Mesoporous zeolites as a high-performance catalyst support

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Abstract: Mesoporous materials can be synthesized with microporous crystalline zeolite frameworks of various types such as MFI, beta and *MRE, using multiammonium surfactants as a micro/meso dual structure-directing agent. Here we show that the mesoporous zeolites have a distinct merit of high catalyst dispersion when used as a support for metal catalysts. The mesoporous zeolite-supported catalysts exhibited high catalytic performances in various reactions.

Keywords: Mesoporous zeolite, supported catalysis, heterogeneous catalysis.

1. Introduction

Zeolites are a family of microporous crystalline aluminosilicate materials with various framework structures. Zeolites are not only important as solid acid catalysts in various petrochemical processes, but also widely used as a metal-catalyst support for hydrogenation, dehydrogenation, hydrogenolysis and oxidation reactions. Platinum and palladium are most widely used among the zeolite-supported metal catalysts. The group-10 heavy metals have high intrinsic catalytic activity and moreover, can easily be supported in a form of nanoparticle with high metal dispersion inside the zeolite micropores. The high dispersion of the heavy metals is due to high atomic polarizability, which allows the stabilization of metal nanoparticles by van der Waals interactions with the micropore walls. Compared to the heavy metals, light transition metals (*e.g.*, Ni and Co) are rarely used as supported on zeolites. This is partly because the light metals have intrinsically low catalytic activity, but a more serious problem arises from their poor dispersion on zeolites. The light metals have a low atomic polarizability, forming large agglomerates at external surfaces of zeolites [1].

In the present work, we have discovered that high dispersion of the light transition metals can easily be achieved when supported on *zeolite nanosponges (ZNS),* which possess secondary mesopores between ultrathin zeolite nanowalls. Such mesoporous zeolites can be synthesized according to a synthesis method using multi-ammonium surfactant as a micro/meso dual structure-directing agent (SDA) [2]. The mesopores in the zeolite nanosponges are disordered in a manner analogous to a sponge, but the pore diameters can be controlled by the size of the SDA surfactant as in MCM-41 mesoporous silica. In addition, the framework structure and thickness of the mesopore walls can be controlled by the zeolite-directing surfactant head. When the metal loading is low (e.g., 2 wt%), the ZNS can support light transition metals, such as Ni and Co in the form of tiny nanoparticles with high metal dispersion inside mesopores [1,3]. When the metal loading is high, the supported metal atoms agglomerate into a nanowire along cylindrical mesopore, or nanosheet within slit-shaped mesopore [4]. However, the thickness of the nanowire or nanosheet is limited to the mesopore size. This encasing or sandwiching effect by the pore walls is important for high metal dispersion. Furthermore, the lateral surfaces of the nanowires and nanosheets are accessible for catalytic reactions through microporous windows in the mesopore walls. We demonstrate the effect of high metal dispersion on ZNS for hydroisomerization of linear paraffins, Fischer-Tropsch (FT) synthesis and benzene hydrogenation. Particularly, in the case of hydroisomerization of *n*-dodecane, the high metal dispersion made it possible to completely replace Pt catalyst by supporting only 2 wt% Ni on MFI ZNS.

2. Experimental

ZNSs of MFI, beta, and *MRE structure were synthesized using micro/meso dual SDA surfactants, following the procedures in our recent works [1,2]. The zeolites were supported with various catalytic components by impregnation, and the reaction measurements were performed as described elsewhere [3,4].

3. Results and discussion

Figure 1 shows the catalytic reaction results for hydroisomerization of *n*-dodecane obtained with 2 wt% Ni/MFI ZNS [3]. As this result shows, the use of ZNS as a catalyst support has two advantages. The first one is high Ni dispersion allowing high catalytic conversion rate. The other is high isomer yield due to the short diffusion path lengths in the ultrathin zeolite framework. This explains why the isomer yield decreased in the order of 2% Ni/ZNS = 1% Pt/ZNS >> 1% Pt/bulk MFI while the catalytic conversion rates were similar for all three catalyst samples.

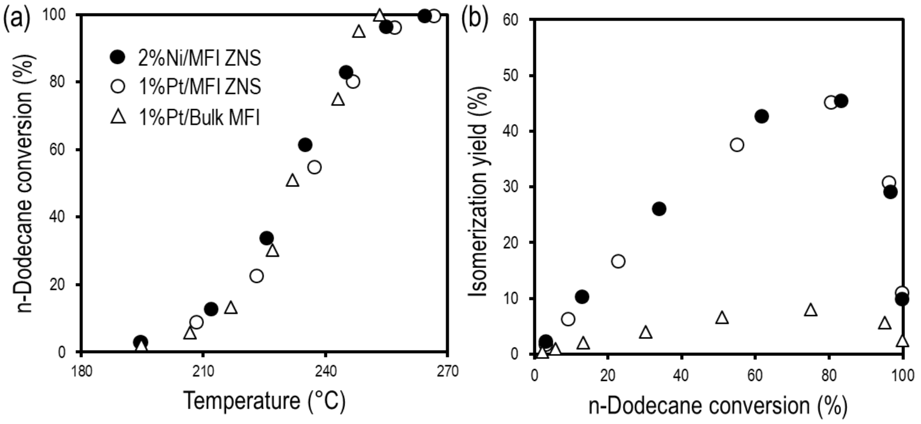

Figure 1. Isomerization of n-dodecane: (a) conversion *vs.* temperature and (b) isomer yield *vs.* conversion [3]

Figure 2 shows the FT synthesis reaction result obtained from Co/beta ZNS catalyst samples with various Co loading amounts from 3 to 30 wt% [4]. The Co/beta ZNS catalysts exhibited much higher CO conversion rates as compared to those of solely mesoporous MCM-48 with the same amount of Co. The difference in the CO conversion rates was increased as the Co loading was increased. This can be explained by the effect of the microporous windows on the mesopore walls of ZNS, when the supported-Co catalysts was in the form of nanowire tightly encased by the mesopore walls at the high metal loading. For the same reason, the ZNS-supported Ni catalysts also showed high catalytic activity in benzene hydrogenation [4].

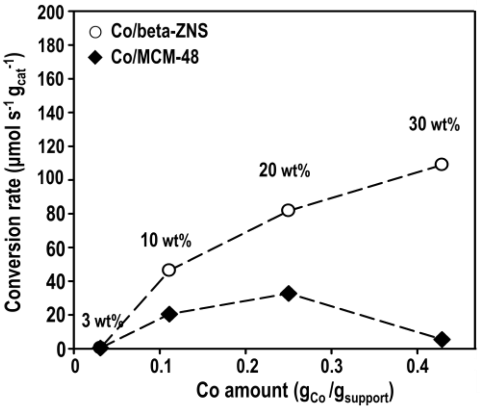

Figure 2. Conversion rate in FT synthesis as a function of Co loading on beta ZNS and MCM-48 [4]

4. Conclusions

The zeolite nanosponges had interconnected mesopore structure, which was built of ultrathin crystalline microporous walls stacked in a disordered manner. Taking advantage of the zeolite nanosponge as a catalyst support, we have demonstrated high-performance catalysis of various reactions, which was difficult to achieve with conventional supporting materials such as mesoporous silica and bulk zeolites.

References

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