914 © 1992 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **65**, 914—916 (1992) [Vol. 65, No. 3

Properties of Acid Sites on TiO_2-SiO_2 and TiO_2-Al_2O_3 Mixed Oxides Measured by Infrared Spectroscopy

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(Received August 28, 1991)

Synopsis. Both Lewis and Brönsted acid sites were found on the surface of TiO_2–SiO_2 mixed oxide, though no Brönsted acid sites were detected on the surface of pure TiO_2 and SiO_2. While on the surface of TiO_2–Al_2O_3 mixed oxide, no Brönsted acid sites were generated. The rate of isomerization of 1-butene was found to be enhanced on the Brönsted acid sites formed on the TiO_2–SiO_2 mixed oxide.

It has been widely accepted[1] that the generation of new and strong acid sites on mixing oxides is ascribed to a charge imbalance, localized on M_1–O–M_2 bonds formed in the mixed oxide, where M_1 is the host metal ions and M_2 the mixed metal ions. Recently, the present author has developed a new idea[2] that new and strong acid sites will be generated on finely-divided pure metal oxides, and has demonstrated an increase in the highest acid strength of TiO_2 paprticles as the particle sizes decreased. In this work the properties of acid sites on the binary oxides, containing finely-divided TiO_2, were measured by infrared spectroscopy for pyridine adsorbed on them.

Experimental

Preparation of Mixed Oxides. The mixed oxides employed were TiO_2–SiO_2 and TiO_2–Al_2O_3, which were prepared by simultaneous hydrolysis of the mixed solution of Ti tetraiso-propoxide and ethyl silicate or Al triiso-propoxide dissolved in *s*-propyl alcohol, respectively. The hydrolysis was carried out at 353 K using an excess amount of distilled water. The precipitates obtained were evaporated and dried in an oven at 383 K, followed by calcination at 773 K for 3 h. The mixed metal oxides were formed so that the molar ratios of both TiO_2/SiO_2 and TiO_2/Al_2O_3 are to be unity. The BET surface areas were estimated by the adsorption of nitrogen at 77 K.

The single metal oxides such as TiO_2, SiO_2, and Al_2O_3 were prepared by hydrolysis of the corresponding metal alkoxide solutions of Ti isopropoxide, ethyl silicate and Al isopropoxide dissolved in *s*-propyl alcohol, respectively. The precipitates were dried and calcined in the similar manner as employed in the preparation of the mixed oxides.

Acid Amounts on Mixed Oxides. The acid amounts on the mixed oxides were calculated from the amounts of ammonia adsorbed at 423 K, using 0.25 g of the sample powders treated in following O_2 at 573 K for 1 h. A certain amount of ammonia was iteratively injected into carrier gas (He), which is introduced onto the sample powders until no more adsorption of ammonia is observed at 423 K. Since ammonia adsorbed at the temperatures lower than 423 K is ascribed to the ammonia physisorbed on the oxides, the acid amounts were obtained from the amounts of ammonia chemisorbed at 423 K. The highest acid strengths of the mixed and the single oxides were determined by observation of the changes in color of the indicators dissolved in benzene.[3]

Infrared Spectra of Pyridine Adsorbed on Mixed Oxides. In order to reveal the type of acid sites on the mixed oxides, an infrared spectrometer (JASCO 7300FT) was employed for pyridine adsorbed on the mixed oxides at various temperatures. The sample powder was pressed into a disc which was treated in flowing O_2 at 573 K prior to the adsorption of pyridine at 423 K. The infrared spectrum of adsorbed pyridine was monitored while the sample disc was evacuated up to 523 K.

Isomerization of 1-Butene on Mixed Oxides. Catalytic activities of the mixed oxides for the isomerization of 1-butene were measured in order to characterize the acid sites generated on the mixed oxides. The reaction was carried out with a closed circulating reactor made of glass, in which 0.2 g of the mixed or the pure oxides were packed, at the temperatures ranging from 393 to 613 K. The initial pressure of 1-butene introduced to the catalysts was 110 Torr (14.7×10^3 Pa) and the products were *cis*- and *trans*-2-butene, analyzed by gas chromatography using a column packed with Uniport C, containing 9% of glutaronitrile and 21% of propyrene carbonate.

Results and Discussion

In Table 1 are given the BET surface areas, the highest acid strengths and the acid amounts measured by ammonia adsorption of all the sample powders examined here. The highest acid strengths of the mixed oxides are higher than those of the constituent pure oxides because of the presence of small size TiO_2 crystallites in the mixed oxides. Although the crystalline size of the pure TiO_2 prepared here is estimated to be 100 Å by measuring an X-ray line broadening at $2\theta=25.3$ and confirmed by TEM (transmission electron microscope),[2] those of TiO_2

Table 1. The BET Surface Areas, Acid Properties, and Catalytic Activities of the Sample Studied

Sample	BET surface area	The highest acid strength	Acid amount	Isomerization rate[a]
	$m^2\ g^{-1}$	(H_0)	$\mu mol\ m^{-2}$	$\mu mol\ min^{-1}\ m^{-2}$
TiO_2–SiO_2	326	−5.6	2.64	7.76
TiO_2–Al_2O_3	224	−5.6	1.80	0.34
TiO_2	120	−3.0	3.14	1.36
SiO_2	665	+3.3	0.62	0
Al_2O_3	184	−3.0	1.33	0.15

a) The reaction was carried out at 453 K.

in the mixed oxides are too small to be detected by an X-ray diffraction.

The acid amounts on the unit surface area of TiO_2–Al_2O_3 are rather less than the arithmetical mean of those of pure TiO_2 and Al_2O_3. This seems to indicate that Al_2O_3 is more concentrated on the surface vicinities of the TiO_2–Al_2O_3 mixed particles.[4] The acid amounts on TiO_2–SiO_2 are, however, a little larger than the arithmetical mean of those on pure TiO_2 and SiO_2, suggesting the generation of new acid sites on this mixed oxide.

The infrared spectra of pyridine chemisorbed either on SiO_2, TiO_2 or Al_2O_3 at elevated temperatures are given in Fig. 1. Three absorption peaks were observed at 1598, 1492, and 1450 cm^{-1}, when pyridine was adsorbed on SiO_2 at 423 K. All the absorption peaks observed are assigned to pyridine weakly bounded to the OH groups on the SiO_2 surface[5] and disappeared when heated up to 523 K. Pyridine adsorbed on TiO_2 at 423 K showed four absorption peaks at 1609, 1575, 1493, and 1448 cm^{-1}, all attributed to pyridine adsorbed on the Lewis acid sites.[5] On Al_2O_3, four peaks assigned to pyridine adsorbed on the Lewis acid sites and a peak, at 1595 cm^{-1}, assigned to pyridine bounded to the OH groups on the Al_2O_3 surface were detected. Accordingly, the Brönsted acid sites were detected neither on the present SiO_2, TiO_2, nor Al_2O_3 by measuring the infrared spectrum of adsorbed pyridine.

For pyridine adsorbed on the TiO_2–Al_2O_3 mixed oxide at 423 K four absorption peaks were observed at 1612, 1576, 1491, and 1450 cm^{-1}, being assigned to pyridine adsorbed on the Lewis acid sites on the mixed oxide.(see Fig. 2) As could be seen in Fig. 2, the peak at 1612 cm^{-1} is prone to be composed of two absorption peaks centered at 1609 and 1620 cm^{-1}, assigned to pyridine adsorbed on the Lewis acid sites formed on TiO_2 and Al_2O_3 in the mixed oxide, respectively. This suggests that the acid sites on the TiO_2–Al_2O_3 mixed oxide are composed of the Lewis acid sites on pure TiO_2 and Al_2O_3, leading to the conclusion that the increase in the highest acid strength of this mixed oxide is caused by the formation of the tiny size TiO_2 crystallites in Al_2O_3 matrices. No interaction between TiO_2 and Al_2O_3 crystallites seems to emerge in the TiO_2–Al_2O_3 mixed oxides prepared in this work. The acid properties of the mixed oxides are concluded to be preferentialy determined by the size of TiO_2 crystallites, dispersed in Al_2O_3. The absorption peaks assigned to pyridine chemisorbed on the Brönsted acid sites were observed at 1636 and 1545 cm^{-1}, when pyridine was introduced on the TiO_2–SiO_2 mixed oxide. The generation of the Brönsted acid sites suggests the presence of some interactions between TiO_2 and SiO_2 particles in the TiO_2–SiO_2, since no Brönsted acid sites are detected on the pure TiO_2 and SiO_2. These interactions may originate in the Ti–O–Si

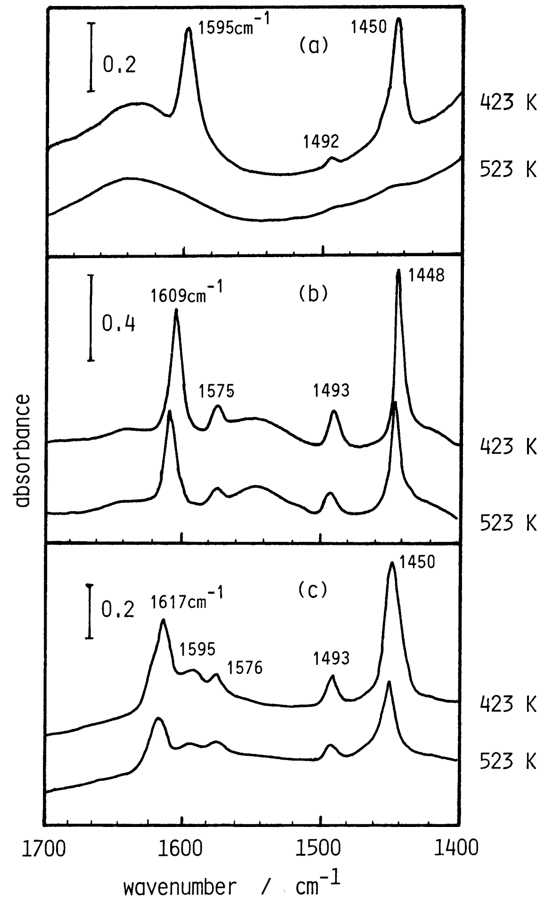

Fig. 1. Infrared spectra of pyridine adsorbed on single metal oxides at elevated temperatures. (a), SiO_2; (b), TiO_2; (c), Al_2O_3.

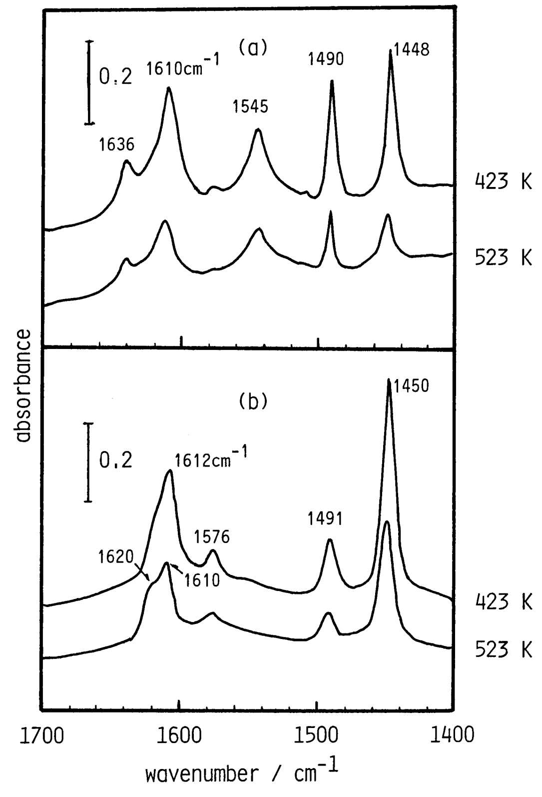

Fig. 2. Infrared spectra of pyridine adsorbed on mixed oxides at elevated temperatures. (a), TiO_2–SiO_2; (b), TiO_2–Al_2O_3.

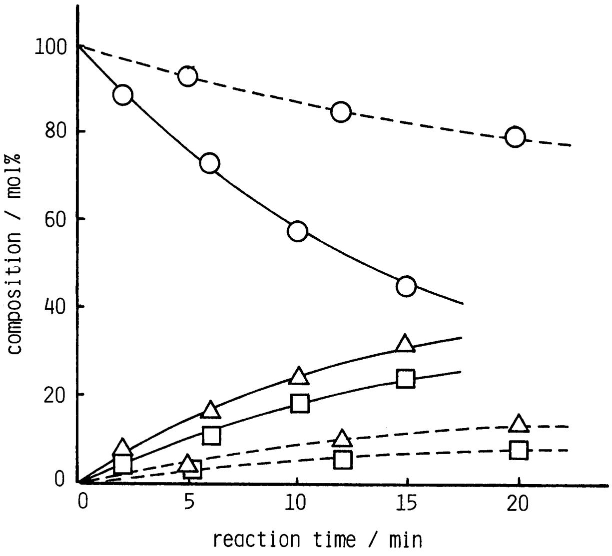

Fig. 3. Isomerization of 1-butene on TiO_2-SiO_2 (—) at 413 K and on TiO_2-Al_2O_3 (----) at 453 K. (○), 1-butene; (△), *cis*-2-butene; (□), *trans*-2-butene.

bonds, probably formed at the fringes of the small TiO_2 particles trapped in SiO_2 matrices. The Ti–O–Si bonds thus produced will generate the Brönsted acid sites in the manner as elucidated by Tanabe.[6] Consequently, the Brönsted acid sities were created on the surface of the TiO_2–SiO_2 mixed oxide, but not on the TiO_2–Al_2O_3, where only the Lewis acid sites were still remained.

In order to understand the differences in the properties of acid sites on the TiO_2–Al_2O_3 and those on the TiO_2–SiO_2, isomerization of 1-butene to *cis*- and *trans*-2-butene was measured at the temperatures ranging from 393 to 613 K. The results obtained at 453 K on the TiO_2–Al_2O_3 and at 413 K on the TiO_2–SiO_2 are shown in Fig. 3. The isomerization rates calculated are also given in Table 1, together with those obtained on the pure TiO_2, Al_2O_3, and SiO_2. The rates observed on these pure oxides are ordered in the sequence of $TiO_2 > Al_2O_3 \gg SiO_2$, where almost no isomerization takes place on the pure SiO_2. The rate on the TiO_2–Al_2O_3 was a little lower than the arithmetical mean of that on the pure TiO_2 and Al_2O_3 because of less concentrated TiO_2 on the surface vicinities of this mixed oxide particles, as noted above. The rate on the TiO_2–SiO_2 mixed oxide was, however, one order of magnitude higher than the arithmetical mean of that on the pure TiO_2 and SiO_2. Since the Brönsted acid sites are newly generated on the TiO_2–SiO_2, the significantly enhanced activity is ascribed to the Brönsted acid sites, which were not detected on the pure TiO_2 and SiO_2. Note that no basic sites are on the surface of both the mixed and pure oxides examined in this work, since the ratio of *cis* and *trans*-2-butene formed was always between 1 and 2. The ratio on the basic sites has been considered to be much larger than the values measured in the present work.[7]

Conclusions

The following conclusions were obtained in this work;

(1) New acid sites classified to the Brönsted acid sites were created on the TiO_2–SiO_2 mixed oxide but not on the TiO_2–Al_2O_3 mixed oxide, where only the Lewis acid sites originated in the pure TiO_2 and Al_2O_3 were recognized.

(2) The properties of acid sites on the TiO_2–Al_2O_3 mixed oxide are controlled by those on the pure TiO_2 and Al_2O_3. While on the TiO_2–SiO_2 mixed oxide, the Brönsted acid sites generated on the Ti–O–Si bonds play an important role.

(3) The isomerization of 1-butene on the Brönsted acid sites generated on the TiO_2–SiO_2 were significantly enhanced.

The author wishes to thank Professor Akifumi Ueno at Toyohashi University of Technology for his helpful discussions.

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