

Abstract

Supported metal nanoparticles are a prominent class of catalysts due to their high activity in redox reactions and wide applications in numerous industrial processes. They often suffer from deactivation by sintering. One of the recognized and effective strategies to prevent sintering is to confine them into a zeolite matrix thus improving the stability of metal nanoparticles. The aim of my Ph. D. thesis was the rational design and synthesis of zeolite-supported metal nanoparticles (metal@zeolite materials). I have put my main focus on the interactions of nanoparticles with the zeolite supports. The essential experimental tool utilized in this work was advanced electron microscopy. I used this method for the investigation of the structure, location, and stability of supported metal species. Synthesized novel metal@zeolite materials were used as model systems for detailed investigation of metal-zeolite interactions. Prepared materials were investigated as heterogeneous catalysts in the hydrogenation of benzonitrile and dry reforming of methane. My thesis covered the following aspects:

i) Rh nanoparticles were incorporated into hierarchical zeolitic materials (Rh@IPCs) *via* swelling of layered zeolite precursor IPC-1P. The final morphology and porosity of prepared materials were tuned by differing the size of used surfactants. Remarkably, using the docosyltrimethylammonium hydroxide for swelling and subsequent calcination resulted in the unprecedented material, denoted as Rh@IPC_C22. The layers in this catalyst were disorderly stacked with each other creating mesoporous voids between layers. Rh nanoparticles in different Rh@IPCs exhibit characteristics desirable for catalytic use, such as small particle size, homogeneous distribution, and resistance to sintering.

In-situ heating STEM was performed to track the behavior of Rh nanoparticles in Rh@IPC_C22, including their locations, stability, and growth while heating up to 750 °C for 6 hours from room temperature. The average sizes of Rh nanoparticles increased only slightly (approx. 5%) after heating, which showed their excellent

sintering resistance. Furthermore, the various Rh@IPCs materials were investigated in the hydrogenation of benzyl nitrile, showing that the sizes of Rh species had not increased significantly in spent catalysts, even after 3 catalytic cycles.

To explain the mechanism of excellent sintering resistance of Rh on the IPC layers, we analyzed prepared materials by the XPS and FT-IR spectroscopy (with CO as a probe molecule). These analyses allowed evaluation of the oxidation states of Rh in prepared materials. Theoretical simulations (DFT) were performed to reveal the binding energies of Rh species on IPC-1P layers, namely to their surface silanols. Finally, we proposed that surface silanols of IPC-1P layers stabilized Rh nanoparticles. We confirmed that the silanols could strongly pin Rh species and stabilize them even at high temperatures.

ii) Commercially available USY zeolites were dealuminated to prepare silanol-rich deAl-USY materials and used as support for Pd nanoparticles. Synthesis of Pd@USY and Pd@deAl-USY was performed by simple impregnation processes. STEM analysis showed that the Pd species were uniformly dispersed in the zeolite crystals. *In-situ* heating STEM experiments were conducted to investigate the thermal stability of Pd nanoparticles in different materials. The average sizes of Pd in Pd@USY increased significantly (from 1.55 nm to 4.03 nm) while heating from room temperature to 700 °C for 4 hours. In contrast to Pd@deAl-USY, it showed a relatively low growth (from 2.49 nm to 3.28 nm) in the average sizes of Pd after the same heating protocol. This anti-sintering effect in Pd@deAl-USY was also observed in the catalytic dry reforming of methane. During a continuous 72-hour test, Pd@deAl-USY showed resistance to deactivation when compared to Pd@USY. Based on the spectroscopic analyses (including solid state NMR, XANES, and XPS) of Pd@deAl-USY and Pd@USY in both reduced and oxidized forms, I confirmed that the improved thermal stability of Pd was due to the enhanced metal-silanols interactions. Silanol-rich supports prepared by demetallation enhanced the sintering resistance of supported metal nanoparticles.

iii) TEM studies were performed to investigate the metal-zeolite interactions in materials composed of bimetallic platinum-cerium (Pt-Ce) alloy particles supported

on degallated **MFI** nanosponge zeolites. ADF-STEM imaging coupled with EDS analysis was used to analyze the structure and chemical composition of these materials. Comparison of ADF-STEM images of fresh and spent catalysts showed high stability of Pt-Ce nanoparticles that were assessed to metal-silanols interactions.

Furthermore, we investigated the influence of the aluminum content and the presence of different cations on Rh particle sizes in *BEA aluminosilicate. ADF-STEM imaging of Rh@H-BEA and Rh@Na-BEA showed that the cation type, as well as Si/Al ratios of the zeolites did not significantly influence the size and stability of supported nanoparticles.