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In situ/operando studies for understanding the metal-support interaction of Ni-based catalysts for ammonia decomposition

Content

Ammonia is considered a promising hydrogen carrier due to its high hydrogen content (17.8 wt%) and ease of transportation at room temperature under moderate pressures [1]. Ammonia decomposition into hydrogen and nitrogen is a carbon-free, endothermic reaction that requires suitable catalysts to lower the reaction temperature. Various supported metal catalysts are tested, and understanding metal-support interactions (MSI) during activation and catalysis is crucial for designing effective catalysts [2]. In this work, Ni catalysts supported on CeO2, TiO2, MgO, Al2O3, and SiO2 are investigated using a combination of in-situ characterization techniques such as X-ray diffraction (XRD), X-ray absorption spectroscopy (EXAFS), X-ray photoelectron spectroscopy (XPS), and total scattering with pair distribution function (PDF) analysis, complemented by transmission electron microscopy (TEM). Wet impregnation is used for the synthesis of 10 at. % Ni on different supports, among which Ni/CeO2 showed the highest ammonia conversion, while Ni/TiO2 showed the lowest.

XRD provides insights into the average crystal structures of the catalyst and the support, whereas EXAFS offers element-specific information on the local coordination environment of Ni. Total scattering with PDF analysis, however, provides understanding of both short- and long-range structural order. In the current study, operando PDF analysis was particularly useful for Ni/SiO2, owing to the amorphous nature of the support, and for Ni/Al2O3, which forms NiAl2O4. Temperature-dependent operando total scattering experiments were conducted at P02.1 (Petra III, DESY), and the structural evolution was compared during the activation and ammonia decomposition processes. Comparative PDF analysis revealed distinct variations in the local Ni environments across different supports. For Ni/CeO_2, the PDF analysis showed well-defined Ni–Ni pair correlations characteristic of metallic Ni nanoparticles. These correlations remained largely unchanged during both activation and ammonia decomposition. This immobilization type-MSI enhanced catalyst stability and activity, resulting in the highest ammonia conversion. However, subtle changes in the structure of the CeO2 support were observed, indicating the partial reduction of Ce4+ to Ce3+ also confirmed by in situ XPS. In contrast, the PDF of Ni/TiO_2 showed sharper Ni–Ni correlations, indicating a well-ordered Ni structure. From in situ XRD, larger crystallite sizes and from TEM analysis, larger particle sizes of Ni nanoparticles indicate sintering. This work emphasizes the importance of using characterization techniques across different length scales, from local coordination to long-range order, combined with in situ/operando studies for a complete understanding of complex metal-support interactions in catalytic reactions.

[1] Y. Kojima, M. Yamaguchi, International Journal of Hydrogen Energy, 2022, 47, 22832-22839.
[2] Liu, L., Corma. A., Chemical Reviews, 2018, 118, 4981–5079.

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