

# **Nanostructured cobalt spinel-based catalysts: correlation between structure, redox and catalytic properties in reactions with small molecules of environmental relevance**

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## **Abstract**

Throughout this doctoral dissertation a research was carried out investigating the relationship between the structure, surface faceting, redox and electronic properties and catalytic activity of spinel systems based on  $\text{Co}_3\text{O}_4$  with different morphologies and chemical compositions (doped with non-redox ions Li, B, K, and redox ions Cr, Mn, Fe, Ni, Cu, Zn). Catalytic properties were evaluated in reactions involving small oxidizing ( $\text{N}_2\text{O}$ ,  $^{18}\text{O}_2/^{16}\text{O}_2$ ) and reducing ( $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2$ ) molecules. Isotopic labeling was employed in order to understand the role of surface (Langmuir-Hinshelwood/Eley-Rideal mechanisms) and interfacial (Mars van Krevelen mechanism) reactive oxygen species in the temperature-dependent reactions.

An optimization of the synthesis of  $\text{Co}_3\text{O}_4$  with controlled crystal morphology was developed (Chapter 7). A series of hydrothermal syntheses were performed with varying concentrations of  $\text{Co}(\text{NO}_3)_2$  and  $\text{NaOH}$  substrates. XRD analysis and microscopy (TEM) and RS/IR spectroscopic studies showed that the crystal shape of  $\text{Co}_3\text{O}_4$  (ranging from cubic, through cuboctahedral, to octahedral) can be controlled by adjusting the reagent concentrations while maintaining a constant molar ratio. Detailed crystal growth studies were conducted on systems with homogeneous faceting (100) and (111). Mechanistic studies were performed using time intervals, and the phase composition of the reaction mixture was analysed at each stage using XRD, IR, RS, and TEM methods. These have revealed that changing the reagent concentration affects the formation of an intermediate phase, on which topotactic nucleation of  $\text{Co}_3\text{O}_4$  crystals with varying morphologies occurs. Cubic crystals are formed from the  $(\text{Co}^{2+}(\text{OH})_{2-x}(\text{NO}_3)_x)$  phase, while octahedral crystals are formed from a mixture of  $\text{CoOOH}$  and  $\text{Co}_2(\text{NO}_3)(\text{OH})_3$ . The concentration of cobalt nitrate has a critical influence on the formation and growth of  $\text{Co}_3\text{O}_4$ . Cubic spinel is formed by the oriented attachment of nanometric crystallites with sizes of 4-5 nm into

submicrometer-sized mesocrystals, which are subsequently consolidated into well-formed  $\text{Co}_3\text{O}_4$  monocrystals with homogeneous faceting (100). The formation of octahedral crystals initially occurs through the aggregation of cuboctahedral nanocrystals. Subsequent hydrothermal etching and recrystallization processes lead to the formation of submicrometer-sized  $\text{Co}_3\text{O}_4$  crystals with faceting (111).

Spinel-based catalysts with different morphologies were evaluated for the effect of  $\text{Co}_3\text{O}_4$  faceting on reducibility ( $\text{H}_2$ -TPR), activation of molecular oxygen ( $^{18}\text{O}_2/^{16}\text{O}_2$  isotopic exchange), and methane oxidation.  $\text{H}_2$ -TPR results have shown the influence of two factors, with grain size being the primary factor (the smallest crystals being reduced at the lowest temperature), and faceting as a secondary factor, with reducibility decreasing in the order cubes > cuboctahedra > octahedra.

An important part of this research stage was methane oxidation tests, during which the use of oxygen with a changing isotopic composition ( $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ ) played a crucial role. This allowed for distinguishing between oxidation mechanisms based on interactions with suprafacial reactive oxygen species (Langmuir-Hinshelwood/Elaya-Rideal mechanism) and intrafacial oxygen anions (Mars-van Krevelen mechanism). The evolution of the  $\text{CH}_4$  oxidation mechanism involving surface  $\text{O}_{\text{ads}}^-$  species (LH/ER), which enable activation of C-H bonds in the low temperature region, and an increasing contribution of  $\text{O}_{\text{surf}}^{2-}$  anions (MvK) with rising temperature, was demonstrated. It was shown that  $\text{Co}_3\text{O}_4$  with cubic morphology exhibits a higher contribution of the MvK mechanism compared to the spinel with octahedral grain shape, throughout the entire temperature range of the reaction, according to the values of  $V_{\text{O}20,1\text{T}}$  oxygen vacancy formation energy.

Another segment of this study (Chapter 9) was focused on the determination of the effect of doping the  $\text{Co}_3\text{O}_4$  spinel with isovalent ( $\text{B}^{3+}$ ) and aliovalent ( $\text{Li}^+$ ) cations. Screening tests of catalytic activity in  $\text{CH}_4$  oxidation, CO oxidation, and  $\text{N}_2\text{O}$  decomposition were conducted. Doping with  $\text{B}^{3+}$  ions in each reaction caused a decrease in activity due to the substitution of redox-active  $\text{Co}^{3+}$  ions located in the 16d positions by non-redox cations. In the case of lithium doping, a decrease in activity was observed during  $\text{CH}_4$  and CO oxidation, and an improvement was observed in  $\text{N}_2\text{O}$  decomposition. Doping with  $\text{Li}^+$

ions was subject to more detailed studies involving a well-defined  $\text{Co}_3\text{O}_4$  spinel with controlled cubic morphology. Doping was carried out in two ways: by surface impregnation and volume doping. Differences in the mechanisms of lithium heteroion incorporation into the spinel structure were demonstrated by XAS spectroscopy and non-contact electrical conductivity measurements. Surface impregnation has resulted in the incorporation of Li in the 8a positions, which lead to the relocation of  $\text{Co}^{2+}$  to the 16c position and the reduction of cobalt located in the 16d position:  $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ . Volume doping lead to the incorporation of  $\text{Li}^+$  in the 16d positions and the oxidation of cobalt:  $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ . As a result, by using a properly chosen lithium doping method, it was possible to control redox processes in the  $\text{Co}_3\text{O}_4$  matrix.

As demonstrated by measurements of the work function, the doping method has a direct influence on the Fermi level, enabling control over the electro-donor properties of spinel and therefore the activity in the  $\text{N}_2\text{O}$  decomposition reaction. Increasing the oxidation state of Co ions (volume doping) lowers the  $E_F$  level, making it difficult for interfacial electron transfer to the  $\text{N}_2\text{O}$  molecule, leading to decreased catalytic activity. On the other hand, reduction of cobalt ions (surface doping) significantly improves catalytic activity by increasing the  $E_F$  level, facilitating the activation of nitrous oxide molecules. Based on the results of  $\text{N}_2\text{O}$  decomposition reaction as a function of temperature, contact time, and pressure, the effect of autogenous poisoning of the catalyst surface by negatively charged  $\text{O}_{\text{ads}}^-$  intermediate reaction products on the catalytic activity was demonstrated. The most active doped system with lithium (i-Li2) was subjected to surface decoration with  $\text{K}^+$  ions. This has enabled to lower the activation energy of  $\text{N}_2\text{O}$  decomposition by simultaneously raising the Fermi level (by targeted doping of Li at the 16d positions) and preventing the formation of a surface potential which is a barrier for electron transfer, resulting from the accumulation of negative charge ( $\text{O}_{\text{ads}}^-$ ) on the surface. As a result, the synergistic effect of double doping (Li + K) of the cubic  $\text{Co}_3\text{O}_4$  led to a significant improvement in the activity of  $\text{N}_2\text{O}$  decomposition reaction.

Mixed spinel catalysts doped with redox-active heteroions (Cr, Mn, Fe, Ni, Cu, and Zn) were obtained by combustion synthesis (Chapter 10). This method was chosen due to its much higher efficiency compared to hydrothermal synthesis, as well as the better phase purity and morphological homogeneity of the obtained spinel compared to the

precipitation method. Systematic analysis of the chemical composition of the internal and surface of mixed spinels (by XRF and XPS methods) and the phase composition by XRD (with a detailed analysis of the diffraction patterns using the Rietveld method) and the valence-coordination states of the dopants (XPS analysis) allowed for the quantitative determination of the heterocation distribution in the spinel lattice. Based on this, taking into account the location of the dopants and the crystal lattice distortions, a group of spinels-B (doped with Cr, Mn, and Fe mainly in the 16d positions) and spinels-A (doped with Ni, Cu, and Zn mainly in the 8a positions) were distinguished. The effect of doping on the position band energy centres of the 2p oxygen and 3d metal bands relative to the Fermi level was analysed. Based on this, a descriptor of surface reducibility  $E_{O_{2p}} + k\Delta\chi$  (the position of the O 2p band modified by the contribution from the average electronegativity of the spinel) was proposed. It was shown that the temperature of the onset of reduction shows a linear dependence on  $E_{O_{2p}} + k\Delta\chi$  for the entire series of  $M_xCo_{3-x}O_4$ .

The relationship between electronic structure and catalytic reactivity of mixed spinel catalysts was investigated using the example of the selective oxidation of CO in a hydrogen rich stream (CO-PROX) - Chapter 11. A correlation was determined between the rates of H<sub>2</sub> and CO oxidation for spinels in groups A and B, as well as the work function ( $\Phi$ ) and the parameter  $\Delta E_{M-O}$  (the difference in the position of the centre of the M 3d and O 2p bands). The selectivity of the CO-PROX reaction analogously to the reducibility, depends on the descriptor  $E_{O_{2p}} + k\Delta\chi$ . To determine the mechanism of the CO-PROX reaction, extensive catalytic studies of mixed spinels were conducted using isotopically labeled <sup>18</sup>O<sub>2</sub>. The analysis of the isotopic composition of reaction products, combined with the simulation of the isotopic composition of products as a function of selectivity, allowed for the identification of the main and side reaction pathways, key intermediate products, and the interplay of LH/ER and MvK mechanisms. The reaction pathway of PROX, which occurs through the evolution of LH/ER- $\alpha_p$  and MvK-LH/ER- $\beta_t/\beta_p'$  mechanisms induced by increasing temperature, was parameterized. The surface carbonate anions play a crucial role as main transient products in the proposed mechanism, determining the isotopic composition of products depending on their current configuration. The observed temperature dependence of selectivity on the C<sup>18</sup>O<sub>2</sub> and C<sup>16</sup>O<sub>2</sub> isotopic spacing, and the complete reproduction of the experimental isotopic composition of CO<sub>2</sub> and H<sub>2</sub>O as a

function of selectivity for the entire series of mixed spinels, provide strong evidence for the validity of the proposed carbonate mechanism as the main pathway of the PROX reaction.