Control and Impact of Nanoscale Distribution of Platinum in Bifunctional Hydrocracking Catalysts

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Introduction

Bifunctional zeolite-based catalysts are of immense importance to industrial processes such as hydrocracking, hydrotreating and hydroisomerization of oil fractions [1]. They are commonly prepared by depositing metal (sulfide) nanoparticles, which provide the (de)hydrogenation function, onto catalyst bodies usually containing zeolite, which provides the cracking function, and alumina binder as the main components. Understanding the mechanism and achieving the control over the metal location and dispersion across the support is crucial for optimizing the catalyst properties [2-4].

Here we present a methodology to deposit Pt nanoparticles either on the zeolite or the alumina phase of extrudates by considering the interplay between ion exchange (IE) and electrostatic adsorption (EA) of Pt-complexes [2,3]. Advanced electron microscopy techniques were essential to unravel the catalyst structural features at nanometer length scales.

Materials and Methods

Cylindrical extrudates containing 50/50 weight ratio of mesoporous zeolite Y (Zeolyst CBV760, Si/Al=30 at/at) and gamma alumina were crushed and sieved to 0.2 - 0.4 mm fractions, here referred as YA support. To deposit Pt exclusively onto the zeolite phase of YA (Pt-YA-Am), Pt(NH3)4(NO3)2 aqueous solution was mixed with YA and left to stir for 3h. The suspension was filtered, washed and YA fractions were dried overnight at 120 °C. Dried fractions were reduced at 600 °C in a flow of H2. In case of depositing Pt exclusively onto the alumina phase (Pt-YA-Cl), H2PtCl6 solution was used as a precursor. Here, pH was adjusted to 3 prior to addition of Pt precursor, and an additional heat treatment of dried and reduced Pt/YA fractions in a N2 with 1% O2 flow was performed. TitanTM G2 80-200 with Chemi-STEM, Tecnai 20 and Tecnai 20F FEI microscopes were used for EDX mapping, electron tomography (ET) and high-angle annular dark field imaging (HAADF), respectively.

Results and Discussion

EDX mapping of 70 nm thick ultramicrotomed sections of YA support showed that most of the zeolite crystals were coated with alumina (Fig. 1a). Electron tomography (Fig. 1b) provided insight into the intimate contact between zeolite and alumina platelets. To deposit Pt particles on exclusively the zeolite component of the YA extrudates, it was assumed that IE of zeolite protons with Pt(NH3)42+ will dominate over EA on alumina if pH is maintained below 9 [2,3]. The previous study [4] showed that direct reduction in H2 promotes the growth of Pt particles to ~3 nm. HAADF images of 70 nm thick ultramicrotomed sections revealed that Pt was successfully deposited on the zeolite crystals exclusively (Fig1c). In case of Pt deposition on exclusively alumina of the YA support, EA of negatively charged PtCl62- complexes on alumina is expected at low pH, while IE between zeolite protons and these negatively charged species is absent [2,3]. Therefore, prior to addition of the H2PtCl6 (aq), the pH of the suspension was lowered to ~3 by adding HCl. Direct reduction in H2 of PtCl62- on alumina and an additional heat treatment in N2 with 1%O2 led to Pt particles of ~3 nm (Fig. 1d).

Figure 1. TEM characterization of Pt-YA catalysts: a) EDX map, b) slice from ET reconstruction, HAADF image of Pt-YA-Am sample (c) and Pt-YA-Cl sample(d).

Significance

This study shows that besides loading and dispersion, the location at the nanometer scale of the metal (de)hydrogenation function in the industrially relevant mixed-phase supports can be controlled and is of great importance. Such control in design offers flexibility in tuning the catalyst properties to meet the requirements of specific processes.

References