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The MoO_3-SnO_2 Catalysts. Acid-Base Properties and Catalytic Activities for 2-Butanol Decomposition and 1-Butene Isomerization

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Synopsis. Acidic and basic properties of MoO_3–SnO_2 catalysts with different compositions of MoO_3 were measured by adsorption of NH_3, CO_2, and acid-base indicators. Acidic property prevailed over basic property for all catalysts. Catalytic activities for 2-butanol dehydration and 1-butene isomerization correlated with the acidities measured under the reaction conditions.

A binary oxide of MoO_3–SnO_2 is known as a catalyst that promotes oxidation of propylene and of methanol.[1–3] Besides oxidation reactions, MoO_3–SnO_2 catalyzed acid-catalyzed reactions such as 1-butene isomerization.[4] Recently, MoO_3–SnO_2 was found to show a high activity for coal liquefaction.[5] Thus, the characterization of the surface property has become necessary.

Okamoto *et al.* studied the relationship between the structure of MoO_3–SnO_2 by XPS and the catalytic activity for 2-butanol decomposition.[6] They carried out the reaction in the presence of oxygen and proposed that the reaction proceeds by a Redox mechanism. Ai measured the acidity and found the correlation between the acidity and the catalytic activity for 1-butene isomerization, which was carried out in the presence of oxygen.[4]

In the present work, the acidic and basic properties of MoO_3–SnO_2 as well as the catalytic activities for 1-butene isomerization and 2-butanol decomposition in the absence of oxygen were studied, and the relationship between the properties and the activities is discussed.

Experimental

The MoO_3–SnO_2 was prepared by hydrolysis of mixed solution of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and tin tetrachloride with ammonia water, the final pH being 8. The precipitate was aged over a water bath for 2 h, then washed with deionized water, dried at 120 °C for 24 h, and finally calcined at 500 °C for 2—3 h in air. The catalysts with different molar ratios of MoO_3 to SnO_2 were prepared from the different mixed solutions. The molar ratios were determined by fluorescence X-ray spectrometry. The MoO_3 was prepared from an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ by precipitation with hydrochloric acid. The SnO_2 was prepared from an aqueous solution of $SnCl_4$ by precipitation with ammonia water. The precipitates were aged, washed, dried, and calcined as above. Acidic and basic strengths of the catalysts were qualitatively determined by use of indicators. A series of Hammett indicators were used for measurement of acidic strength. Bromothymol Blue ($pK_a=7.1$) and phenolphtalein ($pK_a=9$) were used for measurement of basic strength. The amounts of irreversible adsorption of NH_3 at 150 °C were measured by a pulse technique.[7,8] Prior to the measurement, a catalyst was pretreated under a He stream at 500 °C for 2 h or subsequently treated with 2-butanol in a He stream at 200 °C. The adsorption of CO_2 was measured volumetrically at 0 °C. The amount of irreversible adsorption of CO_2 was calculated as the difference in the amount between the first run and the second run which was carried out after outgassing at 0 °C for 30 min.

Reaction Procedures. A recirculation reactor (volume 280 ml) was employed with 0.5 g catalyst for carrying out the isomerization of 1-butene at 100 °C. Prior to the reaction, a catalyst was outgassed at 500 °C for 2 h. For the decomposition of 2-butanol, a microcatalytic pulse reactor was employed at 200 °C. A 10 μl of the reactant was injected in a He stream which flowed at a rate of 85 ml/min over 0.1 g catalyst.

Results and Discussion

The MoO_3–SnO_2 catalysts containing 10, 25, and 40% MoO_3 showed a fairly high acid strength of $H_0=-3.0$—-5.6, and the catalysts containing 50, 70, and 90% MoO_3, the SnO_2 catalyst and the MoO_3 catalyst showed $H_0=+1.5$—-3.0. As the content of MoO_3 in the binary oxide catalysts decreased, the acid sites became strong. The amounts of irreversible adsorption of NH_3 per unit surface area are plotted against the composition of catalyst in Fig. 1. For the catalysts which were pretreated only with a He stream at 500 °C, the amount of NH_3 adsorption exhibited a maximum at 50% of the MoO_3 content, though the amount was less than that for the MoO_3 catalyst. On subsequent treatment with 2-butanol at 200 °C, the amount of NH_3 adsorption decreased for the catalysts containing 25 and 50% MoO_3, and the plot of the amount *vs.* the MoO_3 content showed a monotonous increase with the increase in the MoO_3 content.

Okamoto *et al.* reported on the basis of XPS observation of the MoO_3–SnO_2 catalyst that Mo^{6+} ions in the catalyst containing a small amount of MoO_3 were easily reduced to Mo^{5+} ions which were stable toward further reduction. On the contrary, Mo^{6+} ions in the catalyst containing a large amount of MoO_3 were hardly reduced to Mo^{5+} ions under mild reduction conditions. However, once the Mo^{5+} ions were formed, the Mo^{5+} ions underwent further reduction

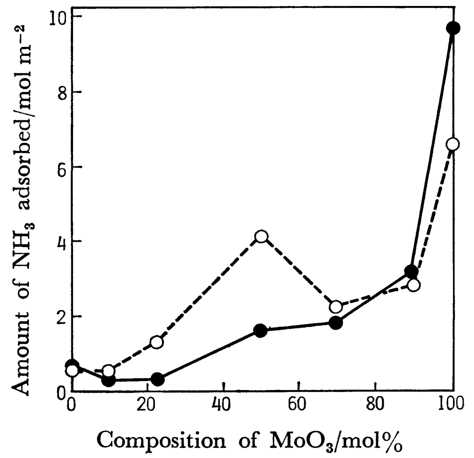

Fig. 1. Variation of the amount of NH_3 irreversibly adsorbed at 150 °C as a function of content of MoO_3 in catalyst.
--○--: Pretreated with a He stream at 500 °C, —●—: subsequently pretreated with a 2-butanol at 200 °C.

to Mo^{4+} ions. This difference in reducibility with MoO_3 content seems to hold in the present case. It is assumed that the decrease in the amount of NH_3 adsorption on pretreatment with 2-butanol is caused by reduction of Mo^{6+} ions to Mo^{5+} ions for the catalysts containing small amounts of MoO_3. For the catalysts containing large amounts of MoO_3, Mo^{6+} ions persisted their oxidation states toward treatment with 2-butanol, and the amount of NH_3 adsorption did not change much.

Existence of weak basic sites ($H_- = 7.1$—9) was observed for all the MoO_3–SnO_2 catalysts, but no basic sites were detected for the MoO_3 catalyst and the SnO_2 catalyst. The amounts of irreversible adsorption of CO_2 at 0 °C were 1.1—7.4 μmol/m², but all the adsorbed CO_2 were easily removed by evacuation at room temperature. This also indicates that basic sites on the catalysts are weak.

The rate of conversion of 1-butene to 2-butenes on unit surface area basis is plotted against the content of MoO_3 in Fig. 2. The catalysts containing 50 and 90% MoO_3 showed maximum activities. The variation of the activity for the isomerization with MoO_3 content correlated roughly with that of the amount of NH_3 adsorption on the catalysts pretreated with He except for MoO_3. This suggests that the active sites for the isomerization are acidic sites present on the MoO_3–SnO_2 catalysts. The higher activity of the catalysts containing 10 and 25% MoO_3 compared with SnO_2 catalyst is considered due to the higher acid strength. On the other hand, the higher activity of the catalyst containing 90% MoO_3 compared with the catalyst containing 50% MoO_3 is supposed to be due to a little cooperation of basic sites, since the acid strength of the former is lower than that of the latter. Since acid-catalyzed isomerization of 1-butene gives the cis/trans ratio in 2-butenes about 1 in most cases, the observed cis/trans ratios 0.9—1.5 also support that the acidic sites on the catalyst are acting mainly for the isomerization.

Degradation of activity for the reaction of 2-butanol with the pulse number was prominent for the catalyst containing 10 and 50% MoO_3, while the activity did not decrease so much for the catalyst containing 90% MoO_3 and the MoO_3 catalyst. The variations of the conversions of 2-butanol to butenes and ethyl methyl ketone at the 5th pulse as a function of the composition of the catalysts are shown in Fig. 3. The conversion to butenes increased monotonously as the content of MoO_3 increased, and attained a maximum at the MoO_3 catalyst. Dehydrogenation to produce ethyl methyl ketone was minor reaction for all the catalysts. Only dehydration was observed on the MoO_3 catalyst. The variation of the conversion to butene with the composition of the catalyst correlated well with that of the amount of NH_3 adsorption on the catalyst pretreated with 2-butanol. During the reaction, a part of Mo^{6+} ions in the catalysts containing small amounts of MoO_3 may be reduced to Mo^{5+} ions. Prominent degradation of activity with increasing pulse number for the catalyst containing 10% and 50% MoO_3 supports the possibility of the reduction of Mo^{6+} ions and elimination of a part of the acidic sites.

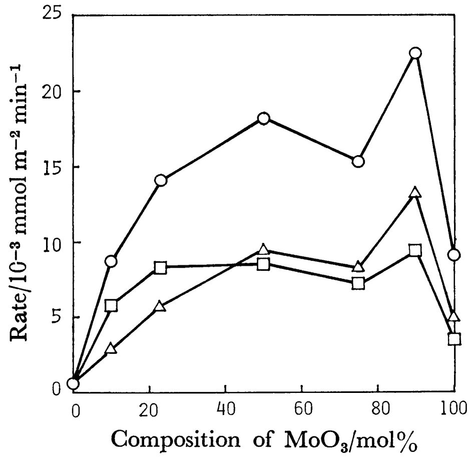

Fig. 2. Variation of the activity for 1-butene isomerization as a function of content of MoO_3 in catalyst.

—○—: Rate of 1-butene conversion, —△—: rate of *cis*-2-butene formation, —□—: rate of *trans*-2-butene formation.

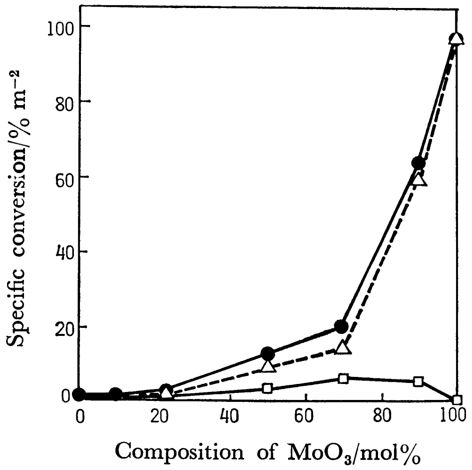

Fig. 3. Variation of the activity for 2-butanol decomposition as a function of content of MoO_3 in catalyst.

—●—: Total conversion, —△—: conversion to butenes, —□—: conversion to methyl ethyl ketone.

Ai reported that the activities of MoO_3–SnO_2 for 1-butene isomerization and dehydration of isopropyl alcohol exhibited maxima at 30—60% of the MoO_3 content and that the activities correlated with the acidity. Taking into account that Ai carried out the reactions in the presence of oxygen, the present results are in accord with his results except for the MoO_3 catalyst. The reason for the discrepancy with MoO_3 is not certain.

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