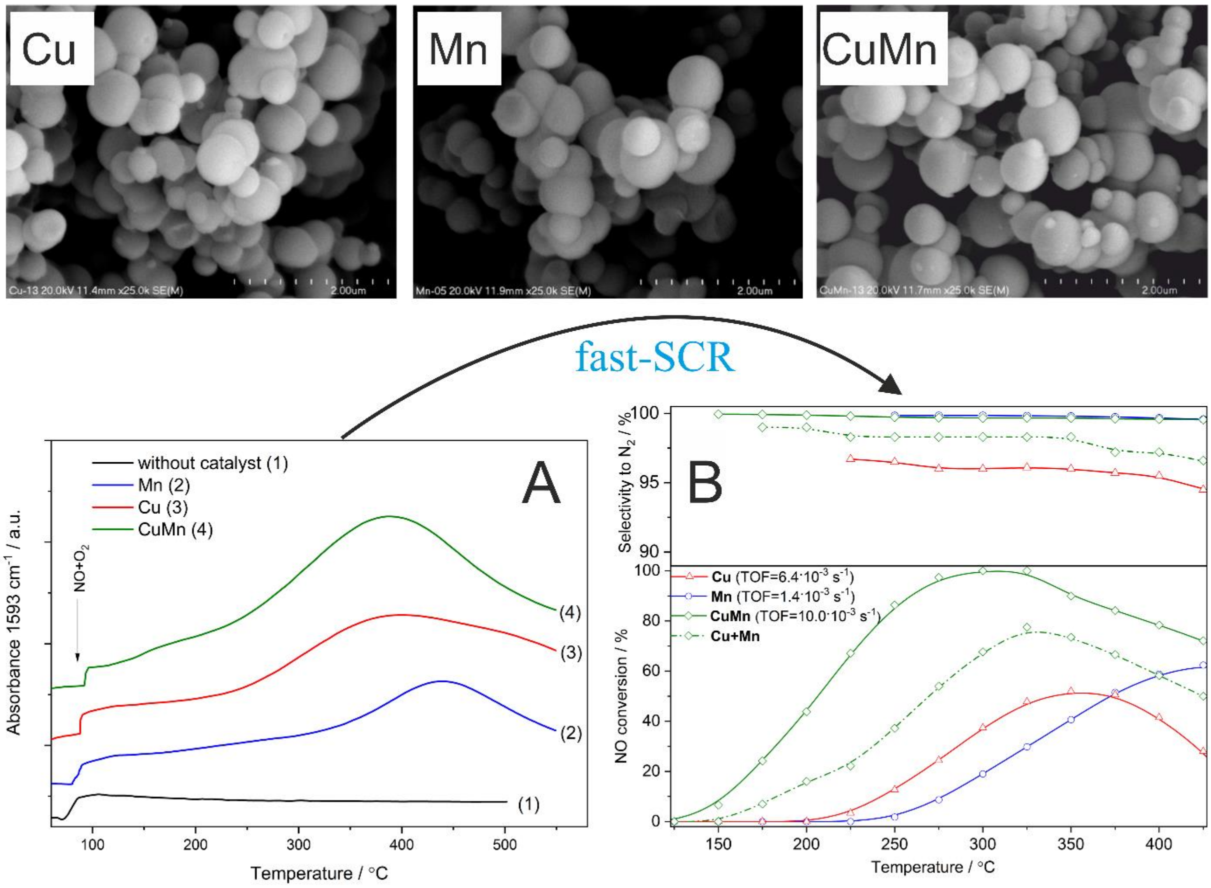

Figure 5.6 SEM images of the selected samples (Cu, Mn and CuMn; **top**), depicted with the results of NO to NO_2 oxidation (**A**), as well as results of the NH_3-SCR catalytic tests (**B**) for Cu, Mn, CuMn and Cu+Mn catalysts. Adapted from illustrations included in the manuscript **P6**.

6. Conclusions and perspectives

The aim of the PhD thesis was to design, synthesise and characterise novel catalytic materials exhibiting an extended temperature range of efficient operation in the NH_3-SCR. The undertaken work was focused on porous silica materials modified with transition metals. The presented studies include MWW zeolites with bimodal porosity modified with iron(III) and mesoporous silicas of MCM-41 with various morphologies, doped with selected transition metals: Cu, Fe or Mn. As a part of the conducted research, studies of the NH_3-SCR activity of obtained materials were performed, which results are supported by the analysis of the possible accompanying processes affecting the overall catalytic efficiency of nitrogen(II) oxide conversion. The obtained materials were found to be active and selective in the process of NO reduction with ammonia. The temperature range of their catalytic operation is strongly related to the type and form of the deposited active phase and the kind of the used catalytic support. The results presented within PhD thesis, consist of six manuscripts (five of which (**P1 - P5**) have been published in high impact scientific journals and one of the papers is currently under review (**P6**)).

Concluding, the outcomes obtained within the framework of the presented doctoral dissertation constitute valuable contributions to the development of novel catalysts based on porous silica systems, useful in the NH_3-SCR process. The obtained materials show promising performance in the low-temperature regime, as well as the high-temperature range NH_3-SCR process. The presented results indicate that the effective operation window of the catalysts was extended compared to the commercially used NH_3-SCR catalytic system. The comparison of such temperature windows of effective catalytic operation for the studied catalysts and commercial catalysts is presented in Figure 6.1. The commercial catalysts based on V_2O_5-TiO_2 oxide system effectively operate in the temperature range of 300-400°C, whereas mesoporous silica of MCM-41 type modified with copper is catalytically active below 300°C. As it was already discussed, increased dispersion and loading of copper species results in a significant shift of the catalyst operation into the low-temperature range. Thus, the methods used for metal deposition in the highly dispersed form are very important for tailoring the catalysts for the low-temperature NH_3-SCR process. On the other hand, mesoporous silica MCM-41 modified with iron presented very promising catalytic activity in the high-temperature NH_3-SCR process (above 400°C). It was shown that the morphology of MCM-41 plays a less significant role, however slightly higher activity was found for silicas in the spherical form.

NH_3-SCR should not be analysed as an independent process. The overall rate of this process depends also on associated reactions that may increase or decrease its efficiency. As it was shown NO to NO_2 oxidation may result in the activation of the low-temperature NO_x conversion according to the so-called fast-SCR pathway. The activity of the catalysts in N_2O decomposition to dinitrogen and oxygen may result in improved selectivity of the NH_3-SCR catalysts into dinitrogen. On the other hand, the activity of the catalysts in direct ammonia oxidation may result in the limitation of the NO conversion at higher temperatures. The presented studies included analysis of these reactions associated with the NH_3-SCR process and therefore more effective designing of the catalysts for the low- and high-temperature NH_3-SCR process was possible.

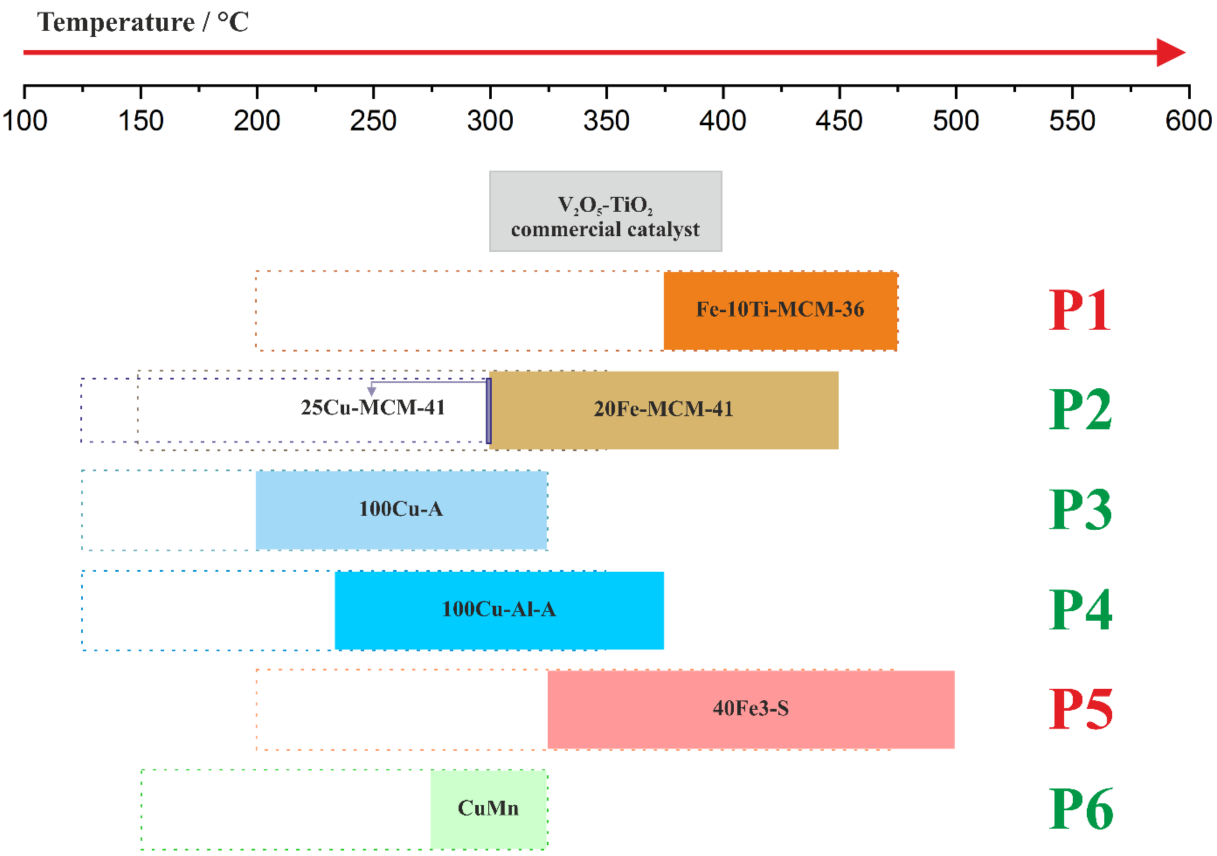

Figure 6.1 Scheme representing a comparison of commercial catalytic system with the most active catalysts described in manuscripts **P1-P6**, tested in the NH_3-SCR reaction, with respect to temperature. The areas marked with the dashed lines represent the range in which the activity of the catalyst increases, while the areas filled with colour correspond to the temperature range in which the NO conversion level above 90% was achieved.

The studies presented in the frame of the doctoral dissertation also show some problems that should be solved in the future. One of them is partial damage of the porous structure of MCM-41 occurring in conditions of ammonia treatment of the samples modified by the TIE-NH_3 method. Thus, the studies focused on replacing ammonia with another complexation agent, but with lower basicity, should be conducted. Another important issue is the verification of the TIE and TIE-NH_3 methods applicability also for other mesoporous silica materials, *e.g.*, MCM-48 or HMS. The important point, focused on the future commercialisation of the studied catalytic system, is the scale-up of the catalyst's synthesis procedures including green chemistry rules.

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9. Attachments

9.1 Co-authors declarations

Declarations of scientific contribution of all co-authors of the manuscripts presented in this doctoral thesis are attached below as follows:

Agata Chłopek

Lucjan Chmielarz

Justyna Ciuba

Barbara Gil

Aleksandra Jankowska

Andrzej Kowalczyk

Shiquan Liu

Marek Michalik

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included:

- Measurements of FT-IR spectroscopy based on adsorption of pyridine used as a probe molecule.

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- H_2-TPR measurements and analysis of the results;
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- Catalytic tests (NH_3-SCR, NO to NO_2 oxidation, ammonia oxidation, N_2O decomposition) - measurements and analysis of the results;
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- Temperature-programmed surface reactions - measurements and analysis of the results;
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Co-author declaration

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concerning her PhD thesis

I declare that my personal scientific contribution to the articles:

P2 Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Shiquan Liu, Lucjan Chmielarz, *Catalytic performance of spherical MCM-41 modified with copper and iron as catalysts of NH_3-SCR process*
Molecules, 2020, **25**, 5651
https://doi.org/10.3390/molecules25235651

included:

- SEM images with EDS analyses.

P3 Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Marek Michalik, Shiquan Liu, Lucjan Chmielarz, *Enhanced catalytic performance in low-temperature NH_3-SCR process of spherical MCM-41 modified with Cu by template ion-exchange and ammonia treatment*
Microporous and Mesoporous Materials, 2021, **315**, 110920
https://doi.org/10.1016/j.micromeso.2021.110920

included:

- SEM with EDS analyses.

P4 Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Lucjan Chmielarz, *Spherical Al-MCM-41 doped with copper by modified TIE method as effective catalyst for low-temperature* NH_3*-SCR*
Molecules, 2021, **26**, 1807
https://doi.org/10.3390/molecules26061807

included:

- SEM images with EDS analyses.

P5 Aleksandra Jankowska, Justyna Ciuba, Andrzej Kowalczyk, Małgorzata Rutkowska, Zofia Piwowarska, Marek Michalik, Lucjan Chmielarz, *Mesoporous silicas of MCM-41 type modified with iron species by template ion-exchange method as catalysts for the high-temperature* NH_3*-SCR process – Role of iron species aggregation, silica morphology and associated reactions*
Catalysis Today, 2022, **390-391**, 281-294
https://doi.org/10.1016/j.cattod.2021.09.033

included:

- SEM images with EDS analyses.

P6 Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Lucjan Chmielarz, *Catalytic performance of bimetallic systems (Cu-Fe, Cu-Mn, Fe-Mn) based on spherical MCM-41 modified by template ion-exchange in* NH_3*-SCR process*
Journal of Porous Materials, *manuscript under review*

included:

- SEM images with EDS analyses.

....

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Prof. dr hab. inż. Włodzimierz Mozgawa
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concerning her PhD thesis

I declare that my personal scientific contribution to the articles:

P1 Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Barbara Gil, Lucjan Chmielarz, *Silica and silica-titania intercalated MCM-36 modified with iron as catalysts for selective reduction of nitrogen oxides – the role of associated reactions*
Catalysis Science and Technology, 2020, **10**, 7940-7954
https://doi.org/10.1039/D0CY01415J

included:

- Participation in the development of the general concept of the performed research;
- Participation in the development of the research methodology;
- Scientific supervision over research;
- Raman measurements;
- Participation in the preparation of manuscript;
- Participation in the correction of the manuscript after reviews and preparing responses for the reviewers.

P3 Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Marek Michalik, Shiquan Liu, Lucjan Chmielarz, *Enhanced catalytic performance in low-temperature* NH_3*-SCR process of spherical MCM-41 modified with Cu by template ion-exchange and ammonia treatment*
Microporous and Mesoporous Materials, 2021, **315**, 110920
https://doi.org/10.1016/j.micromeso.2021.110920

included:

- Participation in the development of the general concept of the performed research;
- Participation in the development of the research methodology;
- Scientific supervision over research;
- Substantive consultations;
- Participation in the preparation of manuscript;
- Participation in the correction of the manuscript after reviews and preparing responses for the reviewers.

Mozgawa

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Prof. dr hab. inż. Włodzimierz Mozgawa

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concerning her PhD thesis

I declare that my personal scientific contribution to the article:

P5 Aleksandra Jankowska, Justyna Ciuba, Andrzej Kowalczyk, Małgorzata Rutkowska, Zofia Piwowarska, Marek Michalik, Lucjan Chmielarz, *Mesoporous silicas of MCM-41 type modified with iron species by template ion-exchange method as catalysts for the high-temperature NH_3-SCR process – Role of iron species aggregation, silica morphology and associated reactions* Catalysis Today, 2022, **390-391**, 281-294 https://doi.org/10.1016/j.cattod.2021.09.033

included:

- TGA-DTG-DTA measurements of the samples.

Piwowarska
....
M.Sc. Zofia Piwowarska

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concerning her PhD thesis

I declare that my personal scientific contribution to the articles:

P1 Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Barbara Gil, Lucjan Chmielarz, *Silica and silica-titania intercalated MCM-36 modified with iron as catalysts for selective reduction of nitrogen oxides – the role of associated reactions*
Catalysis Science and Technology, 2020, **10**, 7940-7954
https://doi.org/10.1039/D0CY01415J

included:

- Nitrogen sorption measurements of the samples.

P2 Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Shiquan Liu, Lucjan Chmielarz, *Catalytic performance of spherical MCM-41 modified with copper and iron as catalysts of* NH_3*-SCR process*
Molecules, 2020, **25**, 5651

https://doi.org/10.3390/molecules25235651

included:

- Nitrogen sorption measurements of the samples.

P3 Aleksandra Jankowska, Agata Chłopek, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Marek Michalik, Shiquan Liu, Lucjan Chmielarz, *Enhanced catalytic performance in low-temperature NH_3-SCR process of spherical MCM-41 modified with Cu by template ion-exchange and ammonia treatment*
Microporous and Mesoporous Materials, 2021, **315**, 110920
https://doi.org/10.1016/j.micromeso.2021.110920

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Molecules, 2021, **26**, 1807
https://doi.org/10.3390/molecules26061807

included:

- Nitrogen sorption measurements of the samples.

P5 Aleksandra Jankowska, Justyna Ciuba, Andrzej Kowalczyk, Małgorzata Rutkowska, Zofia Piwowarska, Marek Michalik, Lucjan Chmielarz, *Mesoporous silicas of MCM-41 type modified with iron species by template ion-exchange method as catalysts for the high-temperature NH_3-SCR process – Role of iron species aggregation, silica morphology and associated reactions*
Catalysis Today, 2022, **390-391**, 281-294
https://doi.org/10.1016/j.cattod.2021.09.033

included:

- Nitrogen sorption measurements of the samples.

JAGIELLONIAN
UNIVERSITY
IN KRAKÓW

P6 Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Lucjan Chmielarz, *Catalytic performance of bimetallic systems (Cu-Fe, Cu-Mn, Fe-Mn) based on spherical MCM-41 modified by template ion-exchange in NH_3-SCR process*
Journal of Porous Materials, *manuscript under review*

included:

- Nitrogen sorption measurements of the samples.

Faculty of Chemistry

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9.2 Scientific curriculum vitae

9.2.1 List of publications not included in the doctoral thesis

Number of publications not included in the doctoral thesis: **6**.

Number of chapters in books not included in the doctoral thesis: **1**.

All journals and chapters in books are indexed by JCR, total impact factor 2020 (IF): **49.43**.

IF including P1-P5, P7-P12 and C1 articles: **76.59**.

PUBLICATION 7 (P7)

Authors: Andrzej Kowalczyk, Aleksandra Borcuch, Marek Michalik, Małgorzata Rutkowska, Barbara Gil, Zbigniew Sojka, Paulina Indyka, Lucjan Chmielarz*

Title: MCM-41 modified with transition metals by template ion-exchange method as catalysts for selective catalytic oxidation of ammonia to dinitrogen

Microporous and Mesoporous Materials, 2017, **240**, 9-21 (IF= 5.455)

PUBLICATION 8 (P8)

Authors: Andrzej Kowalczyk, Aneta Święs, Barbara Gil, Małgorzata Rutkowska, Zofia Piwowarska, Aleksandra Borcuch, Marek Michalik, Lucjan Chmielarz*

Title: Effective catalysts for the low-temperature NH_3-SCR process based on MCM-41 modified with copper by template ion-exchange (TIE) method

Applied Catalysis B: Environmental, 2018, **237**, 927–937 (IF= 19.503)

PUBLICATION 9 (P9)

Authors: Małgorzata Rutkowska*, Aleksandra Borcuch, Anna Marzec, Andrzej Kowalczyk, Bogdan Samojeden, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Influence of iron aggregation on the catalytic performance of desilicated MFI in the $DeNO_x$ process

Microporous and Mesoporous Materials, 2020, **304**, 109114 (IF= 5.455)

PUBLICATION 10 (P10)

Authors: Katarzyna Madej*, Anna Jonda, Aleksandra Borcuch, Wojciech Piekoszewski, Lucjan Chmielarz, Barbara Gil

Title: A novel stir bar sorptive-dispersive microextraction in combination with magnetically modified graphene for isolation of seven pesticides from water samples

Microchemical Journal, 2019, **147**, 962–971 (IF= 4.821)

PUBLICATION 11 (P11)

Authors: Aleksandra Borcuch, Małgorzata Rutkowska*, Anna Marzec, Andrzej Kowalczyk, Marek Michalik, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Selective ammonia oxidation over ZSM-5 zeolite; impact of catalyst's support porosity and type of deposited iron species

Catalysis Today, 2020, **348**, 223-229 (IF= 6.766)

PUBLICATION 12 (P12)

Authors: Małgorzata Rutkowska*, Aleksandra Jankowska, Ewelina Różycka-Dudek, Wiktoria Dubiel, Andrzej Kowalczyk, Zofia Piwowarska, Sebastián Llopis, Urbano Díaz, Lucjan Chmielarz

Title: Modification of MCM-22 zeolite and its derivatives with iron for the application in N_2O decomposition

Catalysts, 2020, **10**, 1139 (IF= 4.146)

CHAPTER 1 (C1)

Authors: Lucjan Chmielarz*, Aleksandra Jankowska

Title: Mesoporous silica-based catalysts for selective catalytic reduction of NO_X with ammonia – recent advances

in: Advances in Inorganic Chemistry, ed. R. van Eldik and C. D. Hubbard, Academic Press, Cambridge, San Diego (United States), Oxford, London (United Kingdom), 2022, vol. 79, ch. 6, pp. 205–241 (IF= 3.282)

9.2.2 List of conference presentations

List of personal conference presentations

Number of international conferences: **12**

Number of national conferences: 7

PRESENTATION 1

Authors: Aleksandra Borcuch, Małgorzata Rutkowska, Anna Marzec, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: The influence of iron aggregation on catalytic performance of micro-mesoporous MFI in the $DeNO_X$ process

Conference: 7th Czech-Polish Catalytic Symposium, 2.02.2018, Ostrava, Czech Republic

Type of presentation / conference status: oral communication / international

PRESENTATION 2

Authors: Aleksandra Borcuch, Andrzej Kowalczyk, Lucjan Chmielarz

Title: Funkcjonalizacja mezoporowatych krzemionek metodą TIE dla potrzeb katalizy środowiskowej

Conference: X Interdyscyplinarna Konferencja Naukowa TYGIEL „Interdyscyplinarność kluczem do rozwoju”, 17-18.03.2018, Lublin, Poland

Type of presentation / conference status: poster / national

PRESENTATION 3

Authors: Małgorzata Rutkowska, Anna Marzec, Aleksandra Borcuch, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Catalytic performance of desilicated ZSM-5 zeolite modified with iron cations and oligocations in SCR-NH_3 process

Conference: International Conference on Catalysis and Surface Chemistry & 50-te OKK, 18-23.03.2018, Kraków, Poland

Type of presentation / conference status: poster / international

PRESENTATION 4

Authors: Małgorzata Rutkowska, Anna Marzec, Aleksandra Borcuch, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Iron aggregation vs. catalytic activity of desilicated ZSM-5 in NH_3-SCR process

Conference: XXII Forum Zeolitowe, 19-23.06.2018, Niepołomice, Poland

Type of presentation / conference status: oral communication / international

PRESENTATION 5

Authors: Aleksandra Borcuch, Małgorzata Rutkowska, Anna Marzec, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Wpływ agregacji żelaza na aktywność katalityczną desilikowanego zeolitu ZSM-5 w procesie $DeNO_x$

Conference: 61 Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 17-21.09.2018, Kraków, Poland

Type of presentation / conference status: poster / national

PRESENTATION 6

Authors: Aleksandra Borcuch, Małgorzata Rutkowska, Anna Marzec, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Catalytic performance of micro-mesoporous MFI modified with iron cations and oligocations in NH_3-SCR process

Conference: EastWest Chemistry Conference of Young Scientists 2018, 10-11.10.2018, Lviv, Ukraine

Type of presentation / conference status: oral communication / international

PRESENTATION 7

Authors: Aleksandra Borcuch, Małgorzata Rutkowska, Anna Marzec, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Catalytic activity of Fe-ZSM-5 zeolite modified by desilication in environmental catalysis

Conference: 8th Czech-Polish Catalytic Symposium, 14.02.2019, Ostrava, Czech Republic

Type of presentation / conference status: oral communication / international

PRESENTATION 8

Authors: Aleksandra Borcuch, Małgorzata Rutkowska, Anna Marzec, Andrzej Kowalczyk, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Micro-mesoporous MFI loaded with iron cations and oligocations as catalyst of NH_3-SCO process

Conference: 51-te Ogólnopolskie Kolokwium Katalityczne, 20-22.03.2019, Kraków, Poland

Type of presentation / conference status: poster / national

PRESENTATION 9

Authors: Małgorzata Rutkowska, Aleksandra Borcuch, Kamil Synowiec, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Modification of layered zeolites with different iron precursors for the catalytic applications

Conference: 51-te Ogólnopolskie Kolokwium Katalityczne, 20-22.03.2019, Kraków, Poland

Type of presentation / conference status: poster / national

PRESENTATION 10

Authors: Aleksandra Borcuch, Małgorzata Rutkowska, Anna Marzec, José María Moreno, Urbano Díaz, Lucjan Chmielarz

Title: Catalytic performance of desilicated MFI modified with iron in environmental catalysis

Conference: Applied Catalysis and Chemical Engineering, 08-10.04.2019, Dubai, United Arab Emirates

Type of presentation / conference status: oral communication / international

PRESENTATION 11

Authors: Aleksandra Borcuch, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Lucjan Chmielarz

Title: Conversion of nitrogen pollutants over transition metal modified porous silica materials

Conference: 9th Czech-Polish Catalytic Symposium, 07.02.2020, Ostrava, Czech Republic

Type of presentation / conference status: oral communication / international

PRESENTATION 12

Authors: Aleksandra Borcuch, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Lucjan Chmielarz

Title: Fe-exchanged MWW derivatives as catalysts of NH_3-SCR process

Conference: 11th International Conference on Environmental Catalysis, 06-09.09.2020, Manchester, United Kingdom (on-line)

Type of presentation / conference status: poster / international

PRESENTATION 13

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Lucjan Chmielarz

Title: Catalytic performance of MCM-22, MCM-36 and Ti-MCM-36 derivatives modified with iron in NH_3-SCR process

Conference: 52-te Ogólnopolskie Kolokwium Katalityczne, 25-27.11.2020, Kraków, Poland (on-line)

Type of presentation / conference status: flash-oral presentation / national

PRESENTATION 14

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Marek Michalik, Shiquan Liu, Lucjan Chmielarz

Title: Functionalization of spherical MCM-41 with Cu by template-ion exchange method for the application in low-temperature NH_3-SCR process

Conference: 8th Conference of the Federation of European Zeolite Associations, 05-09.07.2021, United Kingdom (on-line)

Type of presentation / conference status: poster / international

PRESENTATION 15

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Włodzimierz Mozgawa, Lucjan Chmielarz

Title: Badania aktywności katalitycznej nanosfer MCM-41 dotowanych miedzią za pomocą metody jonowej wymiany templatu (TIE) w niskotemperaturowym procesie NH_3-SCR

Conference: Fizykochemia granic faz - metody instrumentalne, 22-26.08.2021, Lublin, Poland

Type of presentation / conference status: oral communication / national

PRESENTATION 16

Authors: Aleksandra Jankowska, Justyna Ciuba, Andrzej Kowalczyk, Małgorzata Rutkowska, Zofia Piwowarska, Lucjan Chmielarz

Title: Wpływ agregacji żelaza na aktywność katalityczną materiału typu MCM-41 modyfikowanego metodą wymiany jonowej templatu w procesie NH_3-SCR

Conference: Fizykochemia granic faz - metody instrumentalne, 22-26.08.2021, Lublin, Poland

Type of presentation / conference status: poster / national

PRESENTATION 17

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Lucjan Chmielarz

Title: Spherical MCM-41 modified with copper by template ion-exchange (TIE) method as potential catalyst for NH_3-SCR process

Conference: Young Researchers CIS 2021, 06-08.09.2021, Czech Republic, Italy and Spain (on-line)

Type of presentation / conference status: short oral presentation / international

PRESENTATION 18

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Lucjan Chmielarz

Title: Low-temperature NH_3-SCR catalysts based on spherical MCM-41 modified with Cu via template ion-exchange method

Conference: School on catalysis, 24-26.05.2022, Liblice, Czech Republic

Type of presentation / conference status: poster / international

PRESENTATION 19

Authors: Aleksandra Jankowska, Andrzej Kowalczyk, Małgorzata Rutkowska, Marek Michalik, Lucjan Chmielarz

Title: Silica and silica-alumina spherical MCM-41 modified with copper species by template ion-exchange (TIE) method as potential catalysts for low-temperature NH_3-SCR process

Conference: XXIII Forum Zeolitowe, 21-25.06.2022, Niepołomice, Poland

Type of presentation / conference status: oral communication / international

List of contributions to conference presentations of collaborators

Number of international conferences: **4**

Number of national conferences: **2**

PRESENTATION 1

Authors: Andrzej Kowalczyk, Aneta Święs, Aleksandra Borcuch, Małgorzata Rutkowska, Piotr Natkański, Lucjan Chmielarz

Title: MCM-41 based catalysts modified with copper by TIE method for low-temperature SCR-NH_3 process

Conference: International Conference on Catalysis and Surface Chemistry & 50-te OKK, 18-23.03.2018, Kraków, Poland

Type of presentation / conference status: poster presentation of Aneta Święs / international

PRESENTATION 2

Authors: Andrzej Kowalczyk, Aneta Święs, Aleksandra Borcuch, Małgorzata Rutkowska, Barbara Gil, Lucjan Chmielarz

Title: MCM-41 modified by copper by template ion-exchange method as effective catalyst for NH_3-SCR and NH_3-SCO processes

Conference: XXII Forum Zeolitowe, 19-23.06.2018, Niepołomice, Poland

Type of presentation / conference status: oral communication of Aneta Święs / international

PRESENTATION 3

Authors: Aneta Święs, Andrzej Kowalczyk, Barbara Gil, Małgorzata Rutkowska, Aleksandra Borcuch, Marek Michalik, Lucjan Chmielarz

Title: Modyfikacja mezoporowatej krzemionki typu MCM-41 metodą jonowej wymiany templatu dla procesów NH_3-SCR oraz NH_3-SCO

Conference: 61 Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 17-21.09.2018, Kraków, Poland

Type of presentation / conference status: poster of Aneta Święs / national

PRESENTATION 4

Authors: Małgorzata Rutkowska, Aleksandra Borcuch, Urbano Díaz, Lucjan Chmielarz

Title: Modyfikacja nowoczesnych materiałów zeolitowych pod kątem zastosowania w katalizie środowiskowej

Conference: 61 Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 17-21.09.2018, Kraków, Poland

Type of presentation / conference status: oral communication of Małgorzata Rutkowska / national

PRESENTATION 5

Authors: Lucjan Chmielarz, Andrzej Kowalczyk, Aneta Święs, Aleksandra Borcuch, Małgorzata Rutkowska, Shiquan Liu

Title: Strategies for catalytic activation of mesoporous silica materials for NH_3-SCR process

Conference: 11th International Conference on Environmental Catalysis, 06-09.09.2020, Manchester, United Kingdom (on-line)

Type of presentation / conference status: oral communication of Lucjan Chmielarz / international

PRESENTATION 6

Authors: Małgorzata Rutkowska, Wiktoria Dubiel, Aleksandra Jankowska, Zofia Piwowarska, Andrzej Kowalczyk, Krzysztof Maćkosz, Jakub Kawałko, Lucjan Chmielarz

Title: Zeolite spheres. Do they work better in catalysis?

Conference: XXIII Forum Zeolitowe, 21-25.06.2022, Niepołomice, Poland

Type of presentation / conference status: oral communication of Małgorzata Rutkowska / international

9.2.3 International internship

INTERNSHIP

September 2019 (1 month), School of Materials Science and Engineering University of Jinan (West Campus), Jinan, China. Synthesis and characterisation of the mesoporous silica materials with various morphology under supervision of prof. dr Shiquan Liu.

9.2.4 Projects

PROJECT 1

Contractor of project No. 0670/IP3/2016/74, from the Polish Ministry of Science and Higher Education, *Functionalization of micro-mesoporous zeolites for the needs of highly selective processes of environmental catalysis*, February 2017 – July 2020.

PROJECT 2

Contractor of Erasmus+ project No. GREENUS 618173-EPP-1-2020-1-IT-EPPKA2-CBHE-JP funded by the EACEA (Education, Audiovisual and Culture Executive Agency) under the Key Action 2, *GREENUS (GREEN waste management new edUcation System for recycling and environmental protection in asia)*, October 2021 – September 2023.

PROJECT 3

Lider of project No. 2021/41/N/ST5/03358 from the National Science Centre, *Functionalisation of heteroatomic zeolites of MWW family with tailored porous structure for the needs of the low-temperature selective catalytic reduction of NO with ammonia (NH_3-SCR)*, January 2022 – January 2024.

9.2.5 Organisational activity

ACTIVITY 1

Participation in the organization of the national conference: "61 Zjazd Naukowy Polskiego Towarzystwa Chemicznego", 17-21.09.2018, Kraków, Jagiellonian University.

ACTIVITY 2

Co-organisation of the international conference "Green Skills for Sustainable Development", 20-23.03.2019, Kraków, Jagiellonian University.

ACTIVITY 3

Co-organisation of the international meeting "ECTN General Assembly", 12-14.04.2019, Kraków, Jagiellonian University.

ACTIVITY 4

Co-organisation of the international conference "Modernization of Doctoral Education in Science and Improvement Teaching Methodologies (MODEST)", 9-11.07.2019, Kraków, Jagiellonian University.

ACTIVITY 5

Co-organisation of the national conference "I Uczniowska Konferencja Młodych Chemików", 24.09.2021, Kraków, Jagiellonian University.

9.2.6 Award

AWARD

Prize in category 'Best Oral Presentation' entitled *Badania aktywności katalitycznej nanosfer MCM-41 dotowanych miedzią za pomocą metody jonowej wymiany templatu (TIE) w niskotemperaturowym procesie* NH_3*-SCR* presented at the *Fizykochemia granic faz - metody instrumentalne* national conference, 22-26.08.2021, Lublin, Poland.

10. List of abbreviations

BEA – zeolite with the BEA topology

DOMS – deposition of oligomeric metal species

DRIFT – Fourier transform infrared diffuse reflectance spectroscopy

ESP – electrostatic precipitator

FAU – zeolite framework topology of e.g., zeolite Y faujasite

Fe3 – three-nuclear acetate iron oligocations $[Fe_3(OCOCH_3)_7{\cdot}OH{\cdot}2H_2O]NO_3$

FER – zeolite with ferrierite framework type

FT-IR – Fourier transform infrared spectroscopy

GC – gas chromatograph

H_2-TPR – temperature-programmed reduction with hydrogen

ICP-OES – inductively coupled plasma - optical emission spectrometry

ITQ-2 – delaminated derivative of layered MCM-22 precursor

IUPAC – International Union of Pure and Applied Chemistry

M41S – family of mesoporous silica sieves *e.g.*, MCM-41

MCM-22 – Mobile Crystalline Material no. 22 (zeolite with MWW topology)

MCM-41/-48/-50 – Mobil Composition of Matter no. 41/48/50 (hexagonal, cubic, or lamellar ordered mesoporous silicate)

MCM-36 – pillared derivative of layered MCM-22 precursor

MDD – molecular designed dispersion

MFI – zeolite framework topology code, *e.g.*, ZSM-5

MOR – zeolite with mordenite framework type

MWW – zeolite framework topology of *e.g.*, MCM-22

NH_3-SCO – selective catalytic oxidation of ammonia

NH_3-SCR – selective catalytic reduction of nitrogen oxides with ammonia

NH$_3$-TPD – temperature-programmed desorption of ammonia

NO$_x$ – nitrogen oxides, including nitrogen(II) oxide and nitrogen(IV) oxide

P-XRD - powder X-ray diffraction

Py – pyridine

RS – Raman spectroscopy

SAPO-34 – silicoaluminophosphate microporous molecular sieve with the chabazite topology

SBA-15 – Santa Barbara Amorphous type 15 (mesoporous silicate)

SEM – scanning electron microscopy

TCD – thermal conductivity detector

TIE – template ion-exchange

TIE-NH$_3$ – template ion exchange with ammonia treatment

TGA – thermogravimetric analysis

TOF – turn-over frequency

UV-vis DRS – ultraviolet visible diffuse reflectance spectroscopy

QMS – quadrupole mass analyser

11. List of figures