A Novel Shape-Selective Catalyst, Pt-Promoted $Rb_{2.1}H_{0.9}PW_{12}O_{40}$, for Hydrogenation of Aromatic Compounds

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Pt-Promoted $Rb_{2.1}H_{0.9}PW_{12}O_{40}$ was found to possess uniform micropores with the width of about 0.60 nm and a very small external surface area. This catalyst exhibited sharp shape-selectivity in the hydrogenation of aromatic compounds, distinguishing benzene from *m*-xylene and 1,3,5-trimethylbenzene.

Zeolites are typical shape selective catalysts and have widely been used in industry.[1–3] However, they have still disadvantages, that is, the acid strength is not so high and the control of the pore-width is difficult. The control of pore-width is a preferable target in these porous materials.

It was reported that an acidic Cs salt of $H_3PW_{12}O_{40}$ had uniform micropores.[4–6] In addition, the Pt-promoted Cs salt, Pt-$Cs_{2.1}H_{0.9}PW_{12}O_{40}$, showed shape-selectivities for the hydrogenation of small olefins and the oxidation of CO and small hydrocarbons.[7,8] However, the pore-width of this salt (about 0.5 nm) is too small to be applied to aromatic compounds. While many efforts have been done to vary the pore-width of Cs salts by changing the composition and preparation method, it was not able to control the micropore-width.

We attempted to control the pore-width of the microporous heteropoly compounds by changing the counter cation for $H_3PW_{12}O_{40}$, and succeeded in expanding the pore-width by choosing Rb^+ as the counter cation, keeping the uniformity of the micropore-width.

0.5 wt% Pt-$Rb_{2.1}H_{0.9}PW_{12}O_{40}$ (abbreviated as Pt-Rb2.1) was prepared by a titration method as follows.[8] An aqueous solution of H_2PtCl_6 ($0.04\,mol{\cdot}dm^{-3}$) was added to an aqueous solution of $H_3PW_{12}O_{40}$ ($0.08\,mol{\cdot}dm^{-3}$), then an aqueous solution of Rb_2CO_3 ($0.1\,mol{\cdot}dm^{-3}$) was added dropwise to the mixture at a rate of $0.1\,cm^3{\cdot}min^{-1}$ with vigorous stirring at room temperature. The resulting suspension was allowed to stand overnight and evaporated at 318 K to give a pale yellow solid of Pt-promoted acidic salt. As reference, 0.5 wt% Pt/SiO_2 and H-ZSM-5 (HSZ-860 HOA, Tosoh Co., Si/Al = 36.7, $477\,m^2{\cdot}g^{-1}$) were used. 0.5 wt% Pt/SiO_2 was prepared by an impregnation method from the aqueous solution of H_2PtCl_6 ($0.04\,mol{\cdot}dm^{-3}$) and SiO_2 (AEROSIL 300, $274\,m^2{\cdot}g^{-1}$). After drying at 373 K overnight, Pt/SiO_2 was calcined at 773 K for 4 h in air. The dispersions of Pt were determined to be about 20% for 0.5 wt% Pt/SiO_2 and 0.5 wt% Pt-$Rb_{2.1}H_{0.9}PW_{12}O_{40}$ by means of CO-TPD and CO adsorption. Ar and N_2 adsorption-desorption isotherms were obtained by using BELSORP 28SA (BEL Japan, Inc.).

Pt-Rb2.1 gave a Type I isotherm of N_2 adsorption at 77 K, indicating the microporous material. The total surface area was calculated according to the BET method to be $77\,m^2{\cdot}g^{-1}$. It is worthy to note that the external surface area estimated from the adsorption of 1,3,5-trimethylbenzene (molecular size [MS] = 0.75 nm) and *t*-plot method was only about $2\,m^2{\cdot}g^{-1}$ (the fraction of external surface area to the total surface area is about 3%).

In order to determine the pore-width of Pt-Rb2.1, the adsorptions of various molecules having different sizes were systematically measured by use of microbalance (Shimadzu TG-30) directly connected to a high vacuum system.[8] The results for Pt-Rb2.1 are illustrated in Figure 1, where the adsorption areas were calculated from the adsorption amounts and the molecular cross-sectional areas.[1,9,10] As reference, the data of H-ZSM-5 are also shown in Figure 1. Isobutane and *n*-butane were adsorbed at 197 K, and the others at 298 K under the relative pressure (p/p_0) of 0.2. The adsorption amounts were collected after the adsorptions reached equilibrium (2–24 h). Both appreciable amounts of *n*-butane (MS = 0.43 nm) and isobutane (MS = 0.50 nm) were adsorbed on Pt-Rb2.1, which is in contrast with the results of Pt-Cs2.1.[7,8] It was also observed that benzene (MS = 0.59 nm), toluene (MS = 0.59 nm), and *p*-xylene (MS = 0.59 nm) were considerably adsorbed, while *m*-xylene (MS = 0.64 nm), *o*-xylene (MS = 0.67 nm), and 1,3,5-trimethylbenzene (MS = 0.75 nm) were little adsorbed. Considering the molecular sizes, the results of Figure 1 demonstrate that the pore-width of Pt-Rb2.1 is about 0.60 nm. It is noted that the adsorption pattern of H-ZSM-5 was similar to that of Pt-Rb2.1, while the shape selective adsorption was not clear due to a certain external surface area of H-ZSM-5.

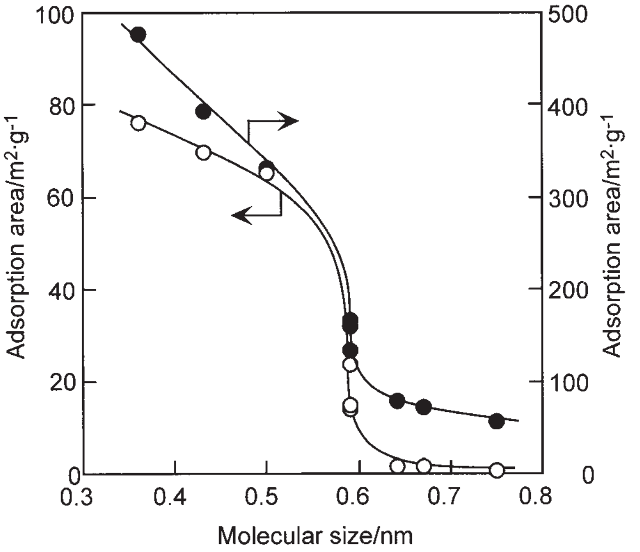

Figure 1. Changes in adsorption area for 0.5 wt% Pt-$Rb_{2.1}H_{0.9}PW_{12}O_{40}$ (○) and H-ZSM-5 (●) as a function of molecular size. The used molecules are described in the text. Adsorption areas are estimated from the adsorption amounts and the molecular cross-sections.

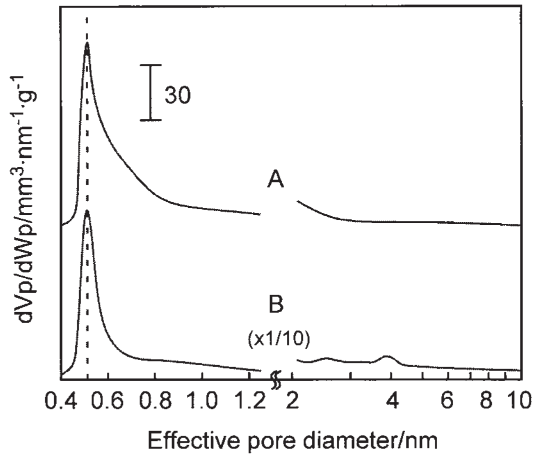

Figure 2. Pore size-distribution curves for (A) 0.5 wt% Pt-$Rb_{2.1}H_{0.9}PW_{12}O_{40}$ and (B) H-ZSM-5.

Figure 2 presents the pore size-distributions in the range from micropore to mesopore, which were obtained from the adsorption isotherm of Ar by Saito-Foley method[11] and the desorption isotherm of N_2 by Dollimore-Heal method,[12] respectively. It is clear that the pores of Pt-Rb2.1 had unimodal distributions and the position of the peak was close to that of H-ZSM-5.

Catalytic hydrogenations were performed in a flow reactor at an atmospheric pressure under the following conditions; total flow rate 20 $cm^3 \cdot min^{-1}$, benzene, *p*-xylene, or *m*-xylene 1% with H_2 90% (He balance), 1,3,5-trimethylbenzene 0.4% with H_2 49% (He balance), Pt-Rb2.1 300 mg (with powdered quartz, 1 g) at 393 K, and Pt/SiO_2 30 mg (with powdered quartz, 300 mg) at 373 K. The catalysts were pretreated in a flow of O_2 (50 $cm^3 \cdot min^{-1}$) for 1 h, He (50 $cm^3 \cdot min^{-1}$) for 0.5 h, and then H_2 (50 $cm^3 \cdot min^{-1}$) for 1 h at 523 K.

Time courses of hydrogenations of benzene, *m*-xylene, and 1,3,5-trimethylbenzene are shown in Figure 3. It should be emphasized that Pt-Rb2.1 gave an activity for the hydrogenation of benzene, but was inactive for the hydrogenations of *m*-xylene and 1,3,5-trimethylbenzene. As was not shown, the hydrogenation of *p*-xylene took place with the rate of about half that of benzene over Pt-Rb2.1. It was confirmed that these aromatics were hydrogenated with the comparable reaction rates over Pt/SiO_2 as shown in Figure 3.[13] Isomerizations of these alkylbenzenes were not detected under these conditions. Therefore, the unique activity pattern obtained on Pt-Rb2.1 is clearly due to the shape-selectivity. The deactivation observed for the hydrogenation of benzene over Pt-Rb2.1 is probably due to a partial blockage of the pores by carbonaceous species.

While TEM gave the image of the aggregates of fine primary crystallites of the Rb salt, the Pt particles were not observed even with about 1 nm resolution. In addition, XRD did not show the peaks due to Pt crystallites, suggesting that Pt is highly dispersed and its crystallite (particle) size is very small. The above sharp shape-selectivity for the hydrogenation also suggests that Pt particles were exclusively located in the pores, but not on the external surface of Pt-Rb2.1.

We have already proposed the mechanism for the formation of pores of Cs salts.[14,15] It is presumed that the micropores are generated between the contact faces of the primary crystallites (12 nm) of Cs salts. The same model can be applicable to the pores of Pt-Rb2.1.

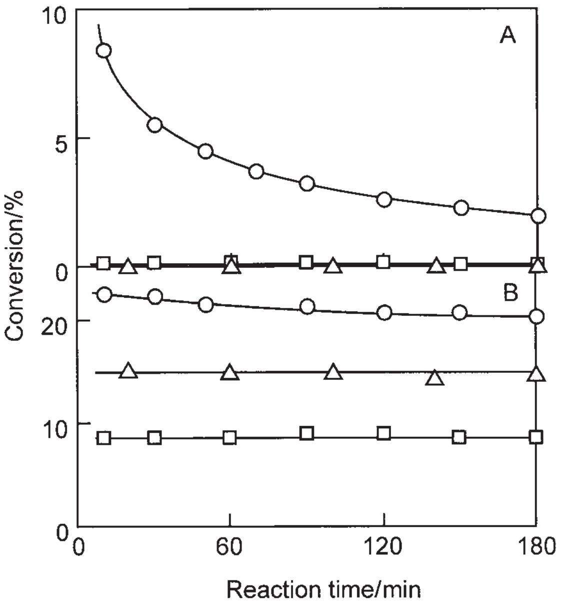

Figure 3. Time courses of hydrogenation of aromatics over (A) 0.5 wt% Pt-$Rb_{2.1}H_{0.9}PW_{12}O_{40}$ and (B) 0.5 wt% Pt/SiO_2. (○): benzene, (□): *m*-xylene, and (△): 1,3,5-trimethylbenzene.

In conclusion, a new functional catalyst, 0.5 wt% Pt-$Rb_{2.1}H_{0.9}PW_{12}O_{40}$ exhibiting shape-selectivity for the hydrogenation of aromatics could be synthesized. This is the first example of the precise control of the pore width of the microporous heteropoly compounds and of shape-selectivity for the aromatics by the Pt-promoted heteropoly compound.

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