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RESEARCH NOTE

Synthetic Smectite-like Materials Containing Different Divalent Cations as Catalysts and Supports for Gas-Phase Hydrogenation of Acetonitrile

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Synthetic smectite-like porous materials including Ni^{2+}, Co^{2+}, Mg^{2+}, and Zn^{2+} cations in the octahedral sheets were used as catalysts and supports for gas-phase hydrogenation of acetonitrile. The Ni^{2+}-containing material itself was active even in the absence of additional active components, while the others were inactive in common with silica, alumina, and NaY zeolite. When platinum was loaded, the smectite-like materials, except those containing Zn^{2+}, exhibited hydrogenation activity, and the platinum-loaded Ni^{2+}-containing material was most active. These catalysts produced a mixture of primary, secondary, and tertiary amines in different selectivities, in contrast to silica-supported platinum catalyst producing mainly tertiary amine. With platinum-loaded Ni^{2+}-containing material, the activity and selectivity can be controlled by changing reduction temperature. © 1999 Academic Press

The hydrogenation of nitriles is an important route for the production of amines. They are hydrogenated industrially in liquid-phase reactions at high pressures of hydrogen (1, 2). Several research groups have studied the gas-phase hydrogenation of nitriles over supported metal catalysts (3–11). In our investigation of these reactions, we have used new synthetic smectite-like porous materials including different divalent cations like Ni^{2+} in their octahedral sheets. It was previously shown that platinum-loaded smectite-like materials were highly active to *n*-butane hydrogenolysis due to concerted metal-support effects (12). During the reduction of Ni^{2+}- and Co^{2+}-containing materials in the presence of platinum, these metal species move from the octahedral sheets and form clusters, which are exposed to foreign gases. As a result, the materials include the two catalytic sites, platinum particles and nickel (or cobalt) clusters, which are different in character for hydrogenation of nitriles. Thus, the present work was undertaken to examine the activities of platinum-loaded and -unloaded smectite-like materials for the atmospheric gas-phase hydrogenation of acetonitrile. It is worth noting here that Ni^{2+}-containing smectite-like material is active in the absence of platinum. Although various metal catalysts have been used in previous works, metal oxides have not been reported so far to be active catalysts. In addition, platinum-loaded smectite-like materials containing Ni^{2+}, Co^{2+}, and Mg^{2+} have been found to be active catalysts and exhibit different selectivities to the formation of amines.

A hydrothermal method previously developed (13–17) was used to prepare four smectite-like porous materials including different divalent cations (Ni^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}) in octahedral sheets. These samples are denoted by SM(Ni), SM(Co), SM(Mg), and SM(Zn) and their BET surface areas are 429, 380, 485, and 153 m^2/g, respectively. For comparison, silica (Aldrich Chemical Co., Davisil grade 646, 300 m^2/g), alumina (Mizusawa Ind. Chem., Neobead C, 126 m^2/g), and NaY zeolite (Toso, HSZ 320 NAA, 700 m^2/g) were also used as catalysts. When these samples were used as catalysts, they were treated in hydrogen at 673 K or above before the hydrogenation of acetonitrile. Platinum was loaded in 1 wt% onto the four smectite-like materials and silica by ion-exchange with tetraamineplatinum dichloride followed by reduction with hydrogen (12). A fixed-bed flow reactor operated at atmospheric pressure was used to test the activities of platinum-loaded and -unloaded samples. The hydrogenation of acetonitrile was carried out according to procedures and conditions similar to those used previously (8, 9, 11): temperature = 383 K, catalyst weight = 15 mg, $CH_3CN : H_2 = 3 : 97$, total flow rate = 35 ml/min.

To examine the acid properties of selected smectite-like materials, SM(Ni) and SM(Co), isomerization of 1-butene was conducted over them using a closed ciculating system at

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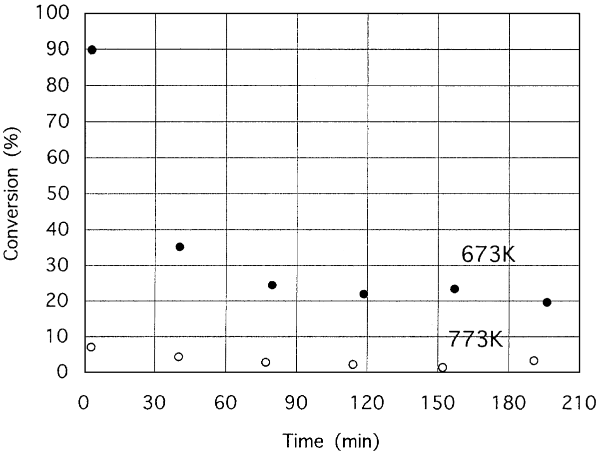

FIG. 1. Total conversion of acetonitrile hydrogenation as a function of time on stream for SM(Ni) pretreated in hydrogen at 673 and 773 K.

323 K. After the sample was treated by dynamic evacuation at various temperatures from 373 to 973 K for 1 h and cooled to a reaction temperature of 323 K, 1-butene was introduced up to a pressure of 13 kPa. The reaction was followed by a gas chromatograph with a flame ionization detector. The activity was evaluated by the initial rates of formation of *trans*-2-butene and *cis*-2-butene.

Figure 1 shows the total conversion in the acetonitrile hydrogenation over SM(Ni) pretreated in hydrogen at 673 and 773 K. The reaction does proceed with this platinum-unloaded sample, and the activity decreases with time on stream in a fashion similar to that of silica-supported platinum catalysts (11). The total conversion and product distribution at 3 and 200 min are given in Fig. 2. The total conversion decreases and the product distribution changes with an increase in the treatment temperature. The sample treated at 673 K produces a mixture of primary, secondary, and tertiary amines, while primary amine is produced mainly after the treatment at 773 K. It is noteworthy that SM(Ni) is an active catalyst even in the absence of additional active components like platinum. SM(Co), SM(Mg), SM(Zn), silica, alumina, and NaY zeolite used in the present work were all found to be inactive. In the literature, it has not been reported so far that oxide materials can be active catalysts for the gas-phase hydrogenation of nitriles. Although Verhaak *et al.* assume that the acidic surface of supports functions as an active site for the condensation, producing the secondary and tertiary amines, the first step in the hydrogenation of acetonitrile takes place on the surface of supported nickel particles (6).

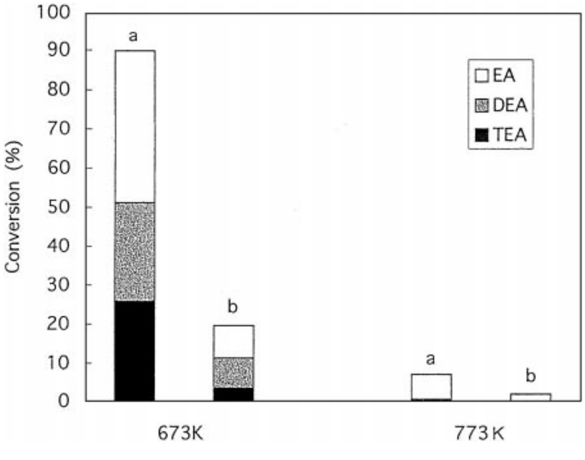

FIG. 2. Activity and selectivity of acetonitrile hydrogenation at 3 min (a) and 200 min (b) on stream for SM(Ni) pretreated in hydrogen at 673 and 773 K. EA, DEA, TEA: ethyl, diethyl, triethylamine.

It should be noted that SM(Ni) itself has peculiar active sites that are absent from the other oxide materials. Nickel is known to be active for the hydrogenation of nitriles (1, 2). SM(Ni) includes the divalent cations, Ni^{2+}, in the octahedral sheets. However, previous EXAFS and TPD measurements do not indicate the presence of nickel–nickel bonds and nickel clusters that are exposed and can catalyze the reaction (12). One reactant, acetonitrile, is basic so that it is adsorbed by acidic sites. The acid properties were then examined by a sensitive reaction, 1-butene isomerization. Figure 3 shows the initial rates of isomerization at 323 K for SM(Ni) and SM(Co) samples treated by evacuation at different temperatures. The activity of SM(Ni) is much higher, by more than two orders of magnitude, than that of SM(Co). When the evacuation temperature is raised, the activity of SM(Ni) becomes much smaller, corresponding to the decreased activity in acetonitrile hydrogenation at 773 K as shown in Fig. 2. The other materials, SM(Mg) and SM(Zn), were also found to be inactive for the isomerization of 1-butene. These results demonstrate that the acid properties of SM(Ni) are significantly different compared with the other materials.

We made FT-IR measurements of adsorbed pyridine and found that Lewis acid sites existed in SM(Ni) as well as the other materials. The FT-IR results indicated no large differences in the amounts of Lewis acid sites between those materials, suggesting that the acidic nature of SM(Ni) was unexpected and the presence of Ni^{2+} was important. There is a possibility that the acidic nature appears around the top surface above the cations in the subsurface layer, while the cations in the bulk do not have such an effect. It is assumed from X-ray diffraction (XRD) data that the SM(Ni) sample is composed of large and small fragments of the same smectite-like structure and the small fragments are intercalated between the large ones. This structure gives a porous nature and high surface area to the SM(Ni) as well as the other smectite-like materials. The materials can have large areas at the basal and edge surfaces. Thus, the number of Ni^{2+} cations in the subsurface layer should be larger than expected from the layered structure of the elementary

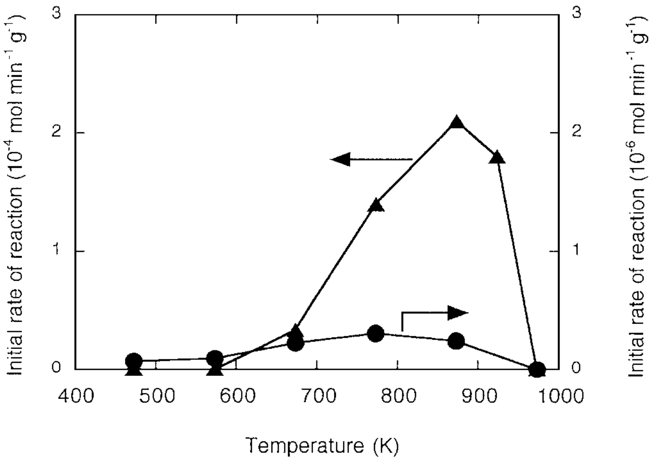

FIG. 3. Initial rate of isomerization of 1-butene at 323 K as a function of evacuation temperature for SM(Ni) (▲) and SM(Co) (●) samples.

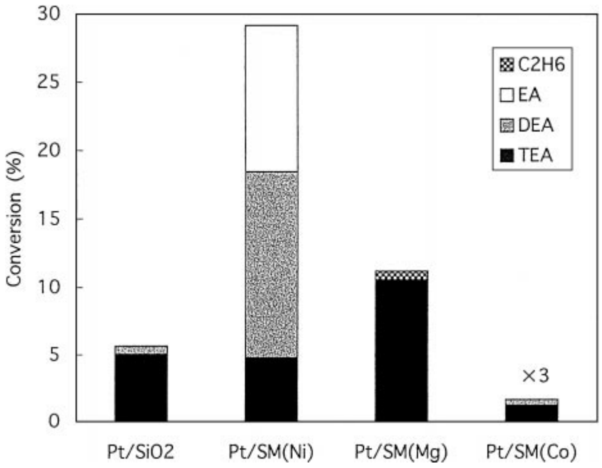

FIG. 4. Activity and selectivity of acetonitrile hydrogenation at 200 min on stream for platinum-loaded catalysts reduced at 673 K.

fragments. It is not clear why SM(Co) does not exhibit acidity similar to that of SM(Ni) despite their similar structures (as examined by XRD).

It is clear that the surface of SM(Ni) has unique Lewis acid sites and they exhibit different catalytic functions compared with the other materials. These acid sites can adsorb acetonitrile molecules and their C–N bonds would be weakened on adsorption and hydrogenated easily, as confirmed in the case of silica-supported platinum catalysts by FT-IR measurements (11, 18). The other reactant, hydrogen, cannot be adsorbed by SM(Ni). One may therefore infer that the reaction occurs between the adsorbed acetonitrile species and the hydrogen gas molecules (Eley–Rideal mechanism). Previously this was also suggested for the same reaction over alumina-supported platinum catalysts (9). As shown from Fig. 3 the Lewis acid properties of SM(Ni) change with evacuation temperature, and this change should occur during hydrogen reduction before the activity measurement in acetonitrile hydrogenation.

Figure 4 shows the steady-state activities and selectivities of platinum-loaded catalysts using smectite-like materials as supports. Platinum-loaded SM(Zn) and NaY zeolite were found to be inactive even after they were reduced at temperatures of 673 to 773 K. Pt/SM(Ni) is more active than the other three samples. The tertiary amine is the major product for Pt/SM(Mg) and Pt/SM(Co), similar to Pt/SiO$_2$, while the secondary and primary amines are also formed for Pt/SM(Ni). Table 1 lists turnover frequencies (TOFs); the active areas were estimated from hydrogen uptakes measured by temperature-programed desorption (12). The TOF values are significantly different between these catalysts. It was previously indicated that the TOF value was larger for smaller degrees of platinum dispersion for Pt/SiO$_2$ catalysts (11). However, Table 1 does not indicate the simple relation that TOF is larger for smaller hydrogen uptake values. This is because the smectite-supported catalysts may have other active sites in addition to platinum.

The influence of reduction temperature on the activity of the most active sample of Pt/SM(Ni) is shown in Fig. 5. The activity increases with increasing temperature from 673 to 773 K, in contrast to SM(Ni) alone (Fig. 2), and further increasing temperature decreases the activity. The selectivity of ethylamine is larger at higher reduction temperature; in other words, the selectivity becomes similar to that of nickel catalysts (1, 2, 8). The selectivity of Pt/SiO$_2$ changes little with reduction temperature as described elsewhere (11). Possible factors for the enhancement from 673 to 773 K are the formation of nickel clusters and the change in the Lewis acidity during reduction. These may contribute to the increase in the selectivity of primary amine judging from the catalytic features of the nickel and Lewis acid sites observed. The decrease in the activity at higher reduction

TABLE 1

TOF Values for Platinum-Loaded Catalysts[a]

Support	Reduction (K)	H_2 uptake[b] (mol g cat^{-1})	TOF[c] (s^{-1})
SiO$_2$	673	4.87×10^{-6}	0.299
SM(Ni)	673	2.23×10^{-4}	0.0339
SM(Mg)	673	3.15×10^{-5}	0.0909
SM(Co)	673	3.64×10^{-5}	0.0115
SM(Ni)	673	2.23×10^{-4}	0.0339
SM(Ni)	773	4.72×10^{-4}	0.0414
SM(Ni)	833	2.97×10^{-4}	0.0483
SM(Ni)	873	7.18×10^{-5}	0.134

[a] Corresponds to the data given in Figs. 4 and 5.
[b] Determined by temperature-programed desorption of hydrogen (12).
[c] Moles of acetonitrile reacted per moles of surface sites determined by H_2 uptake per 1 s.

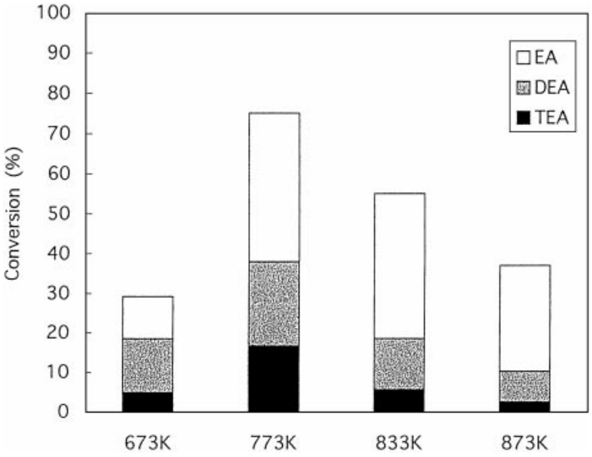

FIG. 5. Influence of reduction temperature on the activity and selectivity at 200 min on stream for platinum-loaded SM(Ni) catalyst for acetonitrile hydrogenation.

temperatures cannot be explained; the number and nature of platinum particles, nickel clusters, and Lewis acid sites should be changing with reduction temperature. Table 1 also presents the TOF values, which increase with an increase in the reduction temperature. The degree of platinum dispersion of Pt/SiO_2 reduced at 673 K given in Table 1 is 0.19. The TOF value should be larger for smaller platinum dispersion (11). We prepared 5% Ni/SiO_2 catalysts by impregnation followed by reduction at 673 and 873 K and used them for the same acetonitrile hydrogenation. The degree of nickel dispersion and TOF were shown to be 0.43 and 0.0284 s^{-1} and 0.22 and 0.0839 s^{-1} for 673 and 873 K-reduced samples. The distribution of the above-mentioned three possible active sites of Pt/SM(Ni) samples is needed to explain the results observed and to obtain the true TOF values for these sites.

In conclution, it is interesting that SM(Ni) itself is an active catalyst for the gas-phase hydrogenation of acetonitrile under mild conditions. The Lewis acid sites are different in nature compared with the other smectite-like materials, and they may be active sites for this reaction. In addition, platinum-loaded SM(Ni) is more active than SM(Ni) and it is the most active among the platinum-loaded catalysts examined. The total activity and product selectivity of this Pt/SM(Ni) catalyst can change with reduction temperature. This is significant from a practical point of view because selectivity does not change that much with reduction temperature for metal catalysts using ordinary oxide supports. In Pt/SM(Ni), high-temperature reduction causes Ni^{2+} to leave its original positions in the octahedral sheets and form some clusters that are exposed to foreign gas species as indicated by EXAFS and TPD measurements (12). Thus, this catalyst has three possible active sites: platinum particles, transition metal clusters, and Lewis acid sites. The present catalyst is a complicated system in that these three sites may have different specific activities, the number and nature of these sites may vary with preparation variables, and adsorbed reactive species may move between these sites.

For the same reaction over supported nickel catalysts, Verhaak *et al.* indicated the importance of acid properties of supports. They proposed that the hydrogenation to the primary amine occurs on the metal while the condensation to the secondary and tertiary amines takes places on the surface of supports (6). However, the present authors observed the influence of supports on the activity but not on the selectivity of supported nickel catalysts (8), similar to previous results reported in the literature (1). The support effect is a current subject in the hydrogenation of nitriles.

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