

Acidic Properties of $\text{SiO}_2\text{-MoO}_3$ and MoO_3 , and Their Catalytic Activities

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MoO_3 , SiO_2 , and $\text{SiO}_2\text{-MoO}_3$ of different compositions were prepared and their surface and catalytic properties examined. A large number of acid sites were generated by mixing SiO_2 with MoO_3 , while each component oxide by itself did not exhibit any appreciable acidic properties. The oxidizing property of MoO_3 was enhanced by mixing with SiO_2 . No new compounds were detected in the oxide mixture by X-ray diffraction. The activity for depolymerization of 2,4,6-trimethyl-1,3,5-trioxane correlated well with the surface acidity. In the isomerization of 1-butene, both MoO_3 and $\text{SiO}_2\text{-MoO}_3$ were active. The active sites on MoO_3 were poisoned by CO_2 but not by NH_3 , while those on $\text{SiO}_2\text{-MoO}_3$ were poisoned by NH_3 but not by CO_2 .

Among the metal oxides most widely used as a component of the multicomponent metal oxide catalysts is MoO_3 , which is usually mixed with other oxides such as SiO_2 , Al_2O_3 , Bi_2O_3 , and SnO_2 . Many metal oxides are known to exhibit acidic properties when they are mixed with other oxides.^{1,2)} The acidic sites play an important role not only in reactions recognized as acid-base catalyzed reactions, but also in those of other types. For instance, the selectivity in the oxidation of olefins depends strongly on the surface acid-base properties.³⁻⁶⁾ However, the acid-base properties of the catalysts containing MoO_3 as a component oxide have not been subjected to extensive study except for $\text{MoO}_3\text{-Al}_2\text{O}_3$.⁷⁾

We have prepared $\text{SiO}_2\text{-MoO}_3$ in various molar ratios and examined their acid-base properties. Two typical acid-base catalyzed reactions, depolymerization of 2,4,6-trimethyl-1,3,5-trioxane and isomerization of butenes, were studied.

Experimental

Catalyst Preparation. SiO_2 and MoO_3 were prepared by precipitation from an isopropanol solution of ethyl orthosilicate and an aqueous solution of ammonium molybdate, respectively, with nitric acid followed by aging at 70–80 °C for 16 h and drying at 110 °C for 24 h.

$\text{SiO}_2\text{-MoO}_3$ was prepared as follows. A mixture of ethyl orthosilicate and 10% aqueous solution of ammonium molybdate was dissolved in isopropanol. To the solution was added dilute nitric acid (pH=1) and the solution was heated at 70–80 °C for 16 h to facilitate gelation. The resulting gel was dried at 110 °C for 24 h. Amounts of the reagents are given in Table 1.

TABLE 1. AMOUNTS OF REAGENTS USED FOR THE PREPARATION OF $\text{MoO}_3\text{-SiO}_2$ WITH DIFFERENT COMPOSITIONS

Composition mol ratio (MoO_3 : SiO_2)	$(\text{C}_2\text{H}_5)_4\text{SiO}_4$ ml	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot$ $4\text{H}_2\text{O}$ g	$(\text{CH}_3)_2\text{-}$ CHOH ml
MoO_3	0	160	0
9:1	13.2	159	14
1:1	167	129	170
1:9	402	35.3	400
SiO_2	400		400

Acidity and Basicity Measurements. Acidity was measured at 55 °C by titration of the suspension in benzene with 0.1 N butylamine benzene solution. The indicators used were

dicinnamylideneacetone ($\text{p}K_a = -3.0$), *p*-(phenylazo)diphenylamine (1.5), Dimethyl Yellow (3.3), Methyl Red (4.8), and Neutral Red (6.8). The existence of basic sites was monitored by dropping a series of benzene solutions of nitroaniline indicators onto a sample.

Surface Area, X-Ray Analysis, DTA, and TG, ESR Measurements. Specific surface areas were determined by applying the BET equation to nitrogen adsorption isotherms at -196 °C. X-Ray diffraction patterns were recorded on a Toshiba ADG-301 with a powdered sample over the range of $2\theta = 10^\circ\text{--}60^\circ$. $\text{CuK}\alpha$ was used as the radiation source.

DTA and TG were performed on a Rigakudenki standard model over the range from room temperature to 720 °C. The rate of temperature rise was 20 °C/min.

For ESR measurements, 20 mg of the sample in a cell with a breakable seal was evacuated at the desired temperature for 3 h and sealed off. ESR spectra of these samples were measured at -196 °C and room temperature. After recording the spectra, samples were exposed to butene, oxygen, nitrobenzene or a benzene solution of perylene through a breakable seal. All the spectra were measured on a Varian E-4 ESR spectrometer.

Reaction Procedure. The benzene solution of 2,4,6-trimethyl-1,3,5-trioxane (paraldehyde) (0.0495 mol/l) was used as a reactant for the depolymerization of paraldehyde. Powdered catalyst was calcined at 500 °C for 3 h in air. To 40 ml of the reactant in a 100 ml flask with a cap was added 0.24 g of catalyst followed by magnetic stirring at 30 °C. Portions of the reaction mixture were periodically withdrawn from the system and subjected to analysis of acetaldehyde by the following method. Excess amount of 0.1 N NaHSO_3 was added to 10 ml of reaction mixture to form a complex with acetaldehyde. After titration of residual NaHSO_3 with I_2 , the $\text{NaHSO}_3\text{-acetaldehyde}$ complex was dissociated by the addition of NaHCO_3 . The amount of NaHSO_3 required for the formation of the complex was determined by titration with I_2 .

A microcatalytic pulse reactor was employed for the isomerization of butenes. The catalyst was sieved to 20–35 mesh and calcined at 500 °C for 3 h. A quarter grams of the catalyst was placed in the reactor and pretreated at 500 °C under a helium stream for 1 h prior to reaction. All the reactions were carried out at 250 °C. Butene (ca. 40 μ mol) was introduced into a helium carrier ahead of the catalyst by manipulating a stop cock. Effluent products were directly introduced into a gas chromatographic column for analysis. The flow rate of the carrier was kept constant (1.1 ml/s). In some experiments, CO_2 or NH_3 was introduced in order to examine a poisoning effect after reaching a steady activity, which was usually attained after 7 or 8 injections.

Results

Surface Area, X-Ray, DTA, and TG. The specific

TABLE 2. SPECIFIC SURFACE AREA (m^2/g) OF $\text{MoO}_3\text{-SiO}_2$ AFTER CALCINATION AT VARIOUS TEMPERATURES^{a)}

Composition ($\text{MoO}_3\text{:SiO}_2$)	Calcination temperature, °C			
	300	400	500	600
MoO_3	4.5	4.8	4.3	2.8
9:1	5.4	4.5	4.0	2.2
1:1	143	92	81	40
1:9	440	376	240	93
SiO_2	—	—	520	375

a) Before measurement, sample was evacuated at 150–170 °C for 1 h.

surface areas of catalysts are given in Table 2. They decrease with an increase in percentage of MoO_3 and with a rise in calcination temperature.

X-Ray diffraction patterns show that all the peaks obtained for $\text{SiO}_2\text{-MoO}_3$ of different compositions calcined at 400, 500, and 600 °C are due to those of MoO_3 , strong peaks being observed at $2\theta=10.17$, 19.90 , and 29.80° . The samples calcined at 300 °C did not show this set of peaks. The peak intensity increases with a rise in calcination temperature and with an increase in MoO_3 content in $\text{SiO}_2\text{-MoO}_3$. No peaks other than those ascribed to MoO_3 were found.

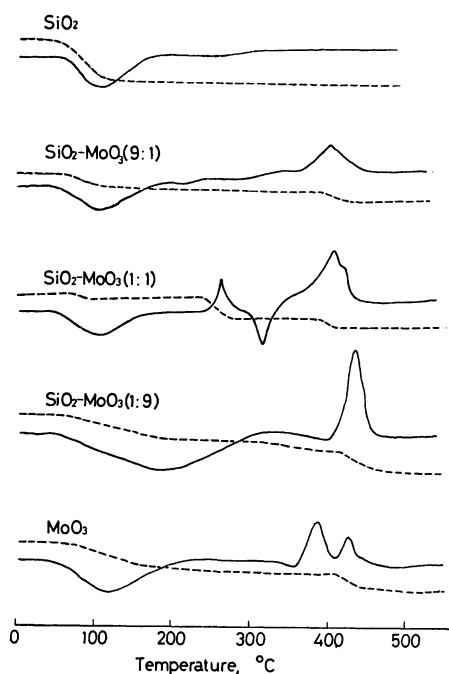


Fig. 1. DTA-TG curves of catalysts. DTA, solid line; TG, broken line.

DTA-TG curves are shown in Fig. 1. All the samples show endothermic peaks by DTA around 50–200 °C with loss of weight. These peaks can be ascribed to desorption of physically adsorbed water. The samples containing MoO_3 show exothermic peaks around 400 °C also accompanied a weight loss.

ESR. $\text{SiO}_2\text{-MoO}_3$ and MoO_3 show ESR signals assigned to Mo^{5+} . The signal for $\text{SiO}_2\text{-MoO}_3$ (9:1) after evacuation at 500 °C is shown in Fig. 2. On ex-

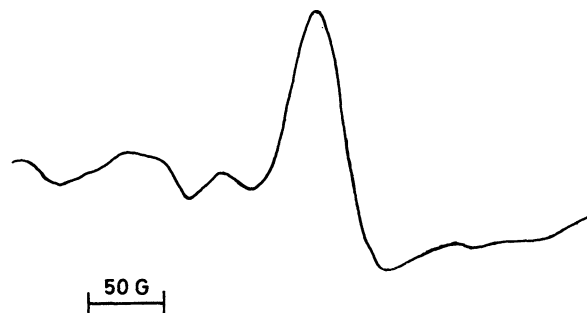


Fig. 2. ESR signal of $\text{SiO}_2\text{-MoO}_3$ (9:1) evacuated at 500 °C.

posure to nitrobenzene, the amplitude of the signal decreased considerably but no signal for nitrobenzene anion radical was observed. On admission of a benzene solution of perylene, a strong signal appeared which could be assigned to perylene cation radical. The signals observed for $\text{SiO}_2\text{-MoO}_3$ 9:1 and 1:1 showed hyperfine splitting into nine peaks. On the other hand, the signals for $\text{SiO}_2\text{-MoO}_3$ (1:9) and MoO_3 were broad singlets. The variation of the integrated signal amplitude of perylene cation radicals with composition is shown in Fig. 3.

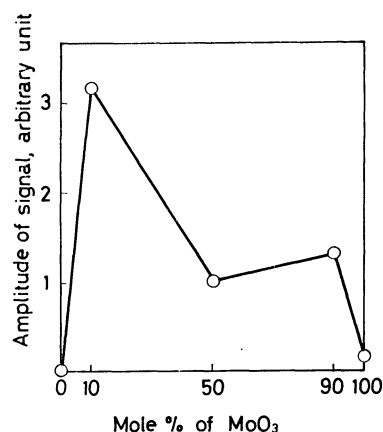


Fig. 3. Numbers of perylene cation radicals on $\text{SiO}_2\text{-MoO}_3$ of different composition. Catalysts had been evacuated at 500 °C.

Admission of butene at 200 °C to $\text{SiO}_2\text{-MoO}_3$ (9:1) evacuated at 500 °C resulted in an increase in the signal amplitude of Mo^{5+} , and the successive admission of O_2 after the excess butene had been trapped in liquid nitrogen resulted in a decrease in the amplitude of the Mo^{5+} signal and the production of O^{2-} .

Acidity. Figure 4 shows the acidity of $\text{SiO}_2\text{-MoO}_3$ having compositions of 9:1, 1:1, and 1:9 as well as that of SiO_2 and MoO_3 , when calcined at 500 °C in air. Although SiO_2 and MoO_3 showed negligible amounts of acid sites stronger than $H_0=3.3$, $\text{SiO}_2\text{-MoO}_3$ with composition 9:1 and 1:1 showed considerable amounts of these acid sites. Change in calcination temperature caused no great change in acidity. An example is shown in Fig. 5 for $\text{SiO}_2\text{-MoO}_3$ (9:1).

Depolymerization of 2,4,6-Timethyl-1,3,5-trioxane. The reaction rate equation was of first order in concen-

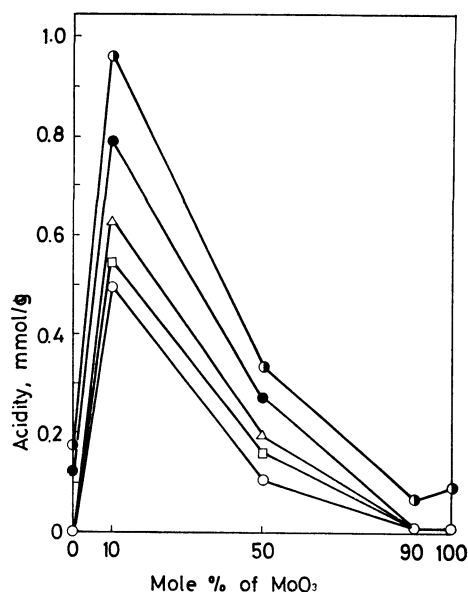


Fig. 4. Acidity of $\text{SiO}_2\text{-MoO}_3$ of different composition. $H_0 = -3.0$ (\circ), $+1.5$ (\square), $+3.3$ (\triangle), $+4.8$ (\bullet), $+6.8$ (\bullet).

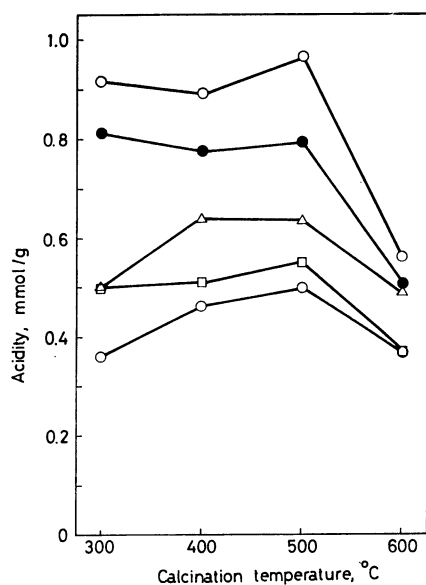


Fig. 5. Changes in acidity of $\text{SiO}_2\text{-MoO}_3$ (9:1) with calcination temperature $H_0 = -3.0$ (\circ), $+1.5$ (\square), $+3.3$ (\triangle), $+4.8$ (\bullet), $+6.8$ (\bullet).

tration of reactant. Activity of the catalyst was expressed by a first order rate constant, k , per unit weight of catalyst. The variation of the activity with composition is shown in Fig. 6, where the catalysts are calcined at 500°C in air. A similarity in the change in activity to that in acidity with composition of the catalyst suggests that the acid sites are active sites for the decomposition of 2,4,6-trimethyl-1,3,5-trioxane to produce acetaldehyde. The activity of the catalysts is more than 10 times greater than that of NiSO_4 and CuSO_4 .⁷⁾

Isomerization of Butene. The conversion of *cis*-2-butene over MoO_3 and $\text{SiO}_2\text{-MoO}_3$ (9:1) is plotted against the pulse number in Figs. 7 and 8. The decrease in conversion with the pulse number is greater for MoO_3 than $\text{SiO}_2\text{-MoO}_3$ (9:1). After the conversion had

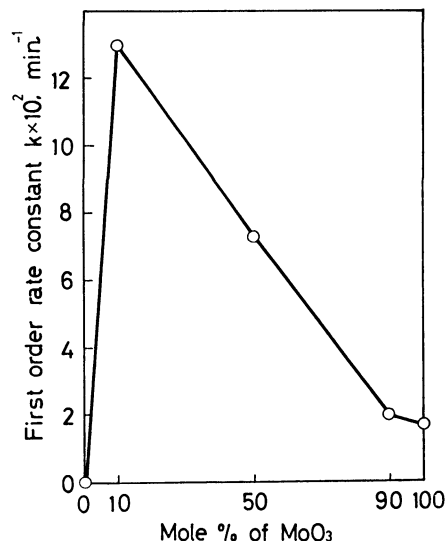


Fig. 6. Variation of activity for depolymerization of 2,4,6-trimethyl-1,3,5-trioxane with composition.

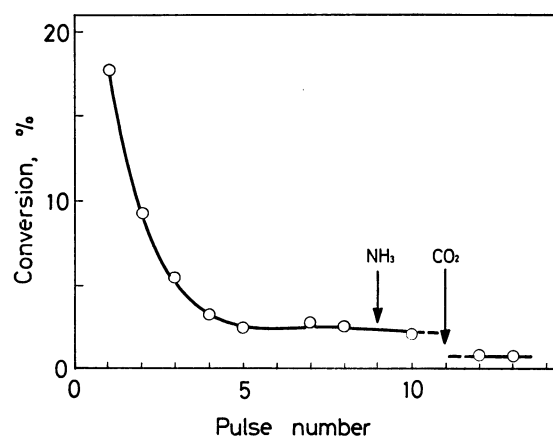


Fig. 7. Activity decrease in isomerization of *cis*-2-butene with pulse number and with NH_3 or CO_2 addition over MoO_3 .

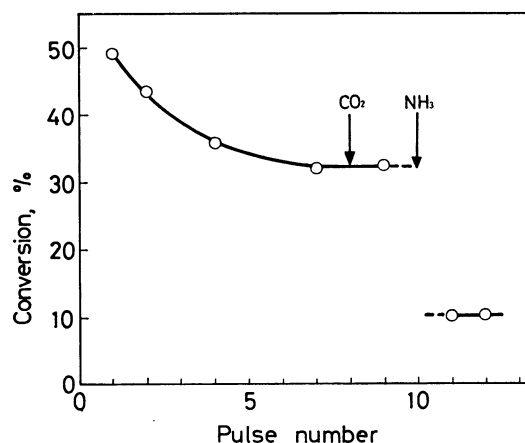


Fig. 8. Activity decrease in isomerization of *cis*-2-butene with pulse number and with NH_3 or CO_2 addition over $\text{SiO}_2\text{-MoO}_3$ (9:1).

attained a constant value, CO_2 or NH_3 was introduced. The active sites of MoO_3 were poisoned by CO_2 , but not substantially by NH_3 . On the other hand, the active

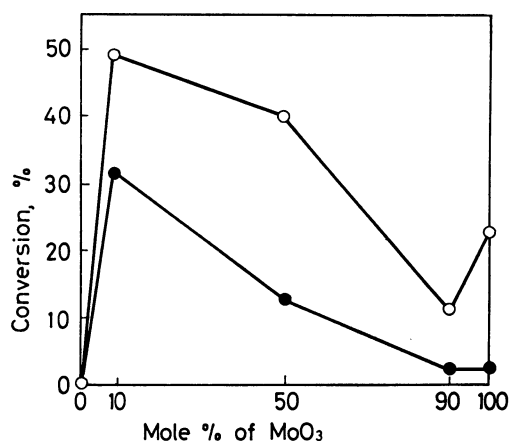


Fig. 9. Initial activity (○) and steady state activity (●) for isomerization of *cis*-2-butene.

sites of $\text{SiO}_2\text{-MoO}_3$ were poisoned by NH_3 , but not by CO_2 .

The conversion at the first pulse and that after several pulses (the constant conversion) are shown in Fig. 9. Except for MoO_3 , the change in conversion with the composition of catalyst is similar to that in acidity.

Discussion

Mixing of SiO_2 and MoO_3 gave rise to new surface and catalytic properties not found in either component oxide, though X-ray and DTA-TG data showed no formation of a new compound. Of these properties acidity is important. A good correlation of acidity with activity for depolymerization of 2,4,6-trimethyl-1,3,5-trioxane indicates that the active sites for the reaction are the acid sites generated by mixing SiO_2 and MoO_3 .

For the isomerization of butene, MoO_3 showed considerable activity though it had no acidic sites stronger than $H_0=4.8$. The catalyst was not poisoned by NH_3 . Thus, the active sites are not acidic. Since CO_2 is an acidic molecule and can be adsorbed on basic sites, and

CO_2 actually poisons the catalyst, the active sites on MoO_3 for the butene isomerization seem to be basic. On the other hand, the activity of the mixed oxides correlates with the acidity and NH_3 poisons the active sites. Thus, the active sites on $\text{SiO}_2\text{-MoO}_3$ are suggested to be acidic sites and the reaction proceeds *via* a carbenium ion mechanism.

An increase in the amplitude of the ESR signal for Mo^{5+} by the admission of butene to $\text{SiO}_2\text{-MoO}_3$ (9:1) indicates that reduction occurred during the course of isomerization of butene. The activity also decreased with successive pulses. It seems that the active sites become less active by reduction. The mechanism of generation of acid sites in a mixed oxide was proposed by one of the authors,^{1,2)} and the concept can be applied to the $\text{SiO}_2\text{-MoO}_3$ system. Acid sites are caused by the excess positive charge on Si^{4+} in the $\text{SiO}_2\text{-MoO}_3$. The reduction of Mo^{6+} reduces the excess positive charge on Si^{4+} by the transfer of negative charge to Si^{4+} through oxygen bridging. This weakens the strength of acid sites or eliminates the acid sites.

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