

Zeolites belong to the group of natural and synthetic porous crystalline aluminosilicates, which, due to their unique properties, are widely used as sorbents and catalysts. The simplicity of their synthesis and modification, resistance to high temperatures, and shape selectivity in a variety of reactions were the reasons for the widespread of their application in the industry, mainly in the processing of crude oil (cracking) and selective conversion of petrochemical products. Zeolites are also intensely tested in the application of biomass conversion addressing the problems of the availability of fossil fuels and their impact on the environment.

Until 1990, zeolites were perceived only as three-dimensional structures (3D). The development of the layered precursor MCM-22P revolutionized this point of view, opening new perspectives in zeolite synthesis, modifications, and consequently their applications. Layered zeolites are often compared to other layered materials - clay minerals. However, despite some similarities, each of these groups has its specific properties. Part of layered zeolites have porous layers, while the porosity of clay minerals is between relatively small (<2 μm), chaotically arranged crystallites, as well as – for some of them – in their interlayer spaces. Clay minerals from the smectite group are spontaneously exfoliating into monolayers, while in zeolites such a phenomenon is not observed. This is the reason why the phenomenon of zeolite exfoliation was intensively studied.

A breakthrough in the exfoliation of zeolites took place in 2020, when the Zeolite Chemistry Group of the Jagiellonian University obtained single-layered MWW[1] and then, a year later double-layered ferrierite [2].

This doctoral dissertation is devoted to the preparation, modification, and catalytic properties of the colloidal suspensions of layered zeolites (2D) from the MWW and FER families.

The research presented in the paper is grouped into four parts. The first part investigates the pillaring of MWW zeolite monolayers using the Keggin Al_{13} oligocations. The obtained results indicate that monolayers are easily swelled using a surfactant. However, the very high pH of the colloidal suspensions makes it impossible to pillar zeolites with Keggin ions. As a result, the amorphous Al_2O_3 is probably formed, which binds to and surrounds MWW layers. The resulting composite is characterized by a significant mesoporosity, which may contribute to better diffusion of substrates and products in catalytic reactions in respect to original materials.

The colloidal suspensions of zeolite monolayers are characterized by a high pH (>12), which is due to the high concentration of tetrabutylammonium hydroxide (TBAOH). Such a high pH hinders further modifications of the material, causing degradation of other substrates (as shown in Chapter 2). Therefore, the second part of this dissertation is carried out to obtain colloidal systems of monolayers with reduced pH. Each addition of a substrate with pH up to 8, disturbs the colloidal systems, causing its immediate flocculation. Therefore, dialysis has been proposed as a method to reduce TBAOH concentration. The zeolite colloids were extracted after dialysis using a freeze-drying method. The freeze-drying method allows to obtain samples with good physical parameters that facilitate further work with the preparates. Dialysis of monolayer suspensions proved also to be effective in removing sodium cations. This further improved the catalytic activity of materials and at the same time allowed the preservation of the high microporosity of the samples. In turn, freeze-drying contributed to the preservation of the disorder in the arrangement of MCM-56 zeolite layers in the samples extracted from the suspensions. It caused also an increase in the share of secondary mesoporosity.

The third part of the dissertation focuses on the preparation of a hybrid catalyst based on MWW monolayers and platinum nanoparticles. The presented results indicate that simple and quick syntheses allow preparing of competitive materials with respect to commercial catalysts. The obtained samples provided 100% conversion of substrates with three times less active phase compared to commercial catalysts, which is important from both, economic and ecological perspectives.

The last part of the dissertation is devoted to hybrid materials that were prepared as a result of the mixing together of colloidal suspensions of layers of two different zeolites – MWW and FER. The resulting composite is characterized by an increased specific surface area and the volume of mesopores with respect to commercially available ferrierite. In addition, the catalytic properties of conversion of benzyl alcohol are improved with respect to the colloidal suspension of MWW monolayers and FER double layers.

This doctoral dissertation is based on the research contained in four articles, which were published in international journals. They are part of the scientific achievements of PhD student, which include a total of seven works (total IF = 59,510, number of citations = 46 according to the Web of Science 10th November 2022).

Articles included in the doctoral dissertation:

1. W. J. Roth, T. Sasaki, K. Wolski, Y. Song, DM. Tang, Y. Ebina, M. Renzhi, J. Grzybek, **K. Kałahurska**, B. Gil, M. Mazur, S. Zapotoczny, J. Cejka
Liquid dispersions of zeolite monolayers with high catalytic activity prepared by soft-chemical exfoliation
Science Advances, 6, 12, 2020
DOI: 10.1126/sciadv.aay8163
IF = 14.980
2. **K. Kałahurska**, P. P. Ziemiański, W. J. Roth, B. Gil
From colloidal dispersions of zeolite monolayers to effective solid catalysts in transformation of bulky organic molecules: role of freeze-drying and dialysis
Molecules, 26, 7, 2076, 2021
DOI: 10.3390/molecules26072076
IF = 4.927
3. **K. Kałahurska**, W. Pajerski, A. Kotarba, M. Kubu, Y. Zhang, M. Mazur, J. Prech, G. Jajko, W. Makowski, W. J. Roth, B. Gil
Platinum nanoparticles supported on zeolite MWW nanosheets prepared via homogeneous solution route
Catalysis Today, 390-391, 335-342, 2022
DOI: 10.1016/j.cattod.2021.09.026
IF = 6.562
4. W. J. Roth, T. Sasaki, K. Wolski, Y. Ebina, DM. Tang, Y. Michiue, N. Sakai, M. Renzhi, O. Cretu, J. Kikkawa, K. Kimoto, **K. Kałahurska**, B. Gil, M. Mazur, S. Zapotoczny, J. Cejka, J. Grzybek, A. Kowalczyk
Exfoliated ferrierite-related unilamellar nanosheets in solution and their use for preparation of mixed zeolite hierarchical structures
Journal of the American Chemical Society, 143, 29, 11052-11062, 2021
DOI: 10.1021/jacs.1c04081
IF = 16.383

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- [1] W.J. Roth, T. Sasaki, K. Wolski, Y. Song, D.-M. Tang, Y. Ebina, R. Ma, J. Grzybek, K. Kałahurska, B. Gil, M. Mazur, S. Zapotoczny, J. Cejka, Liquid dispersions of zeolite monolayers with high catalytic activity prepared by soft-chemical exfoliation, *Sci. Adv.* 6 (2020) eaay8163. <https://doi.org/10.1126/sciadv.aay8163>.

- [2] W.J. Roth, T. Sasaki, K. Wolski, Y. Ebina, D.-M. Tang, Y. Michiue, N. Sakai, R. Ma, O. Cretu, J. Kikkawa, K. Kimoto, K. Kalahurska, B. Gil, M. Mazur, S. Zapotoczny, J. Čejka, J. Grzybek, A. Kowalczyk, Exfoliated ferrierite-related unilamellar nanosheets in solution and their use for preparation of mixed zeolite hierarchical structures, *J. Am. Chem. Soc.* 143 (2021) 11052–11062. <https://doi.org/10.1021/jacs.1c04081>.