Effects of Surface Fluorination on Catalytic Activities and Surface Compositions of TiO_2-Al_2O_3 and TiO_2-SiO_2-Al_2O_3

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Studies showed that the ternary oxide having the atomic ratio of Ti/Si/Al=47.5/47.5/5 exhibited a high catalytic activity for cumene cracking after a surface fluorination using 1 wt% hydrofluoric acid. The catalytic activity for CH_3OH conversion into olefins was highly dependent on the preparation method. That is, the ternary mixed oxide promoted olefin formation slightly when the mixed oxide was prepared only by coprecipitation. Surface treatment, using gaseous CF_3Cl was effective in enhancing catalytic activity. Although the binary oxide, TiO_2-Al_2O_3, itself, was catalytically inactive for olefin formation, TiO_2-Al_2O_3 prepared by coprecipitation became active after the treatment using CF_3Cl. Such an enhancement was found also for the ternary oxide, TiO_2-SiO_2-Al_2O_3, and is ascribable to increased acid strength, as determined by NH_3 adsorptions at various temperatures. The XPS measurements showed that F atoms introduced into mixed metal oxides by the fluorination using CF_3Cl, selectively combined with Al atoms on the mixed oxides prepared by coprecipitation. The XPS measurements of the mixed oxides before and after fluorination using CF_3Cl showed that the coprecipitation preparation is more preferable than the impregnation method in maintaining surface composition during fluorination.

Recently TiO_2-SiO_2[1] and TiO_2-Al_2O_3[2] have been recognized as fairly strong solid acids, like SiO_2-Al_2O_3. Hence, the formation of relatively strong acid sites in the ternary oxide containing TiO_2, SiO_2, and Al_2O_3 seems promising. Furthermore, since the solid acidities of SiO_2-Al_2O_3[3,4] and TiO_2-SiO_2 are enhanced by a surface fluorination, it may be possible to obtain a stronger solid acid by surface fluorination of TiO_2-Al_2O_3 and TiO_2-SiO_2-Al_2O_3.

Since through mixing of the component oxides is very difficult, especially for the ternary oxide, the preparation method may greatly affect the solid acidity and the catalytic activity. Additionally, the method and conditions of the surface fluorination may also have a considerable effect on them.

In general, surface fluorination has been carried out by using aqueous solutions of HF,[5,6] NH_4F,[7] or NH_4HF_2.[8] Recently, gaseous fluorination using fluorohydrocarbons such as CF_3Cl and CF_2ClCF_2Cl has also been found to be effective to increase solid acidity and catalytic activities for CH_3OH conversion into olefins by Al_2O_3-Cr_2O_3,[9] and for paraffin conversion by Al_2O_3.[10]

In this work, the catalytic activities of TiO_2-Al_2O_3 and TiO_2-SiO_2-Al_2O_3 were studied with an emphasis on the effects of the preparation method and surface fluorination. The surface composition and solid acidity, which are closely related to the catalytic activities, were also examined. For comparison, the effect of surface fluorination on the catalytic activities and the surface compositions of TiO_2, Al_2O_3, SiO_2-Al_2O_3, and SiO_2-TiO_2 were investigated. Cumene cracking was selected because it is a typical reaction catalyzed by solid acids, even relatively weak ones.[11] To elucidate the nature of the strong acid sites, the CH_3OH conversion into olefins was adopted because it has been clearly established that the reaction is promoted only by fairly strong Brönsted acid sites.[12] Finally, the cyclopropane isomerization was carried out to elucidate the acid property of sites on the solid surface.

Experimental

Catalysts. Binary oxides of TiO_2 and Al_2O_3 with various atomic ratios of Ti/Al such as 9/1, 5/5, 1/9 were used as catalysts. For the TiO_2-SiO_2 catalyst, a mixed oxide of an atomic ratio of Ti/Si=1 was used as a representative species, since it has been previously determined that this ratio showed the largest acidity.[5] A typical solid acid catalyst, SiO_2-Al_2O_3 (Nikki Chemical Co. N-631L, Si/Al(atomic ratio)=85/15) was used to evaluate catalytic activities of other oxides by comparison of its catalytic activity. To determine the effect of a small Al component addition to the TiO_2-SiO_2(Ti/Si=1), the catalytic activity of the ternary oxide, TiO_2-SiO_2-Al_2O_3, with the Ti/Si/Al atomic ratio of 47.5/47.5/5 was examined.

For preparations of the single and mixed oxides, titanium tetraisopropoxide, aluminum isopropoxide or nitrate, and ethyl silicate were used as starting materials. The single oxides (TiO_2 and Al_2O_3), and TiO_2-SiO_2 were prepared by addition of aqueous solutions of the respective components to water with vigorous stirring, followed by neutralization with 28% aqueous ammonia. The TiO_2-Al_2O_3(TiO_2-Al_2O_3(Cop)) was prepared by addition of 2-propanol, containing definite amounts of alkoxides of Al and Ti, to dilute nitric acid to prevent the formation of deposits during the addition, and to ensure sufficient mixing of the components. One ternary oxide sample (TiO_2-SiO_2-Al_2O_3(Cop)) was prepared from the solution containing ethyl silicate and alkoxides of Ti and Al using the same procedure as that for the binary oxide, TiO_2-Al_2O_3(Cop).

To examine the effect of the preparation method, the mixed oxides were also prepared by impregnation. For the binary oxide, TiO_2-Al_2O_3(Imp), the impregnation was carried out by addition of TiO_2, which was prepared from alkoxide and heat-treated at 500 °C, to the aqueous solution of aluminum nitrate, followed by evaporation to dryness. For the ternary oxide, TiO_2-SiO_2-Al_2O_3(Imp), the impregnation was done in the same way by addition of TiO_2-SiO_2(Ti/Si=1), prepared by coprecipitation from titanium alkoxide and ethyl silicate, to the solution of aluminum nitrate.

All the single and mixed oxides were dried at 120 °C for 24 h and then heat-treated at 500 °C, unless otherwise noted, for 3 h before their use as a catalyst, or before surface fluorination.

Reagents. The CF_3Cl was supplied by the Mitsui Fluorochemical Co., with purity higher than 99.9%. All other reagents were commercial products of the highest grade, and were used without further purification.

Surface Treatment. The oxide surfaces were treated with hydrofluoric acid of different concentrations(0.05—10 wt%), or gaseous CF_3Cl. The treatment with the acid was carried out by immersing the oxides (*ca.* 10 g) in a solution (*ca.* 30 ml) at room temperature for 48 h, followed by evaporation to dryness at 120 °C and heat-treatment at 500 °C for 3 h. The treatment with CF_3Cl was carried out in a reactor at 450 °C immediately before use as catalyst.

Reaction Procedure. The cyclopropane isomerization and the CH_3OH conversion into olefins (abbreviated as MTG) were carried out in a pulse reactor using He as a diluent at 150 or 250 °C, and 400 °C, respectively. The pulse size was about 1.0 µl (for CH_3OH) or 1.1 µl (for cyclopropane), and the weight of catalyst was kept constant at 30 mg (MTG) or 50 mg (cyclopropane isomerization).

The product gas of the cyclopropane isomerization was analyzed by gas chromatography using a column packed with Porapack N at 100 °C. For MTG, the pulse reactor was connected with a modified gas-chromatographic analyzer. The product gas of the MTG, including CO and CH_4, was first condensed at about −196 °C in a 3 m column packed with Tenax GC. Then the condensed products were allowed to evaporate by removal of the liquid nitrogen trap, followed by heat-treatment up to 150 °C. The evaporated gas was passed through TCD, and the composition of the product was analyzed.

The cumene cracking was carried out under ordinary pressure using a conventional flow reactor. The products were analyzed by gas chromatography using a column packed with DC 550 supported on Chromosorb (15 wt%).

Determinations of Surface Properties. Surface areas were determined by applying the BET equation for the adsorption isotherm of N_2 at −196 °C. Surface acidities were measured by the amounts of NH_3 adsorbed at different temperatures. The Brönsted and Lewis acidity was examined by observing the infrared absorption spectra of pyridine adsorbed on oxide samples which were fabricated into discs under a pressure of *ca.* 500 kg cm^{-2}.

Determinations of Surface Composition and Bonding. The compositions in the surface layer were determined by XPS, using a Shimadzu ESCA-750 analyzer. In this determination, the spectra were measured with Mg *Kα* radiation; the base pressure of the spectrometer was usually below 10^{-7} Torr (1 Torr≈133.322 Pa) during the experiments. The peak positions, given by their maxima, were measured with respect to the position of C1s, for which the value of the binding energy was taken as 285 ev. The surface compositions were calculated from the area of the respective peaks (*i.e.*, the maxima in the counting rate) on the basis of photoionization cross sections at 1254 ev, in units of the C1s cross section of 22200 barns.[13] The errors inherent in such a determination are generally 10—30% of the observed value.

Results and Discussion

Catalytic Activities for Cumene Cracking before and after Fluorination Using Hydrofluoric Acid. Similar to TiO_2 and Al_2O_3, the mixed oxides with various Ti/Al atomic ratios, which were prepared from $Al(NO_3)_3$ and titanium tetraisopropoxide by coprecipitation, showed little catalytic activity before fluorination. After fluorination using 1 wt% hydrofluoric acid, only TiO_2-Al_2O_3(Ti/Al=9/1) showed a rather high catalytic activity; the concentration of hydrofluoric acid was found to be optimum at 1 wt% for enhancement of the catalytic activity. However, even the catalytic activity of the TiO_2-Al_2O_3 treated with the hydrofluoric acid at this optimum concentration (1 wt%) was less than that of the component oxide, TiO_2, fluorinated with 1 wt% hydrofluoric acid. Furthermore, the catalytic activity of the fluorinated TiO_2-Al_2O_3(Ti/Al=9/1) was far less than that of the fluorinated TiO_2-SiO_2(Ti/Si=1).[5]

Since cumene cracking can be promoted even by relatively weak Brönsted acid sites,[11] the catalytic activity for cumene cracking may be the measure of the total amount of Brönsted acid sites, including weak ones. Thus, the result indicates that the amount of total Brönsted acid sites formed on TiO_2-Al_2O_3 after fluorination may be less than that on the fluorinated TiO_2 or fluorinated TiO_2-SiO_2.

A catalyst which was more active than the fluorinated TiO_2 or fluorinated TiO_2-SiO_2 was obtained by addition of relatively small amounts of Al_2O_3 to TiO_2-SiO_2. Thus, TiO_2-SiO_2-Al_2O_3(Cop) which contained 5 atom% of Al showed higher initial catalytic activity than that of the fluorinated TiO_2 or fluorinated TiO_2-SiO_2 even before fluorination (Fig. 1). The catalytic activity of the ternary oxide was also higher than that of SiO_2-Al_2O_3 as is shown in Fig. 1. Hence, the higher catalytic activity of the ternary oxide(Cop) may be due to the coexistence of the three components(Ti, Si, and Al) itself. With surface fluorination of the ternary oxide (47.5/47.5/5)(Cop) using 1wt% hydrofluoric acid, both the initial catalytic activity and the activity maintenance were considerably increased. On the other hand, initial catalytic activity of the ternary oxide with the same atomic ratio, prepared by impregnation was noticeably lower than that of the ternary oxide(Cop). Furthermore, the activity of the fluorinated ternary oxide(Imp) decreased significantly with process time (Fig. 1); this evidence indicates the large effect of the preparation method on the catalytic activity of the mixed oxide.

Catalytic Activity for CH_3OH Conversion. Table 1 shows the catalytic activity for the MTG by various oxides, before and after fluorination. Before fluorination, ternary oxide(Cop) promoted the formation of a small amount of propene, although ternary oxide (Imp) promoted only the formation of dimethyl ether, which can be activated even by relatively weak acid

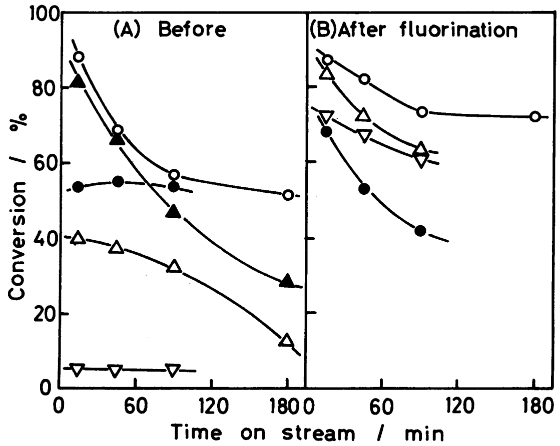

Fig. 1. Catalytic activities for cumene cracking of metal oxides before and after fluorination.
○: TiO_2-SiO_2-Al_2O_3(47.5/47.5/5)(Cop); ●: TiO_2-SiO_2-Al_2O_3(47.5/47.5/5)(Imp); △: TiO_2-SiO_2(1/1)-(Cop); ▲: SiO_2-Al_2O_3(85/15)(N-631L); ▽: TiO_2. Reaction temperature; 350 °C, W/F: 51.6 g h mol^{-1}.

Table 1. Catalytic activities of metal oxides for CH_3OH conversion

Catalyst[a)]	Yield/mol%[b)]					
	CO	CH_4	$CH_2=CH_2$	$CH_3CH=CH_2$	Butene	CH_3OCH_3
TiO_2-SiO_2-Al_2O_3 (Cop)						
Before fluorination	0	13.6	Trace	3.3	0	48.8
Treated with CF_3Cl	0	13.4	2.2	18.4	0.4	38.9
Treated with HF acid	0	33.6	4.3	0	0	58.8
TiO_2-SiO_2-Al_2O_3 (Imp)[c)] treated with CF_3Cl	0	8.3	2.8	0	0.8	88.0
TiO_2-Al_2O_3 (Ti/Al=9/1) treated with CF_3Cl	5.2	19.0	21.4	5.2	0	42.9
SiO_2-Al_2O_3						
Before fluorination	0	0	Trace	Trace	0	76.1
Treated with CF_3Cl	0	0	5.1	11.4	0	66.8
TiO_2-SiO_2 (Ti/Si=1)						
Before fluorination	6.3	36.1	0	0	0	52.3
Treated with CF_3Cl	0	13.9	1.4	0	2.1	80.4
Al_2O_3 treated with CF_3Cl	0	0	3.6	7.9	Trace	55.4
TiO_2 treated with CF_3Cl	0	6.8	Trace	0	Trace	0

a) TiO_2 and Al_2O_3 were heat-treated at 600 °C (and the others at 500 °C) for 3 h before use as catalyst. b) These data were measured for the third pulse. c) Untreated TiO_2-SiO_2-Al_2O_3 showed little catalytic activity for CH_3OH conversion.

sites.[12)] After fluorination, all oxides, except TiO_2, exhibited some degree of catalytic activity. In particular, mixed oxides containing Al and prepared by coprecipitation, such as TiO_2-Al_2O_3(Cop) and TiO_2-SiO_2-Al_2O_3(Cop), showed high activity after fluorination using CF_3Cl. The ternary oxide fluorinated with hydrofluoric acid, however, was significantly less active. Since MTG is known to be promoted only by strong acid sites,[12)] these facts suggest that fluorination using CF_3Cl may be effective, but that using hydrofluoric acid is almost completely ineffective in the formation of strong acid sites.

Although TiO_2 was markedly active as a catalyst for cumene cracking after fluorination using hydrofluoric acid, it was quite inactive for the MTG after fluorination using the acid or CF_3Cl. This is plausibly ascribable to the low acid strength of the sites formed on TiO_2 by treatment with hydrofluoric acid, even though the number of these relatively weak acid sites might be fairly large.

TiO_2 fluorinated using CF_3Cl could not promote even the formation of dimethyl ether, in contrast the fluorinated Al_2O_3 appreciably increased formation of olefins besides dimethyl ether. Thus, the Al component seems important for the formation of acid sites strong enough to promote the MTG.

Acid Properties of Mixed Oxides. Infrared studies of the adsorption of pyridine were performed on TiO_2-Al_2O_3(9/1) (Cop) and TiO_2-SiO_2-Al_2O_3(47.5/47.5/5) (Cop) or (Imp) to know about the acid properties. After evacuation at 300 °C for 2 h, the sample was left in contact with 5 Torr of pyridine at room temperature for 0.5 h, and then further evacuated at 170 °C for 1 h.

TiO_2-Al_2O_3(9/1): This mixed oxide gave only bands at about 1600, 1580, 1490, and 1440 cm^{-1} which were all attributable to pyridine on Lewis acid sites.[14)] Although the band at 1540 cm^{-1} due to pyridinium ion[14)] was scarcely observable for the evacuated samples before and after fluorination, it became clearer after sample contact with H_2O vapor(5 Torr) for 1 min. Together with the band at about 1640 cm^{-1}, these bands indicate that Brönsted acid sites were abundantly formed on the fluorinated mixed oxide by interaction of H_2O with the surface.

Table 2. Catalytic activities for cyclopropane isomerization

Catalyst	Reaction temperature	Conversion[a)]
	°C	%
TiO_2-Al_2O_3 (Ti/Al=9/1)		
Before fluorination	150	1.0
	250	15.5
	150	19.2
Fluorinated with 1 wt% HF acid	250	93.0

a) The conversion was calculated from the result of the first pulse (for 150 °C reaction) or the third pulse (for 250 °C reaction).

The catalytic activities of mixed oxides for cyclopropane isomerization (150 and 250 °C), which is promoted not by Lewis, but by Brönsted acid sites,[15)] were remarkably increased by surface fluorination, as is shown in Table 2. This fact further verified the formation of Brönsted acid sites after surface fluorination.

TiO_2-SiO_2-Al_2O_3(47.5/47.5/5): Like the spectrum for TiO_2-Al_2O_3 described above, that obtained for the ternary oxide prepared by impregnation showed the presence of only Lewis acid sites. After surface fluorination using hydrofluoric acid, a weak band specific to pyridinium ion appeared at 1540^{-1}.

On the other hand, the spectrum for the ternary oxide prepared by coprecipitation showed the bands at 1550 and 1640^{-1} due to Brönsted acid sites in addition to those due to Lewis acid sites, even before surface fluorination. The formation of the Brönsted acid sites on the unfluorinated ternary oxide may have resulted from sufficient mixing of the component metal atoms (or ions); the Brönsted acid sites may function as active sites not only for the cumene cracking but also for MTG.

NH_3 Adsorption: In order to know the strengths and numbers of acid sites, adsorption of NH_3 on various oxides, including SiO_2-Al_2O_3, was carried out at temperatures from 100 °C to 500 °C.

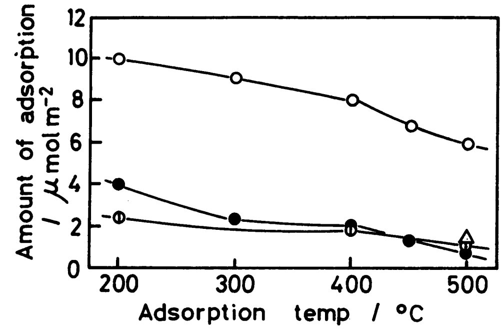

Fig. 2. NH_3 adsorptions at various temperatures. ●: TiO_2-SiO_2-Al_2O_3(47.5/47.5/5)(Cop); before treatment; ○: TiO_2-SiO_2-Al_2O_3(47.5/47.5/5)(Cop) treated with CF_3Cl; △: TiO_2-SiO_2-Al_2O_3(47.5/47.5/5)-(Cop) treated with 1 wt% hydrofluoric acid; ○: SiO_2-Al_2O_3(85/15)(N-631L).

As is shown in Fig. 2, the ternary oxide prepared by coprecipitation showed a notably high adsorptive activity for NH_3 after the surface fluorination using CF_3Cl. In particular, the amount of adsorption on the fluorinated ternary oxide at 500 °C was about 6 times that of the typical strong solid acid catalyst, SiO_2-Al_2O_3, and was higher than Al_2O_3-Cr_2O_3 fluorinated with CF_3Cl, which has been reported to be a strong acid catalyst for MTG.[9] The amount of adsorption at 500 °C on the ternary oxide(Cop), fluorinated using hydrofluoric acid, was only about the same as that on SiO_2-Al_2O_3. These facts support the suggestions that remarkably strong acid sites may be formed on the ternary oxide(Cop) treated with CF_3Cl, and that surface fluorination using CF_3Cl is far more effective in strengthening solid acidity than that using hydrofluoric acid.

Surface Compositions. Table 3 shows the surface compositions which were examined by recording the XPS spectra. As the results show, the surface composition generally differs from the designed one to a considerable extent. In particular, the Al component tends to concentrate in the surface layer, even for mixed oxides prepared by coprecipitation. Such a tendency has also been observed for the binary oxides, TiO_2-Al_2O_3, which is coprecipitated from the solution containing equimolar aluminum nitrate and

Table 3. Surface composition of various oxides

Oxide	surface composition/atom%[a]					
	O	F	Cl	Ti	Si	Al
Before fluorination						
TiO_2	74.1			25.9		
Al_2O_3	65.5					34.5
TiO_2-Al_2O_3	72.0			20.1		7.9
(9/1, Cop)				(7.2)		(2.8)
TiO_2-SiO_2	77.8			15.8	4.4	
(9/1, Cop)				(7.8)	(2.2)	
SiO_2-Al_2O_3	67.4				28.4	4.2
(8.5/1.5)					(8.7)	(1.3)
TiO_2-SiO_2-Al_2O_3	70.6			8.6	16.8	4.0
(47.5/47.5/5, Cop)				(2.9)	(5.7)	(1.4)
TiO_2-SiO_2-Al_2O_3	77.0			10.1	8.4	4.5
(47.5/47.5/5, Imp)				(4.4)	(3.6)	(2.0)
After fluorination						
TiO_2	67.5	8.4	1.4	22.7		
Al_2O_3	35.4	37.5	0			27.1
TiO_2-Al_2O_3	22.0	56.7	0	6.2		15.1
(9/1, Cop)				(2.9)		(7.1)
TiO_2-SiO_2	59.8	11.5	1.5	27.2	Trace	
(9/1, Cop)				(10.0)		
SiO_2-Al_2O_3	50.9	19.3	0		24.8	5.0
(8.5/1.5)					(8.3)	(1.7)
TiO_2-SiO_2-Al_2O_3	64.7	5.2	0	8.1	17.2	4.8
(47.5/47.5/5, Cop)				(2.7)	(5.7)	(1.6)
TiO_2-SiO_2-Al_2O_3	60.5	11.7	0	6.6	12.4	8.8
(47.5/47.5/5, Cop)				(2.3)	(4.5)	(3.2)
(HF-treated)						
TiO_2-SiO_2-Al_2O_3	61.8	20.5	0	17.7	Trace	Trace
(47.5/47.5/5, Imp)				(10.0)		

a) The numbers in parentheses indidate the atomic ratio of Ti, Si, and Al components.

ethyl silicate.[16] The higher concentration of Al component in the surface layer may possibly be due to a difference in the pH value for the precipitation as hydroxides. That is, for the precipitation of Al^{3+} as $Al(OH)_3$, the solution must be more alkaline than for Ti^{4+} and Si^{4+}; thus Al^{3+} tends to deposit as a hydroxide on the surface of the hydroxides of Ti and Si, which have already formed in the neutralization using aqueous ammonia.

Although the Al content in the surface layer of the fresh ternary oxide(Cop) is less than that in the fresh ternary oxide(Imp), the difference is relatively small. However, for the samples fluorinated with CF_3Cl, the surface composition greatly differs depending on the preparation methods. That is, during fluorination, the Al and Si components in the ternary oxide prepared by impregnation were lost largely from the surface layer, resulting in a remarkable increase of Ti content in the surface layer. On the other hand, the surface composition of the ternary oxide prepared by coprecipitation was scarcely changed by surface fluorination.

Similarly, the surface composition of SiO_2-Al_2O_3 was not appreciably changed by surface fluorination using CF_3Cl; The Si component in TiO_2-SiO_2 was lost mostly during the surface fluorination. Nevertheless, the mixed oxides were prepared by coprecipitation.

These results suggest that Al atoms may firmly combine with F atoms, especially in preference to Si atoms, and thus prevent the formation of volatile SiF_4. However, such Al atom behavior may be displayed only when the Al atoms are sufficiently close to Si atoms, so that the effect of Al component on the retention of Si component was fully exhibited in the mixed oxide prepared by coprecipitation.

Bonding in Surface Layer. Figures 3 and 4 give the detailed F1s and O1s peaks of various oxides.

F1s Peaks: The peaks due to F1s in the spectra for SiO_2-Al_2O_3, TiO_2-Al_2O_3(Cop), and the ternary oxide(Cop) were found only at 687.9, 686.9, and 687.4 eV, respectively, after fluorination using CF_3Cl. Since the peak positions are all close to that for AlF_3(687.3 eV) or Al_2O_3 fluorinated using CF_3Cl(687.4 eV), this indicates that F atoms introduced by the fluorination are selectively bound to the Al atoms in the mixed oxides.

The binding energies of the F1s peaks in the fluorinated ternary oxide(Imp) are found at 684.9 and 688.5 eV. Since the binding energy in TiO_2 fluorinated using CF_3Cl is found at 684.5 eV, the stronger peak at 684.9 eV is assignable to the F atom bound to a Ti atom in the ternary oxide(Imp), Observation of the peak due to Ti–F bonding on the surface of the ternary oxide prepared by impregnation may result from the removal of a larger amount of Al atoms as volatile aluminum chloride.

O1s Peaks: The spectrum for O1s of the fresh ternary oxide(Imp) gave two peaks, their maxima being observed at 530.3 and 532.7—533.0 eV. The former peak at 530.3 eV almost coincided with that due to TiO_2 or TiO_2-Al_2O_3, while the latter peak coincided

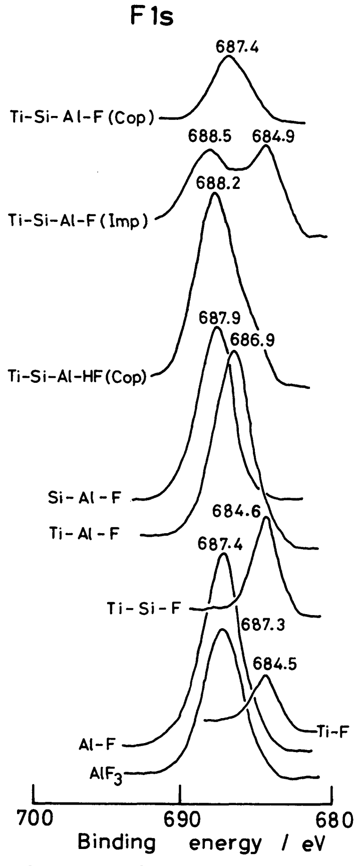

Fig. 3. XPS spectra of F1s.
Ti, Si, and Al indicate the samples of TiO_2, SiO_2 and Al_2O_3, respectively, and "-F" indicates the samples treated with CF_3Cl.

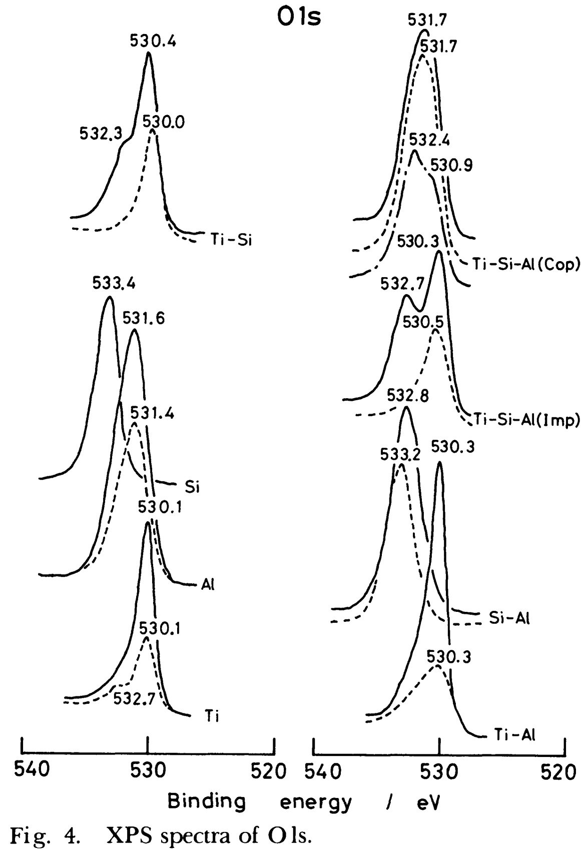

Fig. 4. XPS spectra of O1s.
Full lines and broken lines indicate the spectra for fresh oxides and treated oxides, respectively.

with that due to SiO_2 or SiO_2-Al_2O_3.

After fluorination using CF_3Cl, the ternary oxide(Imp) gave only one peak at 530.5 eV, that position almost coinciding with one obtained for fresh ternary oxide(Imp) at 530.3 eV. Furthermore, this peak position is close to that obtained for fluorinated TiO_2-(530.1 eV). Hence, the peak at 530.0 eV is assignable to the O atom bound to a Ti atom; the absence of other peaks except that 530.5 eV is compatible with the previous assumption that the surface layer of the fluorinated ternary oxide(Imp) is composed mainly of fluorinated titanium oxide.

On the other hand, for the ternary oxide(Cop), only one broad peak was given at around 531.7 eV. The peak position and shape of the peak were not changed by surface fluorination using CF_3Cl. Namely, the concentration of Ti component by the fluorination with CF_3Cl appeared improbable for the mixed oxide prepared by coprecipitation.

Thus, the preparation of the ternary oxide by coprecipitation was essential for maintaining the homogeneity in the surface compositions. The fluorination of the homogeneous surface using, not hydrofluoric acid, but gaseous CF_3Cl was remarkably effective for the formation of strong acid sites on the mixed oxide surface.

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