

Catalytic Evidence of Formation of Water-Induced Silicomolybdic
Acid on a $\text{MoO}_3/\text{SiO}_2$ Catalyst

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The formation of silicomolybdic acid induced by the preadsorbed or catalytically formed water on $\text{MoO}_3/\text{SiO}_2$ 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 $\text{MoO}_3/\text{SiO}_2$ 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 $\text{MoO}_3/\text{SiO}_2$ 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% $\text{MoO}_3/\text{SiO}_2$ 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 ($\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, 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 molybdenum species in water extract from $\text{MoO}_3/\text{SiO}_2$, since the molybdenum species thus reacted with water was expected to be converted to SMA. The sample was prepared as follows; (1) the $\text{MoO}_3/\text{SiO}_2$ (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 $\nu(\text{Mo}=\text{O})$, $\nu(\text{Si}-\text{O})$, and $\nu(\text{Mo}-\text{O}-\text{Mo})$ in a Keggin structure, respectively.⁷⁾ Thus, a part of molybdenum species on $\text{MoO}_3/\text{SiO}_2$ is shown to react readily with water to give SMA, in agreement with the literatures.¹⁻³⁾

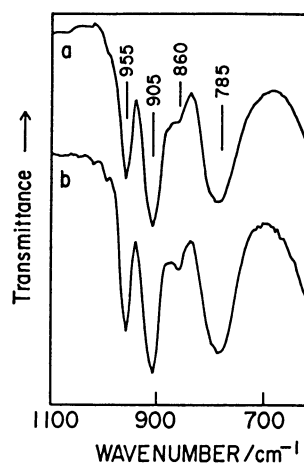


Fig.1. IR spectra of molybdenum species.

(a) water extract from $\text{MoO}_3/\text{SiO}_2$,

(b) SMA ($\text{H}_4\text{SiMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$).

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 $\text{MoO}_3/\text{SiO}_2$ and on the SMA/SiO_2 in the conventional recirculating system (302 ml) with an online-gas chromatograph (VZ-8 column, 6 m, 0 °C). Figure 2a shows the effect of the water-

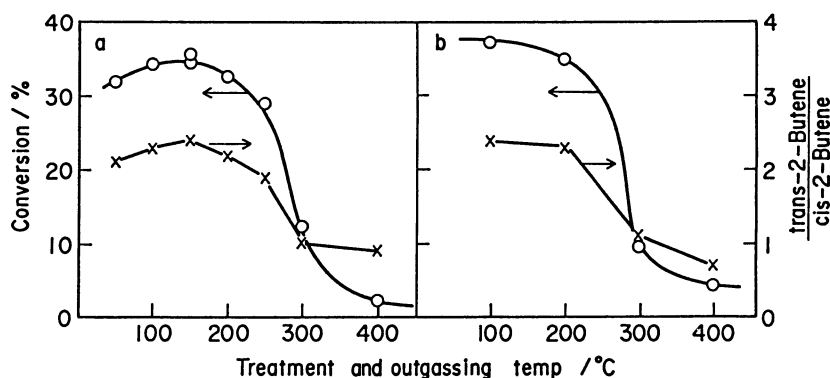


Fig.2. Effect of water-treatment temperature and outgassing temperature on catalytic activity (O) or selectivity (x) for isomerization of 1-butene to trans-2-butene or cis-2-butene. (a) $\text{MoO}_3/\text{SiO}_2$, (b) SMA/SiO_2 .

treatment temperature of $\text{MoO}_3/\text{SiO}_2$ 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 $\text{MoO}_3/\text{SiO}_2$ sample not treated with water was found to give almost the same results to those on the 400 °C water-treated $\text{MoO}_3/\text{SiO}_2$ 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 $\text{MoO}_3/\text{SiO}_2$, (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 $\text{MoO}_3/\text{SiO}_2$, the 150 °C water-treated $\text{MoO}_3/\text{SiO}_2$ 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 EX-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.

In order to see the molybdenum species besides SMA, IR spectra of the adsorbed pyridine on the water-treated $\text{MoO}_3/\text{SiO}_2$ was studied and compared with those on the non-treated $\text{MoO}_3/\text{SiO}_2$ 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 $\text{MoO}_3/\text{SiO}_2$, and the non-treated $\text{MoO}_3/\text{SiO}_2$, 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

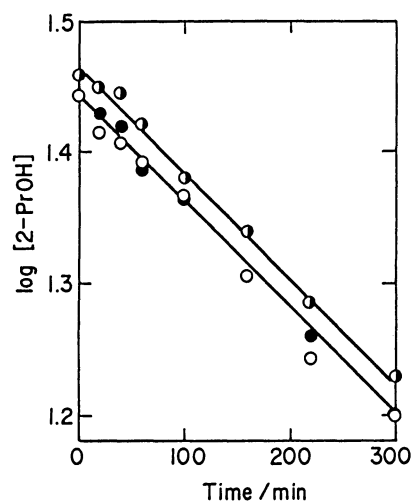


Fig.3. Dehydration of 2-propanol at 150 °C.
 (○) $\text{MoO}_3/\text{SiO}_2$ calcined in O_2 at 500 °C,
 (◐) 150 °C water-treated $\text{MoO}_3/\text{SiO}_2$,
 (●) 150 °C outgassed SMA/SiO_2 .

$\text{MoO}_3/\text{SiO}_2$ (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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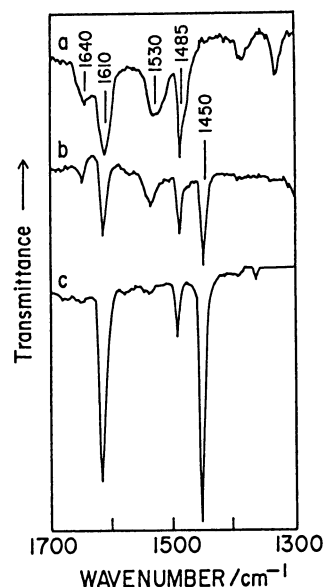


Fig.4. IR spectra of adsorbed pyridine.

(a) silicon-supported SMA,

(b) 100 °C water-treated $\text{MoO}_3/\text{SiO}_2$,

(c) $\text{MoO}_3/\text{SiO}_2$ calcined in O_2 at 500 °C.

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