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Characterization of TiO_2–SiO_2 Modified with H_2SO_4 and Activity for Acid Catalysis

Recently, many kinds of mixed oxides have been reported to show surface acidity (*1–3*). In cumene dealkylation the more acidic the catalysts, the higher the catalytic activity they show (*4, 5*). On the other hand, *tert*-butanol dehydration takes place on relatively weaker acid sites, while skeletal isomerization of isobutylene requires exceedingly strong acid sites (*6*). Thus to incorporate more acidity and stronger acid strength, single or binary oxide catalysts are often modified with sulfuric acid (*7–9*). High catalytic activity of catalyst modified with sulfuric acid is attributed to the enhanced acidic property by the inductive effects of S=O bonds of the complex formed by the interaction of oxides with sulfate ion (*8, 10*).

The present paper is concerned with the characterization of TiO_2–SiO_2 series catalysts modified with H_2SO_4 and activity for acid catalysis. For this purpose, the 2-propanol dehydration and cumene dealkylation were used as test reactions.

The coprecipitate of $Ti(OH)_4$–$Si(OH)_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and sodium silicate solution at room temperature with stirring until the pH of the mother liquor reached 8. The dired coprecipitate was again washed with successive portions of a 5% ammonium nitrate solution and then with hot distilled water to remove sodium ion in the coprecipitate. To obtain the modified catalysts, 2 g of each dried precipitate was treated with each 30 ml of 1 *N* sulfuric acid followed by drying the sample in air as described elsewhere (*8*). The dried solid powders were used as modified catalysts after calcination at 400°C for 1.5 h. The catalysts are denoted by following a mole percentage of TiO_2. That is, 92-TiO_2–SiO_2 represents the catalysts having 92 mol% of TiO_2 and 92-TiO_2–SiO_2/SO_4^{2-} represents 92-TiO_2–SiO_2 catalyst modified with 1 *N* H_2SO_4. The reactions for 2-propanol dehydration and cumene dealkylation were carried out at 180 and 400°C, respectively. During the 2-propanol dehydration reaction a diethyleneglycol succinate on a Shimalite column at 150°C was employed, while for the cumene dealkylation reaction a Bentone 34 on a Chromosorb W column at 130°C was used. Conversions for both reactions were taken as the average of the first to sixth pulse values. IR spectra were recorded using Mattson Galaxy-6030E FT–IR spectrometer. X-ray diffractograms of the catalyst were taken by a Jeol Model JDX-88 X-ray diffractometer using a copper target and nickel filter at 30 kV and 1000 cps.

TiO_2/SO_4^{2-} and 92-TiO_2–SiO_2/SO_4^{2-} showed infrared absorption bands at 1200–1225, 1140–1130, 1060–1040, and 990–980 cm^{-1}, which are assigned to bidentate sulfate ion coordinated to the metal such as Ti^{+4} and Si^{+4} (*11*). Strong absorption bands of sulfate ion still remained even after evacuation at 400°C, indicating a very strong interaction between the sulfate ion and metal. For the samples modified with H_2SO_4 followed by calcination at 400°C, based on infrared spectra results, the sulfur is considered to reach the highest oxidation state, S^{6+} of SO_4^{2-}. To obtain further information on the oxidation state of sulfur, X-ray photoelectron spectroscopic investigation was performed. As expected, all samples modified with H_2SO_4 gave the signal attributed to S^{6+} (*10*), suggesting the oxida-

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TABLE 1

Acid Strength of Catalysts

Hammett indicator	pK_a value of indicator	SiO_2	SiO_2/SO_4^{2-}	TiO_2	TiO_2/SO_4^{2-}	73-TiO_2–SiO_2	73-TiO_2–SiO_2/SO_4^{2-}
Dimethyl yellow	+3.3	+	+	+	+	+	+
Dicinnamalacetone	−3.0	−	+	+	+	+	+
Benzalacetophenone	−5.6	−	+	−	+	+	+
Antraquinone	−8.2	−	−	−	+	+	+
Nitrobenzene	−12.4	−	−	−	+	−	+
2,4-Dinitrofluorobenzene	−14.5	−	−	−	+	−	+

tion state of sulfur as SO_4^{2-} as the main species. The S_{2p} binding energy of S^{6+} was 168.8 eV (*10, 12*), calculated in reference to the C_{1s} binding energy of 285.0 eV. The crystalline structures of catalysts calcined in air at 400°C for 1.5 h were checked by X-ray diffraction. The catalysts containing TiO_2 content lower than 50% were amorphous to X-ray diffraction, but a tiny amount of the anatase form of TiO_2 was observed with the samples containing higher TiO_2 content.

The acidity of TiO_2–SiO_2 and TiO_2–SiO_2/SO_4^{2-} series catalysts after evacuation at 400°C for 1 h was determined by the amine titration method at $H_0 = -3.0$, where H_0 is the Hammett acidity function. Although single component SiO_2 showed little acidity, mixing of the two components, TiO_2 and SiO_2, resulted in a remarkable increase in acidity. The acidity increased gradually upon the addition of TiO_2 to SiO_2 reaching a maximum at 73-TiO_2–SiO_2. The combination of TiO_2 and SiO_2 generated stronger acid sites and more acidity as compared with the single components. Moreover, the modified catalysts had much more acidity than the unmodified catalysts. These results mean that the weak acid sites of unmodified catalysts are converted into strong acid sites by means of modifying the sample with H_2SO_4. The acid strength of the catalysts was examined by the color change method using the Hammett indicator (*13*), when a powdered sample was added to an indicator dissolved in dried benzene. In Table 1, + indicates that the color of an indicator base form was changed to that of the conjugated acid form. TiO_2 prepared by evacuating titanium hydroxide at 400°C had acid strength of $H_0 \leq -3.0$, while SiO_2 had very weak acid strength of $H_0 \leq +3.3$ (*14*). However, 73-TiO_2–SiO_2 was estimated to be $H_0 \leq -8.2$, indicating the formation of new acid sites stronger than those of the single oxide components. The other binary oxides also had the same acid strength of $H_0 \leq -8.2$ as 73-TiO_2–SiO_2. The acid strength of SiO_2/SO_4^{2-} was estimated to be $H_0 \leq -5.6$, and that of TiO_2/SO_4^{2-} and 73-TiO_2–SiO_2 was $H_0 \leq -14.5$. Acids stronger than $H_0 = -11.93$, which corresponds to the acid strength of 100% H_2SO_4, are superacids (*15*). Consequently, TiO_2/SO_4^{2-} and 73-TiO_2–SiO_2/SO_4^{2-} would be solid superacids. The increase of acid strength in the modified catalysts is attributed to the double bond nature of S=O, which strengthens the acid sites by the inductive effect (*8*).

We examined the infrared spectra of pyridine adsorbed on catalysts evacuated at 400°C for 1.5 h. The coordinated pyridine band at 1445 cm^{-1} was found with TiO_2, while both the pyridinium ion band at 1541–1543 cm^{-1} and the coordinated pyridine band at 1447 cm^{-1} were found with TiO_2/SO_4^{2-}, TiO_2–SiO_2, and TiO_2–SiO_2/SO_4^{2-}. It is clear that the new Brønsted acid site, which is not present on pure TiO_2, is formed by modifying TiO_2 with H_2SO_4 or by mixing TiO_2 and SiO_2.

The catalytic activities for the 2-propanol dehydration are measured and the results are illustrated as a function of TiO_2 content in Fig. 1. In view of measured acidity, the variations in catalytic activities of unmodified TiO_2–SiO_2 catalysts are roughly correlated with the changes of their acidity. As shown in Fig. 1, the catalysts modified with H_2SO_4 exhibit higher catalytic activity than unmodified catalysts. The modification effect on the catalytic activity was much greater in the catalysts having high TiO_2 content. Actually, the catalytic activity of 92-TiO_2–SiO_2/SO_4^{2-} was 20 times as high as that of 92-TiO_2–SiO_2, while 10-TiO_2–SiO_2/SO_4^{2-} exhibited only 1.5 times as high an activity. We could guess from these results that TiO_2 has more of an effect on the modification than SiO_2. However, in the case of modified catalysts, the correlation between catalytic activity and acidity does not hold good. Although the acidity of TiO_2/SO_4^{2-} is the highest, its catalytic activity is relatively low. It is known that 2-propanol dehydration takes place very readily on weak acid sites (*16, 17*). Therefore, it seems that in the case of TiO_2/SO_4^{2-}, the number of weak acid sites decreased due to the conversion of weak acid sites into strong acid sites by the modification with H_2SO_4.

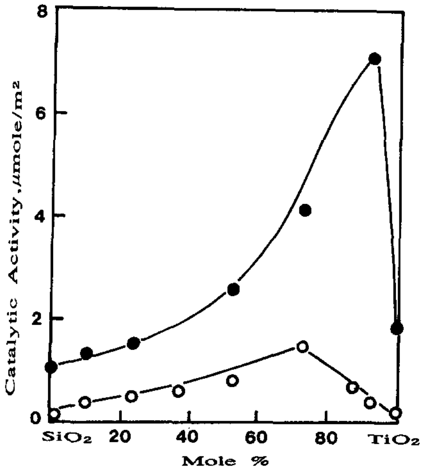

FIG. 1. Variations of catalytic activity for 2-propanol dehydration with TiO_2 content: ○, unmodified catalyst; ●, modified catalyst.

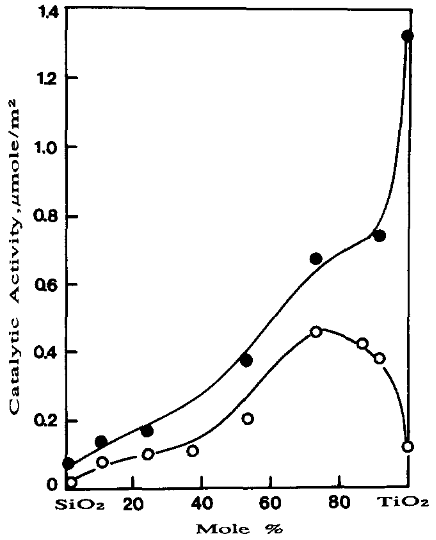

FIG. 2. Variations of catalytic activity for cumene dealkylation with TiO_2 content: ○, unmodified catalyst; ●, modified catalyst.

Cumene dealkylation takes place on relatively strong acid sites of the catalysts (*16, 17*). Catalytic activities for cumene dealkylation against TiO_2 content are represented in Fig. 2. Comparing Figs. 1 and 2, the catalytic activity for cumene dealkylation is much lower than that for 2-propanol dehydration. This result may be attributed to the fact that TiO_2–SiO_2 catalysts have a small amount of relatively strong acid sites necessary for cumene dealkylation, while the number of weak acid sites necessary for 2-propanol dehydration is relatively abundant. However, regardless of modification, the catalytic activities are correlated with acidity of two series catalysts. The modification effect on catalytic activity also increased with increase of the TiO_2 content, showing a maximum effect in a single oxide of TiO_2.

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REFERENCES

1. Damon, J. P., Delmon, B., and Bonnier, J. M., *J. Chem. Soc. Faraday Trans. 1* **11**, 372 (1976).

2. Holm, V. C. F., Bailey, G. C., and Clark, A., *J. Phys. Chem.* **63,** 129 (1959).
3. Dzisko, V. A., "Binary Oxide Catallysts Based on Silica," pp. 422–432. Academic Press, New York, 1970.
4. Tamele, M. W., *Discuss. Faraday Soc.* **8,** 270 (1950).
5. Johnson, O., *J. Phys. Chem.* **59,** 827 (1955).
6. Tanabe, K., Seiyama, T., and Hueki, K., "Metal Oxide and Mixed Oxides." Kodansa Tokyo, 1978.
7. Hino, M., and Arata, K., *Chem. Lett.,* 477 (1976).
8. Sohn, J. R., and Kim, H. J., *J. Catal.* **101,** 428 (1986).
9. Sohn, J. R., Kim, H. W., and Kim, J. T., *J. Mol. Catal.* **41,** 375 (1987).
10. Sohn, J. R., and Kim, H. W., *J. Mol. Catal.* **52,** 361 (1989).
11. Nakamoto, K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed. Wiley, New York, 1964.
12. Ito, M., Hattori, H., and Tanabe, K., *J. Catal.* **35,** 225 (1974).
13. Hammett, L. P., and Deyrup, A. J., *J. Am. Chem. Soc.* **54,** 272 (1932).
14. Miura, M., Kubota, Y., Iwaki, T., Takimoto, K., and Muraoka, Y., *Bull. Chem. Soc. Jpn.* **42,** 1476 (1969).
15. Olah, F. G. A., Prakash, G. K. S., and Sommer, J., *Science* **206,** 13 (1979).
16. Sohn, J. R., and Jang, H. J., *J. Mol. Catal.* **64,** 349 (1991).
17. Decanio, S. J., Sohn, J. R., Paul, P. O., and Lunsford, J. H., *J. Catal.* **101,** 132 (1986).

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