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Correlation between the Infrared Band Frequency of the Silanol Bending Vibration in TiO_2–SiO_2 Catalysts and Activity for Acid Catalysis

It is well known that the surface acidity of a metal oxide is improved with the incorporation of another metal oxide to form a binary oxide. Thus, recently many kinds of mixed oxides were reported to show catalytic activity for particular reactions (*1–5*). Titania–silica mixed oxides are interesting materials. The combination of TiO_2 and SiO_2 generated very strong acid sites and showed high catalytic activity and selectivity for the amination of phenol with ammonia to produce aniline (*6*). In this paper we report the correlation between the band frequency of the silanol bending vibration in TiO_2–SiO_2 catalysts and acid catalytic activity. For this purpose, the 2-propanol dehydration and cumene dealkylation were used as test reactions.

The coprecipitate $Ti(OH)_4$–$Si(OH)_4$ was obtained by adding aqueous ammonia slowly to a mixed aqueous solution of titanium tetrachloride and sodium silicate at room temperature with stirring until the pH of the mother liquor reached 8. The coprecipitate thus obtained was washed thoroughly with distilled water, and 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. This series of catalysts calcined at 450°C for 1.5 hr are denoted by their mole percentage of TiO_2. Catalytic activities for 2-propanol dehydration and cumene dealkyaltion reactions were measured in a pulse microreactor. Pulses of 1-μl reactant were injected into a N_2 gas stream which passed over 1–3 mg catalyst activated at 400°C. 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 Shimalite column at 150°C was employed, while for the cumene dealkylation reaction a Bentone 34 on Chromosorb W column at 130°C was used. Conversions for both reactions were taken as the average of the first to sixth pulse values. The specific surface area was determined by applying the BET method to the adsorption of nitrogen at −196°C. 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.

The crystalline structure of catalysts calcined at 450°C for 1.5 hr was checked by X-ray diffraction. Most of the binary oxide catalysts except for 92-TiO_2–SiO_2 were amorphous to X-ray diffraction, but a tiny amount of the anatase form of TiO_2 was observed with 92-TiO_2–SiO_2.

A series of TiO_2–SiO_2 calcined at 400°C was examined by IR absorption in the mid-infrared region, using the KBr disc technique. There were no new bands due to the chemical compound between TiO_2 and SiO_2, indicating no formation of a new phase between them. The spectra of bands around 1200–1100 cm^{-1} due to Si–O stretching vibrations were sharper with increasing TiO_2 content because of the higher degree of order (*7*). The band of SiO_2 at 974 cm^{-1} is assigned to the O–H bending vibration of the silanol group (*8*). As shown in Fig. 1,

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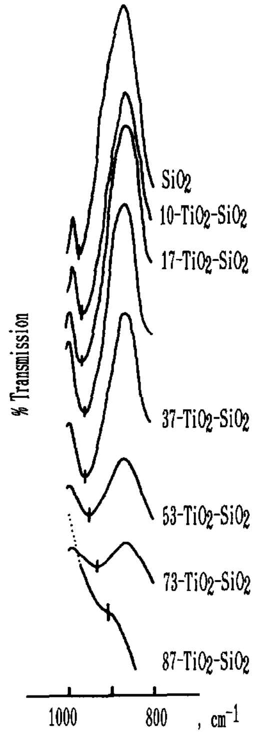
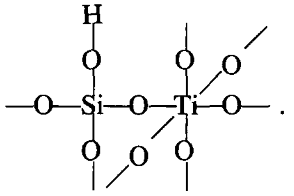


FIG. 1. Infrared band shift of silanol bending vibration in TiO_2–SiO_2 series catalysts.

however, the bending vibration band was shifted to a lower frequency and became broader with increasing TiO_2 content. This means that the O–H bond of the silanol group was weakened by adding TiO_2 component to SiO_2 and by withdrawing electrons in the O–H bond due to the interaction between them as the following model:



Tanabe *et al.* suggested similar model regarding the acidity generation of binary oxides (*9*). For 87–TiO_2–SiO_2, a shoulder band at 925 cm^{-1} appeared, while for 92–TiO_2–SiO_2 the bending band of the silanol group was not observed due to the high content of TiO_2. It is expected that the weakness of the O–H bond does influence both acidity and acid catalytic activity of the catalyst.

Catalytic activities for both 2-propanol dehydration and cumene dealkylation reactions and acidity of catalysts are listed in Table 1, together with the bending fre-

TABLE 1

Surface Area, Acidity, Bending Frequency, and Catalytic Activity of TiO_2–SiO_2 Series Catalysts

Catalyst	Surface area (m^2/g)	Acidity ($\mu eq/m^2$)	Bending frequency (cm^{-1})	Catalytic Activity ($\times 10^{-3}$ $\mu mol/m^2$)	
				Cumene dealkylation	2-Propanol dehydration
SiO_2	361.9	0	974	0	0
10–TiO_2–SiO_2	550.7	0.58	968	57	400
17–TiO_2–SiO_2	518.6	0.73	964	65	503
23–TiO_2–SiO_2	487.0	0.81	962	73	587
37–TiO_2–SiO_2	485.9	1.24	960	93	652
53–TiO_2–SiO_2	372.7	2.15	956	182	821
73–TiO_2–SiO_2	338.5	3.55	939	449	1,503
87–TiO_2–SiO_2	156.1	3.20	925	436	653
92–TiO_2–SiO_2	134.5	2.97	—	379	364
TiO_2	96.6	1.31	—	114	83

quency of the silanol group, and acidity and surface area of catalyst. Acidity of the catalyst was determined by the *n*-butylamine titration method, using Hammett indicator, dicinnamalacetone having a p*Ka* value of −3.0 (*10*). The IR spectra of pyridine adsorbed on the catalysts were examined. Both the pyridinium ion band at 1543 cm^{-1} and the coordinated pyridine band at 1445 cm^{-1} were found with all binary oxide catalysts evacuated at 400°C for 1 hr, indicating the presence of both Brønsted and Lewis acid sites. It is clear that the addition of TiO_2 to SiO_2 causes the increase of acidity and the shift of the bending band of the silanol groups to a lower frequency over the range of 0–73% TiO_2. Consequently, catalytic activities for both reactions increased in relation to the increase of acidity and the band shift to a lower frequency. It seems likely that the addition of TiO_2 to SiO_2 produces new acid sites by weakening the O–H bond of the silanol group. The correlation between catalytic activity and acidity holds better for cumene dealkylation than for 2-propanol dehydration, indicating that the acid strength required to catalyze an acid reaction is different depending on the type of reactions. In fact, it has been known that 2-propanol dehydration takes place very readily on weak acid sites, while cumene dealkylation does so on relatively moderate acid sites (*11*). As seen in Table 1, the catalytic activity for cumene dealkylation, in spite of a higher reaction temperature, is much lower than that for 2-propanol dehydration.

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