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Silica-Supported MoO_3 Catalyst Prepared by Alkoxide Method

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Highly dispersed silica-supported molybdenum catalysts were prepared by an alkoxide method, using ethylsilicate and ammonium paramolybdate dissolved in ethylene glycol. By comparing temperature-programmed sulfiding(TPS) spectra of the catalysts with those of alumina or silica-supported catalysts formed by an impregnation method, the structures and the dispersion states of molybdenum oxide in the catalysts prepared by the alkoxide method were discussed.

One of the essential roles of carriers in the supported catalysts is to highly disperse the catalytically active metal or metal oxide particles on the surfaces. The dispersion state of active components strongly depends on the carriers used. In the case of a hydrodesulfurization (HDS) catalyst currently employed, two-dimensionally dispersed polymolybdates1) have been considered to be produced on alumina supports, but not on silica supports.

Recently, a new method has been developed to prepare a silica-supported catalyst, where small-size metal or metal oxide particles are dispersed in a homogeneous size level.2) This is called an alkoxide method, since metal alkoxides, yielding silica powder and catalytically active metals or metal oxides, are employed as starting materials. The purpose of this work was to prepare a silica-supported molybdenum oxides catalyst by the alkoxide method,3) and to compare the dispersion states of molybdenum oxides in the catalyst with those on silica- and alumina-supported catalysts prepared by a conventional impregnation method.

Three kinds of the molybdenum oxide catalysts were prepared as follows; one is named "alk-S", which is prepared by the alkoxide method. Ammonium paramolybdate ($(NH_4)_6Mo_7O_{24}\cdot 6H_2O$) dissolved in ethylene glycol at 80 °C was poured into a solution comprising ethylsilicate, ethanol, water and nitric acid with a molar ratio of $1/10/10/3.6\times10^{-2}$, followed by brisk stirring at

80 °C, resulting in the formation of transparent gels. The gels were dried under reduced pressure and, subsequently, in an oven at 110 °C, followed by calcination at 500 °C for 4 h. The others are designated "imp-S" and "imp-A", which were prepared by immersing silica or alumina, respectively, with an aqueous solution of ammonium paramolybdate. The conditions employed for drying and heating the immersed powder were the same as those employed for the preparation of "alk-S". The BET surface areas of silica and alumina used for the impregnation are 300 and 150 m^2g^{-1}, respectively. The loading of molybdenum oxide in the catalysts prepared here was settled to be 10 wt% of the catalysts; calculated as MoO_3.

The dispersion states of the molybdenum oxides were discussed by a TPS spectrum, obtained by an apparatus illustrated somewhere.4) The catalyst (0.1 g) was placed in a reactor, where gases composed of $H_2/H_2S/Ar$ with a vol% of 3.3/28.1/68.9 were introduced in order to reduce and sulfurize the catalyst. The temperature was raised up to 1100 °C with a rate of 10 °C/min. The amount of H_2S consumed to sulfurize the molybdenum oxide was estimated by measuring a UV-absorption intensity at 212 nm, although H_2S has an absorption peak centered around 195 nm.4) The amount of H_2 consumed for the reduction of the molybdenum oxide was measured by a TCD cell. In front of the TCD cell, a trap packed with molecular sieves 5A was placed to eliminate the residual H_2S and the water vapor formed during the reduction.

The reduction and the sulfiding of MoO_3 have been considered to proceed as follows;5)

step 1-1: $MoO_3 + H_2S \rightarrow MoO_2 + S + H_2O$ step 2: $MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O$
step 1-2: $MoO_3 + H_2 \rightarrow MoO_2 + H_2O$ step 3: $MoO_2 + 2H_2 \rightarrow Mo + 2H_2O$
step 1-3: $S + H_2 \rightarrow H_2S$ step 4: $Mo + 2H_2S \rightarrow MoS_2 + 2H_2$

In Fig. 1-a is shown the TPS spectrum of pure MoO_3 powder as a standard material. A peak at 180 °C for H_2S consumption is ascribed to the reaction of $H_2S + MoO_3 \rightarrow MoO_2 + S + H_2O$(step 1-1), since the reduction of MoO_3 by H_2S has been reported to be much enhanced by the coexistence of H_2.5) A rapid consumption of H_2 observed at 330 °C is attributed to the reduction of MoO_3 to MoO_2(step 1-2). A slow consumption of H_2 was observed about 500 °C, which indicates the reduction of MoO_2 to metallic molybdenum (step 3),as well as the reaction of $H_2 + S \rightarrow H_2S$(step 1-3). The hydrogen sulfide, thus formed, resulted in an appearance of a shoulder around 500 °C in a large consumption peak of H_2S at 700 °C, where a generation of H_2 was simultaneously observed. This means the sulfiding of metallic molybdenum and unreduced MoO_2 in the following manners; $Mo + 2H_2S \rightarrow MoS_2 + 2H_2$ and $MoO_2 + 2H_2S \rightarrow MoS_2 + 2H_2O$, as given in the step 2 and step 4,respectively.

A TPS spectrum of molybdenum oxides in the "imp-S" catalyst is shown in Fig. 1-b, which is very close to the TPS spectrum of pure MoO_3. This seems to indicate that the molybdenum oxides on the "imp-S" are bulk-like MoO_3 crystallites, which was confirmed by an X-ray powder diffraction.

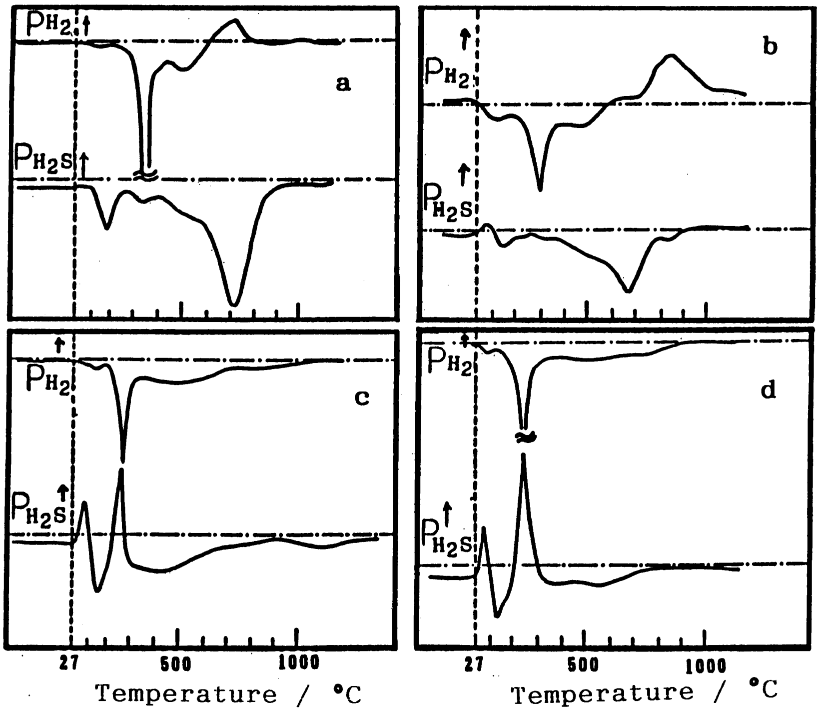

Fig.1. TPS spectra of (a):pure MoO_3, (b):imp-S, (c):alk-S and (d):imp-A, respectively.

Therefore, the structures and the dispersion states of molybdenum oxides on the catalysts would be partially reflected on the TPS spectra, though the spectra depend strongly on the interactions between molybdenum oxides and the supports used. The TPS spectra of molybdenum oxides in the "alk-S" and on the "imp-A" are given in Figs. 1-c and 1-d, respectively. These spectra resembled quite well with each other, and were definitively different from those of pure MoO_3 and of molybdenum oxides in the "imp-S" catalyst. The peak detected at 90 °C for H_2S evolution in these spectra was assigned to the desorption of physisorbed and/or weakly chemisorbed H_2S, and the successive peak at 130 °C might be ascribed to the progress in the reduction of molybdenum oxides by H_2S, shown in the step 1-1, since no simultaneous evolution of H_2 was observed. The hydrogen consumption accompanied by an H_2S formation at 260 °C seems to be ascribed to the reaction, given in the step 1-3. A broad peak, caused by H_2 and H_2S consumption, similarly observed at temperatures higher than 350 °C in these TPS spectra was hard to be assigned to the reactions in the step 1 to 3.

Since the structures and the dispersion states of molybdenum oxides are conceived to be partially reflected on the TPS spectra, those in the "alk-S" are timidly expected to be similar as those on the "imp-A". Though the structures of molybdenum oxides in these catalysts were not revealed, high dispersion states of these molybdenum oxides were confirmed by XRD spectra shown in Fig. 2, where no diffraction peaks were detected. Peaks assigned to MoO_3 were observed for both catalysts, when MoO_3 loading was increased to be 20 wt%.

Thus, the high dispersion of molybdenum oxides on silica supports could be achieved by the alkoxide method, and the catalytic activity was evaluated after treatments in 6.7 vol% H_2S/H_2 at 400 °C. A reaction used was hydrodesulfurization of thiophene, pulsed with 40 vol% H_2/Ar carrier into the catalyst at 400 °C (Fig. 3). All of the molybdenum oxides are not necessarily on the surface of silica in the "alk-S" catalyst, and some of them are inside the silica support. This means that only a part of the molybdenum oxide loaded can participate the catalysis. The activity of the "alk-S" was, however, higher than that of the "imp-S" and was close to the activity of the "imp-A", suggesting high dispersion states of the molybdenum oxide in the "alk-S".

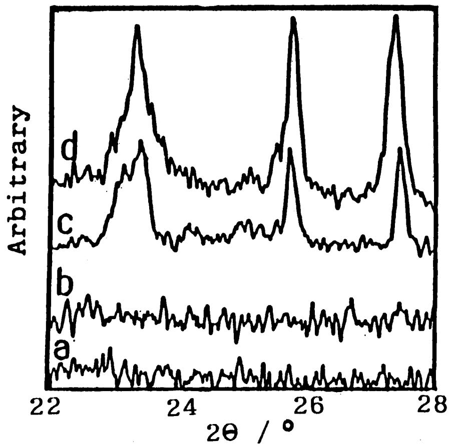

Fig.2. XRD spectra of MoO_3 in catalysts.
a:10 wt% MoO_3 in "imp-A"
b:10 wt% MoO_3 in "alk-S"
c:20 wt% MoO_3 in "imp-A"
d:20 wt% MoO_3 in "alk-S"

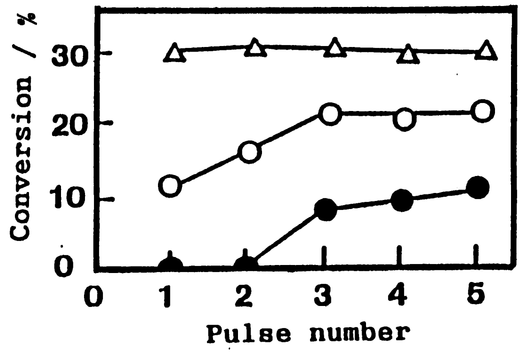

Fig.3. Activity for HDS of thiophene(10 wt% MoO_3).
●: imp-S, ○: alk-S, △: imp-A

References
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