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SUPPORT EFFECT ON THE HYDROCRACKING ACTIVITY OF MOLYBDENUM CATALYSTS

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Hydrocracking reactions of diphenylmethane under high H_2 pressure were carried out to elucidate the requisite properties of the support for molybdenum catalysts. The effectiveness order of the supports was $TiO_2 > SiO_2 > ZrO_2 > \gamma\text{-}Al_2O_3 > MgO$.

Molybdenum catalysts supported on γ-Al_2O_3 have long been used for hydrodesulfurization of petroleum fractions. Recently, an application of molybdenum catalysts to hydrotreating of petroleum residue or coal derived oil[1)] has made it desirable for these catalysts to have good performances in asphaltene conversion or nitrogen removal. It is known that the molybdenum catalysts have several different active sites where hydrocracking, hydrogenation or hydrodesulfurization is catalyzed.[2,3)] Therefore, in order to get a catalyst of high selectivity, it would be most practical to try to find the most proper support by which the favorable and proper chemical properties of the catalyst can be attained. Previous investigations of the support effects have been almost exclusively undertaken under atmospheric pressure, although high hydrogen pressures are required for practical use. In the present paper, the activities of supported molybdenum catalysts under high hydrogen pressure were investigated using hydrocracking of diphenylmethane (DPM).

Commercially available supports were used for γ-Al_2O_3 (Sumitomo Aluminum Smelting Co. ltd.), SiO_2 (Davison grade 57) and MgO (Nakarai Chemicals Co. ltd., reagent grade). TiO_2 and ZrO_2 supports were prepared by a precipitation technique from aqueous solutions of $Ti(SO_4)_2$ and $ZrOCl_2$, respectively. The supports prepared were impregnated in a solution of ammonium paramolybdate to contain 10 wt% of molybdenum as MoO_3. After impregnation, the catalysts were dried at 110 °C and then calcined at 500 °C for 3 h. The catalysts were then presulfided in a stream of 10 vol% of H_2S (balance H_2) at 430 °C for 1 h before reactions.

The surface area and pore volume of each catalyst were measured by a nitrogen adsorption technique and BET method. Temperature programmed desorption (TPD) of NH_3 was employed to measure the acid properties of the catalyst. The electronic states of the molybdenum ions were analyzed using an X-ray photoelectron spectrometer (XPS, Shimadzu, ASIX-1000) with Mg anode.

For the hydrocracking of DPM, the microautoclave (50 cm^3) containing 10 cm^3 of DPM and 0.5 g of the catalyst was charged with H_2 to an initial pressure of 70 kg/cm^2. The unit was then heated to 400 °C and held for 60 min. The liquid products were analyzed by using a gas chromatograph equipped with an OV-1 capillary column (50 m).

The catalytic activities for hydrocracking of DPM are given in Table 1, which indicates the great differences in both the activity and the selectivity among the catalysts on different supports. The TiO_2 support gave the highest hydrocracking activity, while the MgO support gave no activity. Both the catalysts supported on the Al_2O_3 and the SiO_2 showed high selectivities of hydrogenation, neither giving high hydrocracking activity in spite of their high surface areas.

Table 1. Hydrocracking of diphenylmethane with molybdenum catalysts

Support	S.A.[a]	P.V.[b]	Conv.[c]	CKG[d]	HYD[e]	Others[f]	CKG/HYD
	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	%	%	%	%	-
Al_2O_3	170	0.47	2.9	2.0	0.86	0.0	2.3
TiO_2	66	0.17	28.1	27.3	0.48	0.32	56.9
SiO_2	266	1.09	6.5	5.3	1.1	0.10	4.8
ZrO_2	53	0.06	4.4	3.6	0.76	0.0	4.7
MgO	51	0.16	0.0	0.0	0.0	0.0	-

a) Surface area. b) Pore volume. c) Total Conversion.

d) Hydrocracking = yields of toluene and benzene.

e) Hydrogenation = yields of hexahydrodiphenylmethane.

f) Other products were methyldiphenyls and methyldiphenylmethanes.

The relevant active sites of molybdenum catalysts for hydrocracking have been considered to be acidic. Kimura et al.$^{4)}$ reported that the hydrocracking of DPM at atmospheric pressure was accelerated by the acid sites. However, the TPD measurement showed that the total amount of acid sites on the Mo/TiO_2 catalyst was much less than that on the Mo/Al_2O_3 and the acid strength of the former was also smaller than that of the latter (Fig. 1). This result suggests that all the acid sites cannot be active for hydrocracking of DPM under high hydrogen pressure.

In the hydrocracking of DPM under high hydrogen pressure, other properties of the catalyst such as favorable reduction states of molybdenum may be required. The XPS analysis showed that the binding energy of Mo 3d $_{5/2}$ line for Mo/TiO_2 was 0.8 eV lower than that for Mo/Al_2O_3 (Fig. 2), indicating the more electronegative state of the molybdenum ion on TiO_2. While, the molybdenum ion on the MgO support was less electronegative than that on the Al_2O_3. The dependence of the electronic state of the active component on the support will be correlated with the recent discussions made by Swanson et al.,$^{6)}$ in which they state that the reduction behavior of the active component was

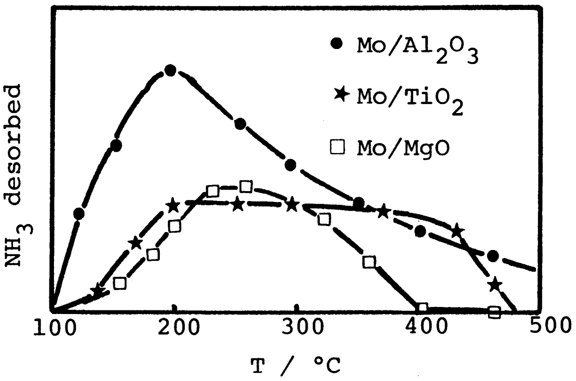

Fig. 1. TPD profiles of NH_3 from the oxide catalysts.

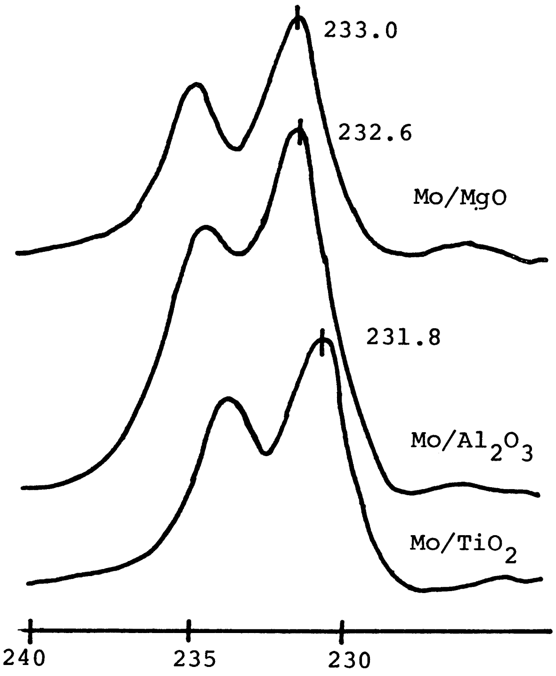

Fig. 2. Mo 3d photoelectron spectra for the oxide catalysts. The binding energies are referenced to the gold (Au 4f 7/2 ; 83.8 eV) which was evaporated on the catalyst surface.

dependent upon the interaction between the support and the molybdenum.

Sonnemans and Mars$^{6)}$ reported that one Mo atom would occupy 0.17 - 0.25 nm^2 on the support surface depending on the deposition condition. Basing on this assumption, 10 wt% of MoO_3 is beyond the monolayer of loading on the TiO_2, ZrO_2, and MgO supports, and the excess molybdena would aggregate. The interaction between Mo and support would affect the structure of the molybdate formed on the support and result in the large difference of the catalytic activities.

The present study showed that the hydrocracking activity of the molybdenum catalyst is highly dependent upon its support and that TiO_2 gives the most favorable support effect on the hydrocracking acvtivity of DPM. The superiority of TiO_2 support as the catalyst for hydrotreating of heavy feedstocks$^{7)}$ will be partly attributed to this hydrocracking activity. Further characterization of molybdenum catalysts on various kinds of supports are now in progress.

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