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Synthesis and Size-Selective Application of Palladium Metal Particles Intercalated in Mesopore-Size Controlled Smectite

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(In final form June 28, 1999)

Mesoporous smectite-type materials (SM) were synthesized with a hydrothermal method from water glass, magnesium chloride and alkyl ammonium salt. The mesopore diameter of SM was controlled from 30 to 130 Å by changing the reaction temperature, pH and the template materials during hydrothermal treatment. Palladium metal particles were intercalated in the mesopores of SM with an ion-exchanging of $[Pd(NH_3)_4Cl_2]$ on them and hydrogen reduction treatment. The size-selective hydrogenation of butadiene-acrylonitrile rubbers (NBR) in carbon tetrachloride was studied using palladium loaded smectite catalysts (Pd-SM). The reaction was controlled by the sizes of mesopore of Pd-SM, which determine the diffusion of polymer molecules onto the dispersed palladium particles within the pores.

Keywords: smectite; mesoporous materials; metal loaded catalysts; size-selectivity; polymer hydrogenation

INTRODUCTION

Mesoporous materials can be envisaged to be potential supports of heterogeneous catalysts for reactions of large molecules [1]. Synthesized smectite materials have mesoporous structures, in which the mesopore diameter can be controlled from 30 to 130 Å by changing the reaction

temperature, pH, and template materials during hydrothermal treatment[2,3]. In the present work, we report the preparation of well dispersed palladium metal particles intercalated in mesopore size-controlled smectite materials and their application for hydrogenation of polymer molecules.

EXPERIMENTAL

Smectite samples were synthesized with a hydrothermal method[2,3]. A slurry from water glass, magnesium chloride (Si/ Mg = 8/ 6) and alkyl ammonium salt was hydrothermally treated between 373 and 573 K for 2 h in an autoclave. Following drying at 353 K, the precursor was annealed at 873 K for 2 h. Then, we obtained smectite samples of different pore sizes. $[Pd(NH_3)_4Cl_2]$ was loaded on the smectite samples with an ion-exchanging method[4]. Following evacuation of the palladium-exchanged samples at 393 K for 1 h, they were reduced at 773 K for 1 h under flowing hydrogen.

RESULTS AND DISCUSSION

The XRD pattern shows that SM33 has smectite structure (Figure 1). The symbol, SM, denotes the smectite sample and the following figures mean its average pore size. All the samples prepared in this study showed similar XRD patterns.

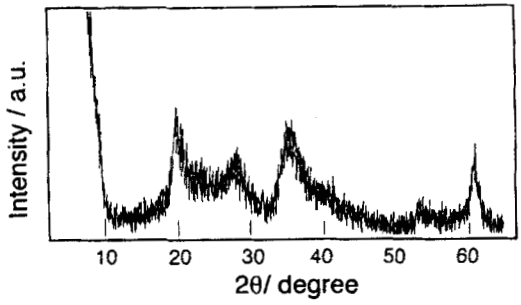

FIGURE 1 X-ray powder diffraction pattern of SM33.

Table 1 summarizes the characteristics of palladium-loaded smectite catalysts prepared in this study. All the prepared samples show high surface areas and large pore volumes. Figure 2 shows several results of the pore size distribution of smectite supports prepared. In the case of SM with average pore size below 80 Å, their pore size distributions were narrow. For SM85 and SM132, pore size distributions were wide. However, the volumes of their pores larger than the average diameters are very small.

TABLE 1 Results of characterization of smectite supports

Catalysts	Surface area (m^2g^{-1})	Pore volume ($cm^3\ g^{-1}$)	Amount of Pd (wt%)	Pd-Pd coordination number [a)]
SM31	658	0.516	1.0	6.5
SM33	485	0.396	1.1	-
SM43	751	0.804	1.0	-
SM53	576	0.767	1.0	-
SM63	477	0.752	1.1	-
SM79	236	0.465	1.0	-
SM85	340	0.726	1.0	6.5
SM125	252	0.790	0.9	-
SM132	220	0.724	0.8	6.5

a) -: not measured.

EXAFS experiments were performed to determine the dispersion of palladium metal particles in SM. The Pd-Pd coordination numbers of palladium particles loaded on SM supports were independent of the size of mesopores in smectite catalysts and estimated to be 6.5, indicating that the intercalated palladium particles are icosahedron clusters of 13 metal atoms [5]. The degrees of dispersion of palladium metal were determined with a static volumetric hydrogen adsorption method. The dispersion of palladium metal in SM31,

SM85 and SM132 is 1.0. EXAFS and hydrogen adsorption results show that palladium metal particles are well dispersed in the mesopores of smectite catalysts.

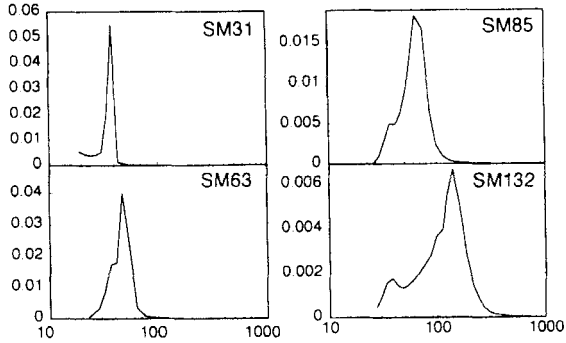

FIGURE 2 Pore size distributions of smectite supports.

The hydrogenation of NBR molecules in carbon tetrachloride was conducted at 323 K either in a glass reactor (volume 300 ml) under flowing hydrogen at atmospheric pressure or in an autoclave (volume 100 ml) under 50 atm hydrogen. The average molecular weight of NBR used was 3000 (NIPPON ZEON). The size distribution of NBR molecules used in catalytic reaction was in the range of 35-77 Å and the average was 42 Å. The catalytic hydrogenation activities were determined from the number of C=C bonds of NBR molecules. The number of C=C bonds was determined from the number of protons which were located near C=C bonds in NBR molecules with a ^{1}H-NMR technique. Hydrogenation of cyano group to amine group did not proceed on palladium loaded smectite catalysts[6]. Figure 3(a) shows the conversion of NBR hydrogenation after 20 h under flowing hydrogen at atmospheric pressure. The palladium supported catalysts in which the average pore sizes are above 79 Å were found to give similar conversions around 30 %.

However, NBR polymers are little hydrogenated with catalysts of pore sizes below 33 Å. The hydrogenation did not proceed on the supports without palladium, so that the active sites for the hydrogenation are palladium metal surfaces. Figure 3(b) shows the conversion of the hydrogenation after 15 h at 50 atm hydrogen. Most of C=C bonds of NBR were hydrogenated with the catalysts in which the average pore sizes of supports were above 63 Å, while the conversions were only 40 % with the smectite catalysts in which the average pore sizes were below 53 Å. The conversion was found to be zero over palladium supported NaY catalysts.

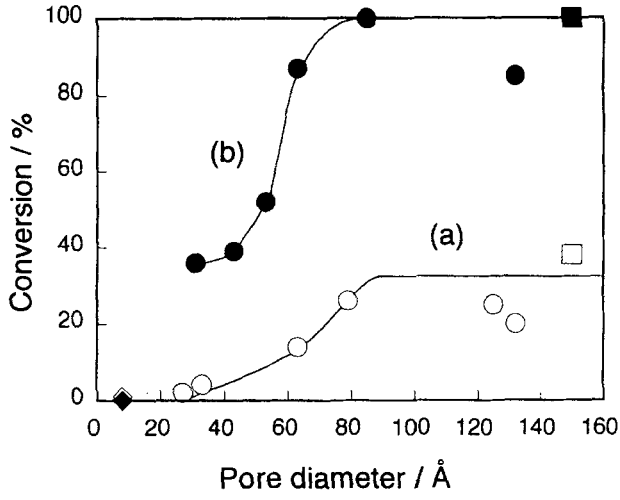

FIGURE 3 Conversion of NBR hydrogenation after 20h under 1 atm hydrogen (a) and after 15 h under 50 atom hydrogen (b): (◆,◇) Pd/NaY8, (●,○) Pd/SM, (■,□) Pd/$SiO_2$150.

The hydrogenation of NBR proceeds over palladium metal particles dispersed in the smectite catalysts in which pore sizes are larger than the NBR molecules with the size of 42 Å; however, the NBR molecules do not enter into mesopores smaller than 40 Å.

Acknowledgment

EXAFS experiments were carried out under the approval of the PF advisory committee (No. 97G022).

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