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The Conversion of CH_3OH into Olefins over Al_2O_3–Cr_2O_3 Treated with CF_3Cl

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A mixed oxide of Al and Cr having an atomic ratio(Al/Cr) of around 9 showed catalytic activity for the conversion of CH_3OH into olefins and aromatic compounds after treatment with CF_3Cl at 450 °C. The mixed oxide treated with CF_3Cl adsorbed a considerable amount of NH_3, even at temperatures as high as 500 °C. Analyses of the compositions on the surface layer by using XPS showed that the F component was predominantly bound to Al, not to Cr. Strong acid sites related to the less crystallized AlF_3 seemed to be able to promote the conversion of CH_3OH.

Hydrocarbon production from methanol has become an important process for obtaining materials such as ethylene and propylene from coal, instead of petroleum. The catalytic activity of metal oxides in the conversion of CH_3OH into olefins have, however been little reported on, work having been limited to certain zeolites[1–2] such as ZSM-5 (Mobil Oil Company),[3] heteropolyacids and/or their salts,[4–5] and aluminum dihydrogenphosphate.[6] Sufficiently strong acid sites seem to be essential for the promotion of the reaction.

It has been previously found that Al_2O_3–Cr_2O_3 promotes the disproportionation of CF_3Cl into CF_4 and CF_2Cl_2 at temperatures higher than 400 °C.[7] The scission of the strong C–F bond in the CF_3 group[8] is essential for the disproportionation, and the surface of Al_2O_3–Cr_2O_3 should be first fluorinated when the mixed oxide is used as a disproportionation catalyst. Accordingly, the Al_2O_3–Cr_2O_3 surface treated with CF_3Cl, is considered to have strong acid sites and may be expected to promote the conversion of CH_3OH into olefins. Consequently, the catalytic activities of treated Al_2O_3–Cr_2O_3, with various Al/Cr atomic ratios, were examined and compared to those of unfluorinated Al_2O_3–Cr_2O_3, Al_2O_3, and Cr_2O_3. The effects of CF_3Cl treatment on the surface activation were compared with those of treatment with other chlorofluoromethanes and CCl_4. The surface compositions and properties of treated single and mixed oxides were investigated in connection with the catalytic activities.

Experimental

Materials. Various oxides were prepared from their nitrates through the respective hydroxides. The mixed hydroxides were prepared from aqueous solutions of nitrates by coprecipitation with 28% aqueous ammonia, the final pH being adjusted to 8.0—9.0. The precipitates of the mixed hydroxides were thoroughly washed with deionized water and separated by decantation. After drying at 120 °C for 12 h, the mixed hydroxides were heat-treated in air at 600 °C for 3 h; they were then converted to the mixed oxides. Just before their use as catalysts, the oxides were compressed to 30—40 mesh granules under pressure; they were then submitted to surface treatments with a flow of halogen-substituted methane diluted with He at 450 °C for 30 min in a flow reactor. Although mainly CF_3Cl was used as the surface-treatment agent, other chlorofluoromethanes (CF_2Cl_2 and $CFCl_3$) and CCl_4 were also used for comparison with CF_3Cl. All the chlorofluoromethanes (supplied by the Mitsui Fluorochemical Co.) were of purities higher than 99.9%.

Reaction Procedure. The conversion of CH_3OH was carried out in a pulse reactor connected with a modified gaschromatographic analyzer at 400 °C, using He as the diluent. The pulse size was 1 μl; the weight of the catalyst and the velocity of the diluent were kept constant at 30 mg and 35 ml/min respectively.

The product gas, 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 removing the liquid nitrogen trap; the column was subsequently heat-treated up to about 150 °C. The evaporated gas flowed through TCD, and the composition of the product was analyzed.

Also, the conversion of the dimethyl ether to olefins was carried out in the same reactor by an operation similar to that described above. In these operations, the low-boiling components, such as CO and CH_4, were almost entirely recovered in a column immersed in the liquid-nitrogen trap. The material balances for the conversions of CH_3OH and CH_3OCH_3 were more than 70% and about 85% respectively.

Determinations of Surface Compositions and Properties. The compositions in the surface layer were determined by XPS using a Shimadzu ESCA-750 apparatus. The spectra were measured with Mg $K\alpha$ radiation. The base pressure of the spectrometer was usually below 10^{-7} Torr (1 Torr $\approx$133.322 Pa) during the experiments. The compositions were calculated from the area of the peaks (*i.e.*, the maxima in the counting rate) in the spectra on the basis of photoionization cross-sections at 1254 eV in units of the C 1s cross-section of 22200 barns.[9] The errors inherent in such a determination are generally 10—30% of the observed value.

The surface areas were determined by applying the BET method to the adsorption isotherm of N_2 at −196 °C. The structures of Al_2O_3 and Al_2O_3–Cr_2O_3 were determined from the powder-diffraction patterns obtained with a Rigaku Denki Gigerflex X-ray diffractometer using filtered Cu $K\alpha$ radiation. The surface acidities were measured by means of the amounts of NH_3 adsorbed at different temperature.

Results and Discussion

Effects of Atomic Ratio (Al/Cr). Table 1 shows the effect of the mixed oxide atomic ratio on the catalytic activity before and after treatment with CF_3Cl. For comparison, SiO_2–Al_2O_3 (N-631, Nikki Chemical Co.), which is a typical strong solid acid, was also used. Except for SiO_2–Al_2O_3, which caused the formation of a slight amount of olefin, none of the single and mixed oxides promoted any olefin formation. On the other hand, except for Cr_2O_3, when the oxides were pretreated with CF_3Cl at 450 °C and then used as catalysts, considerable amounts of ethylene and propene were formed from CH_3OH. The catalytic

TABLE 1. DECOMPOSITION OF CH_3OH OVER VARIOUS CATALYSTS AT 400 °C

Catalyst	Product distribution (mol%)							
	CO	CO_2	CH_4	C=C	C=C-C	C_{6-7} b)	DME	CH_3OH
Al_2O_3	6.2	0	20.4	0	0	0	53.8	19.0
Cr_2O_3	51.0	32.4	3.5	0	0	0	0	14.1
SiO_2-Al_2O(N-631)	0	0	0	Trace	Trace	0	76.1	23.9
Al/Cr:9.5/0.5a)	15.1	41.4	6.0	0	0	0	0	37.8
9/1	20.4	44.3	7.4	0	0	0	0	27.9
8.5/1.5	16.7	39.6	6.7	0	0	0	0	37.0
8/2	14.4	38.9	5.7	0	0	0	0	41.0
Al_2O_3-F	0	0	0	3.6	7.9	Trace	55.4	32.9
Cr_2O_3-F	7.9	8.7	0.8	0	0	Trace	0	79.6
N-631-F	0	0	0	5.1	11.4	0	66.8	16.7
Al/Cr:9.5/0.5-F	0	0.6	0	7.3	10.9	1.4	60.2	19.6
9/1-F	0	1.2	0	7.1	12.9	1.8	55.4	21.6
8.5/1.5-F	0	1.0	0	7.0	6.8	1.8	55.9	27.5
8/2-F	0	1.1	0	5.6	9.6	1.6	50.5	31.6

a) Al/Cr denotes the Al_2O_3-Cr_2O_3 mixed oxide catalyst; -F denotes the catalyst treated with CF_3Cl. b) C_{6-7} denote benzene and/or toluene.

TABLE 2. DECOMPOSITION OF CH_3OH OVER Al_2O_3-Cr_2O_3 (Al/Cr=9/1) TREATED WITH VARIOUS CHLOROFLUOROMETHANE OR CCl_4

Treatment species	Product distribution(mol%)							
	CO	CO_2	CH_4	C=C	C=C-C	C_{6-7}	DME	CH_3OH
No treatment	20.4	44.3	7.4	0	0	0	0	27.9
CCl_4	2.6	2.1	3.6	29.5	0	0	62.2	0
$CFCl_3$	2.2	1.8	4.0	13.1	0	0.3	75.7	2.8
CF_2Cl_2	0	1.2	Trace	12.5	Trace	1.1	63.7	21.5
CF_3Cl	0	1.2	0	7.1	12.9	1.8	55.4	21.6

TABLE 3. EFFECT OF CF_3Cl-TREATMENT TEMPERATURE ON CATALYTIC ACTIVITY

Temperature/°C	Product distribution(mol%)a)						Conversion of disproportionation of CF_3Cl/%4)
	CO_2	C=C	C=C-C	C_{6-7}	DME	CH_3OH	
400	2.6	7.0	0.9	1.8	66.2	21.5	26.5
450	1.2	7.1	12.9	1.8	55.4	21.6	30.8
500	1.0	3.5	6.9	1.8	32.8	54.0	19.5

a) CO and CH_4 were not observed in the product gases for any of the runs.

activity of Cr_2O_3 for the formations of CO and CO_2 decreased remarkably with the pretreatment, suggesting that the active O atoms on the Cr_2O_3 surface may be removed by the reaction with CF_3Cl.

A maximal conversion of CH_3OH into olefins was obtained with the mixed oxide having the atomic ratio of Al/Cr=9/1. The same atomic ratio also gave a maximum disproportionation for CF_3Cl.7) Since the disproportionation can be promoted only by the strong acid,7) the strong acid sites must be formed most abundantly on Al_2O_3–Cr_2O_3 (9/1) after treatment with CF_3Cl.

Comparison of Treatment Using CF_3Cl with Those Using Other Chlorofluoromethanes or CCl_4. The catalytic activities of Al_2O_3–Cr_2O_3 treated with different chlorofluoromethanes or CCl_4 are shown in Table 2 for the CH_3OH conversion. The Al_2O_3–Cr_2O_3 treated with CCl_4 showed the highest activity at the first pulse of the reactant. However, large amount of deposits, which seemed to be aluminum chloride and/or chromium chloride, were formed on the reactor walls and finally clogged the reactor outlet. The deposited amounts decreased with an increase in the number of F atoms in the chlorofluoromethane molecule used for the surface treatment. Thus, when CF_3Cl was used for the treatment, there were hardly any deposits found during the reaction.

When the mixed oxide treated with CCl_4, $CFCl_3$, or CF_2Cl_2 was used as a catalyst, ethylene was obtained as the main olefinic product. On the other hand, a good deal of propene was produced, together with ethylene, when the mixed oxide was treated with CF_3Cl.

Effect of CF_3Cl-treatment Temperature on Catalytic Activity. The effect of the treatment temperature with CF_3Cl on the catalytic activity for the conversion

Table 4. Surface composition of treated component or mixed oxide

Oxide	Composition(atom%)					Atomic ratio	
	O	F	Cl	Cr	Al	Cr/Al	F/Al
Al/Cr:9/1	69.9	0	0	3.1	27.0	0.11	—
-treated with CCl_4	57.7	0	5.8	2.9	33.6	0.09	—
-$CFCl_3$	46.2	20.5	1.7	3.5	28.1	0.12	0.7
-CF_2Cl_2	36.8	21.6	1.8	3.5	36.3	0.10	0.6
-CF_3Cl	31.2	37.7	0	3.7	27.4	0.13	1.4
Al_2O_3	63.7	0	0	0	36.3	—	—
-treated with CF_3Cl	44.3	23.2	0	0	32.5	—	0.7
Cr_2O_3	67.3	0	0	32.7	0	—	—
-treated with CF_3Cl	65.3	0	0	34.7	0	—	—

Table 5. Conversion of DME over oxides before and after treatment with CF_3Cl

Oxide^a)	Product distribution(mol%)						
	CO	CO_2	CH_4	C=C	C=C-C	C_{6-7}	DME
Al_2O_3	18.4	0.5	55.0	0	0	0	26.1
Cr_2O_3	7.6	3.2	2.6	0	0	0	86.6
Al/Cr:9/1	7.2	84.6	8.2	0	0	0	0
Al_2O_3-F^b)	0	0	0	6.7	0.6	0	92.7
Cr_2O_3-F	7.1	2.6	3.7	0.6	0	0	86.0
Al/Cr:9/1-F	0	1.7	1.7	2.4	5.6	0	88.6

a) All the oxides were heat-treated at 600 °C for 3 h before the treatment with CF_3Cl or use as a catalyst. b) -F denotes a catalyst treated with CF_3Cl similarly to that shown in Table 1. The treatment conditions with CF_3Cl were the same as for the conversion of CH_3OH.

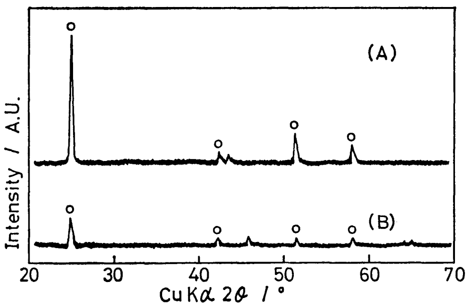

Fig. 1. X-Ray diffraction patterns.
(A): Al_2O_3 treated with CF_3Cl, (B): Al_2O_3–Cr_2O_3 treated with CF_3Cl. (O): Peaks due to α-AlF_3.

of CH_3OH is shown in Table 3. The CF_3Cl treatment was most effectively carried out at 450 °C to give an increase in the catalytic activity for the CH_3OH conversion similar to that for the CF_3Cl disproportionation.

Effect of H_2-treatment before the Treatment with CF_3Cl. To know the effect of reduction on the catalytic activity, Al_2O_3–Cr_2O_3 (9/1) was treated with H_2 at 450 and 600 °C before the treatment with CF_3Cl at 450 °C. The catalytic activity for the formation of olefins was remarkably decreased by the pretreatment with H_2 at 450 °C. Particularly, the formation of propene was not observed when the mixed oxide was pretreated with H_2, although the amount of dimethyl ether formed increased with the pretreatment. The catalytic activity of the mixed oxide treated with CF_3Cl remained for the formation of dimethyl ether, even when the mixed oxide was pretreated at as high a temperature as 650 °C.

Surface Composition and Degree of Crystallization of the Oxide after Treatments. The surface compositions determined by XPS, after treatment with chlorofluoromethanes or CCl_4, are shown in Table 4. In the mixed oxides treated with $CFCl_3$ or CF_2Cl_2, only a small amount of the Cl component was found, together with a much larger amount of the F component. Furthermore, the Cl component was not detected in the mixed oxide treated with CF_3Cl. The F component in the mixed oxide (Al/Cr=9/1) increased with an increase in the number of F atoms in the molecule used for the surface treatment. As is shown in the last line in Table 4, Cr_2O_3 did not bind the F component at all during the treatment with CF_3Cl. In contrast to Cr_2O_3, Al_2O_3 bound a good deal of the F component, as is shown in the seventh line of Table 4. This fact suggests that the F atoms in the mixed oxide may combine with Al, not Cr, atoms.

The X-ray diffraction analysis of Al_2O_3 and Al_2O_3–Cr_2O_3 after treatment with CF_3Cl (Fig. 1) showed that α-AlF_3 formed on both oxides and that the degree of crystallization of the aluminum fluoride on the treated mixed oxide was far less than that on the treated Al_2O_3. The X-ray diffraction patterns ascribable to

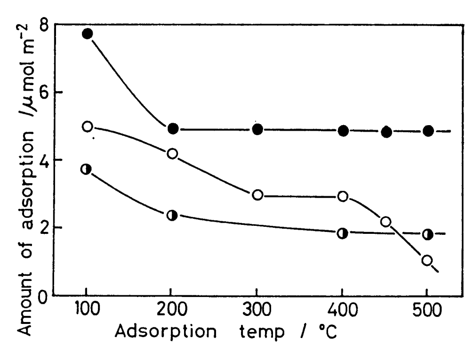

Fig. 2. Adsorption of NH_3 at various temperatures. ◑: SiO_2–Al_2O_3 (N-631), ○: Al_2O_3–Cr_2O_3(9/1), ●: Al_2O_3–Cr_2O_3 treated with CF_3Cl.

metal chlorides and the chromium compound was not observed at all. The absence of the Cl component in the most active oxide, *i.e.*, Al_2O_3–Cr_2O_3 (Al/Cr=9/1) treated with CF_3Cl, has also been shown by the results obtained by using XPS (Table 4). Thus, the high catalytic activity of the treated mixed oxide may be due not to aluminum chloride, but to the less crystallized, and so active, aluminum fluoride formed on the surface by the treatment.

Conversion of DME over Oxides before and after Treatment with CF_3Cl. As Table 5 shows, Al_2O_3, Cr_2O_3, and Al_2O_3–Cr_2O_3 (Al/Cr=9/1) promote only the conversion of dimethyl ether to CO, CO_2, and CH_4 before treatment with CF_3Cl. After such a treatment, Al_2O_3 and Al_2O_3–Cr_2O_3 showed activities for the conversion of dimethyl ether into olefins. In particular, the Al_2O_3–Cr_2O_3 promoted a formation of propene similar to that observed in the conversion of CH_3OH.

For the conversion of CH_3OH catalyzed by ZSM-5 or other zeolites, it is generally accepted that the formation of hydrocarbons proceeds according to the pathway shown below:[1,5,6]

$$CH_3OH \rightleftharpoons CH_3OCH_3 \longrightarrow C_2H_4,\ C_3H_6,\ \text{and } C_4H_8\ \textit{etc.} \begin{array}{l} \nearrow \text{Paraffins} \\ \searrow \text{Aromatics.} \end{array}$$

The fact that dimethyl ether gives a similar or essentially the same product distribution as methanol (shown in Table 1) shows that the pathway described above may be acceptable also for the conversion catalyzed by the treated Al_2O_3–Cr_2O_3 or the treated Al_2O_3. The strong acid sites formed by treatment with CF_3Cl should promote the slowest step in the reaction sequence.

Surface Properties and Formation of Active Sites. The specific surface areas of the mixed oxides before and after treatment with CF_3Cl were almost completely independent of the atomic ratio in the Al/Cr range from 1/0 to 8/2. Hence, the specific surface area does not seemed to be a factor determining the mixed oxide catalytic activity, which is maximal when the atomic ratio of Al/Cr equals 9/1.

As is shown in Fig. 2, the amount of NH_3 adsorbed on treated Al_2O_3–Cr_2O_3 (9/1) at temperatures higher than 450 °C was much more than that on SiO_2–Al_2O_3 or untreated Al_2O_3–Cr_2O_3 (9/1). This fact shows that fair amounts of strong acid sites should be formed on the mixed oxides treated with CF_3Cl at 450 °C.

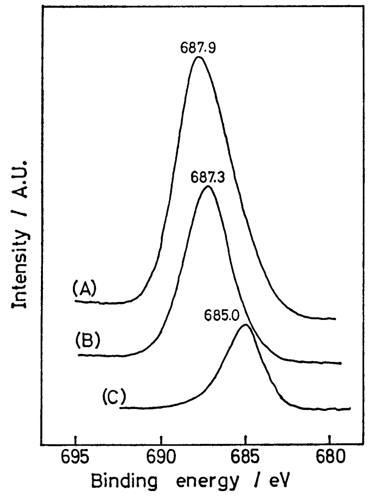

Fig. 3. F 1S peaks in XPS.
(A): Al_2O_3–Cr_2O_3 treated with CF_3Cl, (B): AlF_3, (C): CrF_3.

Figure 3 shows that the position of the F is peak (687.9 eV) in the spectrum of Al_2O_3–Cr_2O_3 (9/1) treated with CF_3Cl is close to those of AlF_3 (687.3 eV) or Al_2O_3 treated with CF_3Cl (687.1 eV), while it is far from that of CrF_3. Thus, it is elucidated that the active sites should be related to aluminum fluoride or to Al atoms (or ions) bonded to F atoms (or ions) on the surface.

Because AlF_3 has the highest positive partial charge (0.72) among the typical strong electron-acceptors, such as BF_3 (0.56), $AlCl_3$ (0.57), BCl_3 (0.41), and $GaCl_3$ (0.32),[10] it should be an extremely strong solid acid. However, it tends to form stable crystals due to the very small radius of the F ion and its large electronegativity and, further, the large ion potential, *i.e.*, the ratio of the ionic valence to the ionic radius, of the Al ion. Consequently, it is desirable to prevent the crystallization for aluminum fluoride to fully function as a strong solid-acid catalyst.

By considering also that Cr_2O_3 itself did not catalyze the formation of olefins at all, even after treatment with CF_3Cl (Table 1), and that no F component was found in Cr_2O_3 treated with CF_3Cl (Table 4), the major effect of Cr_2O_3 in the treated mixed oxide seems to be only structural. That is, the crystal structure of Cr_2O_3 is a corundum type in which O atoms are appeared in an approximately hexagonal close-packed arrangement and Al^{3+} ions are situated in two-thirds of the octahedral holes;[11] furthermore, the ionic radius (0.63 Å[12]) is comparatively close to that of Al^{3+} (0.51 Å[12]). Hence, small amounts of Cr^{3+} ions added to Al_2O_3 may be thoroughly mixed with Al^{3+} and may thus suppress the crystallization of AlF_3 by intervening between Al^{3+} ions. However, Cr_2O_3 itself is catalytically far less active for the formation of olefins from CH_3OH, even after treatment with chlorofluoromethanes. Accordingly, the addition of Cr^{3+} in a larger amount was not beneficial for the enhancement of the catalytic activity because an excess Cr_2O_3 component hinders the formation and the function of active aluminum fluoride on the surface. Thus, an optimal amount of Cr constituent was observed at around 10 atom% in the CF_3Cl-treated mixed oxide.

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