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Catalytic Evidence of Formation of Water-Induced Silicomolybdic Acid on a MoO_3/SiO_2 Catalyst

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The formation of silicomolybdic acid induced by the preadsorbed or catalytically formed water on MoO_3/SiO_2 was evidenced by typical heteropoly acid catalysed reactions, isomerization of 1-butene or dehydration of 2-propanol.

Silicomolybdic acid, one of heteropoly acids, has been detected using several spectroscopic techniques on a MoO_3/SiO_2 catalyst preadsorbed with water.[1-3] This appears to be important in a view that the catalyst is often applied to reactions which contain water in reactant or product. A large amount of water, for example, is needed in methanol formation from methane.[4-6] Heteropoly acids, on the other hand, have recently attracted attention for their interesting catalytic nature.[7]

The present work is aimed at obtaining a catalytic evidence of the formation of silicomolybdic acid (designated as SMA) on the MoO_3/SiO_2 preadsorbed with water or used in a reaction involving water. For this purpose, the catalyst preadsorbed with water was employed for reactions which heteropoly acids are known to catalyse,[7] isomerization of 1-butene and dehydration of 2-propanol, in comparison with a silica-supported silicomolybdic acid catalyst (designated as SMA/SiO_2).

An 8 wt% MoO_3/SiO_2 catalyst was prepared by a conventional impregnation technique and calcined in O_2 at 500 °C, as described previously.[8,9] The water treatment of the sample was carried out by recirculating a mixture of water vapor and He (20 Torr : 40 Torr) over it in the range of 50 to 400 °C for each 1 h, followed by successive outgassing under the same conditions. The SMA/SiO_2 (8 wt% of Mo) was prepared by a similar impregnation technique with SMA ($H_4SiMo_{12}O_{40}$ nH_2O, Nippon Muki-Kagaku-Kogyo Co. Ltd), followed by drying it at 50 °C for several hours using a rotary evaporater. This was used after outgassing in the range of 50 to

400 °C for 1 h.

Prior to catalytic experiments, an IR spectroscopic study was carried out on a molybdenunm species in water extract from MoO_3/SiO_2, since the molybdenum species thus reacted with water was expected to be converted to SMA. The sample was prepared as follows; (1) the MoO_3/SiO_2 (ca. 0.5 g) calcined in O_2 was washed onto a filter funnel with 20-30 ml of distilled water, (2) the filtrate of yellow color was dried at ca. 80 °C overnight, (3) the resulted solid was diluted with KBr and pressed into a pellet. As shown in Fig.1, the spectrum was almost the same as that obtained on SMA; the absorption bands are at 955, 905, and 860 and 785 cm^{-1}, which have been assigned to ν(Mo=O), ν(Si-O), and ν(Mo-O-Mo) in a Keggin structure, respectively.[7] Thus, a part of molybdenum species on MoO_3/SiO_2 is shown to react readily with water to give SMA, in agreement with the literatures.[1-3]

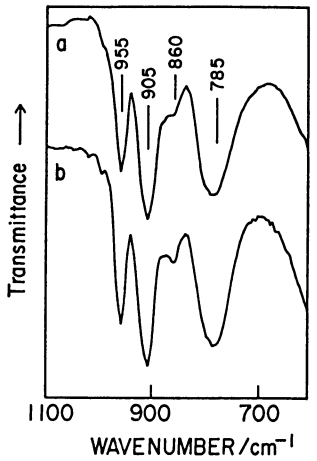

Fig.1. IR spectra of molybdenum species. (a) water extract from MoO_3/SiO_2, (b) SMA ($H_4SiMo_{12}O_{40}\cdot nH_2O$).

Isomerization of 1-butene to cis- and/or trans-2-butene was carried out with 18 Torr of 1-butene at 50 °C on 0.4 g of the water-treated MoO_3/SiO_2 and on the SMA/SiO_2 in the coventional recirculating system (302 ml) with an online-gas chromatograph (VZ-8 column, 6 m, 0 °C). Figure 2a shows the effect of the water-

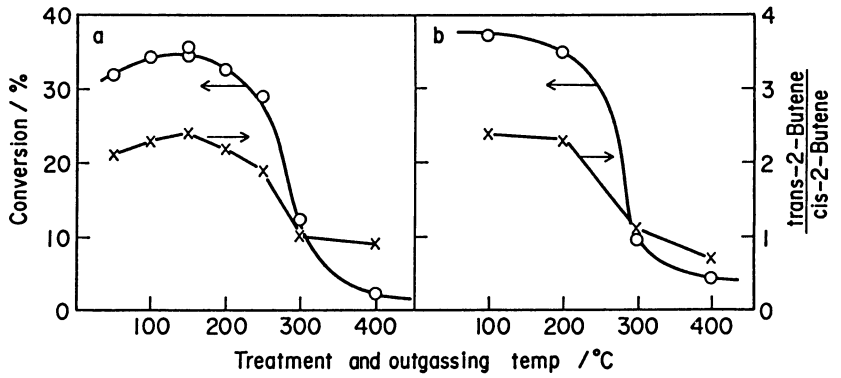

Fig.2. Effect of water-treatment temperature and outgassing temperature on catalytic activity (O) or selectivity (x) for isomerization of 1-butene to trans-2-butene or cis-2-butene. (a) MoO_3/SiO_2, (b) SMA/SiO_2.

treatment temperature of MoO_3/SiO_2 on the activity and selectivity of the reaction, given in terms of the conversion yield of 1-butene and the trans-2-butene/cis-2-butene ratios in 3 h of the reaction time. They exhibited a sharp variation in the range of 200 to 300 °C. A very similar profiles were observed on the SMA/SiO_2 outgassed in the range of 50 to 400 °C, as shown in Fig. 2b. Also, a MoO_3/SiO_2 sample not treated with water was found to give almost the same results to those on the 400 °C water-treated MoO_3/SiO_2 or the 400 °C outgassed SMA/SiO_2. The following conclusions may be drawn; (1) SMA species is the active species to isomerization of 1-butene, (2) the preadsorbed water induces the formation of SMA on MoO_3/SiO_2, (3) it is decomposed in the temperature range of 200 to 300 °C.

As a typical catalytic reaction containing water in its product, dehydration of 2-propanol was studied by recirculating a mixture of 2-propanol and He (30 Torr : 40 Torr) at 150 °C over three samples, the non-treated MoO_3/SiO_2, the 150 °C water-treated MoO_3/SiO_2 and the 150 °C outgassed SMA/SiO_2. Propylene was found to be the main product with a trace of acetone by the gas chromatographic analysis with a BX-10 column (6 m, 85 °C). As shown in Fig. 3, each sample gave practically the same catalytic activity. This would indicate that the water produced from 2-propanol induced the formation of SMA as active sites for this reaction.

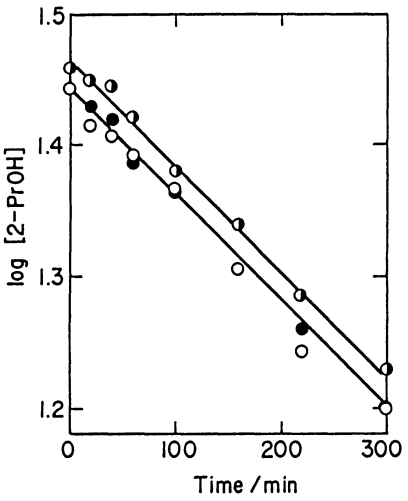

Fig.3. Dehydration of 2-propanol at 150 °C.
(○) MoO_3/SiO_2 calcined in O_2 at 500 °C,
(◑) 150 °C water-treated MoO_3/SiO_2,
(●) 150 °C outgassed SMA/SiO_2.

In order to see the molybdenum species besides SMA, IR spectra of the adsorbed pyridine on the water-treated MoO_3/SiO_2 was studied and compared with those on the non-treated MoO_3/SiO_2 or on a silicon-supported SMA.[10] These were obtained after exposing each sample to several torr of pyridine, and then evacuating the physisorbed pyridine at 100 °C for 1 h. In Fig. 4, the spectra a, b, and c were observed on the 150 °C outgassed silicon-supported SMA, the 100 °C water-treated MoO_3/SiO_2, and the non-treated MoO_3/SiO_2, respectively. The SMA gave the absorption bands due to pyridinium ions at 1640, 1610, 1530, and 1485 cm^{-1}.[10] On the water-treated sample, on the other hand, the intense absorption band was obtained at 1450 cm^{-1} besides those due to pyridinium ions. This band was observed also on the non-treated

MoO_3/SiO_2 (Fig. 4c), and could be assigned to the pyridine adsorbed on Lewis acid sites. This would indicate that a part of molybdenum species was still remained as molybdenum oxide species even after the catalysts was exposed to water vapour.

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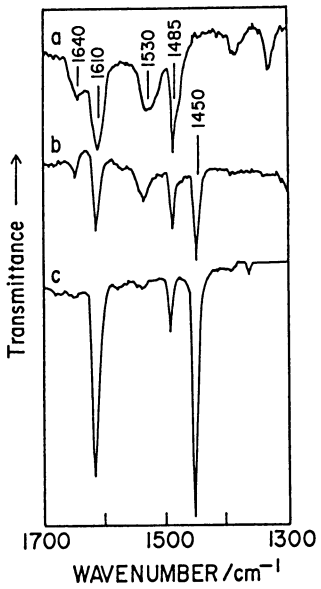

Fig.4. IR spectra of adsorbed pyridine.
(a) silicon-supported SMA,
(b) 100 °C water-treated MoO_3/SiO_2,
(c) MoO_3/SiO_2 calcined in O_2 at 500 °C.

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