Effect of Surface Fluorination with $CClF_3$ on Catalytic Activity of SiO_2-Al_2O_3 for Alkylation of Benzene with Propene

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For surface modification, the vapor-phase fluorination of SiO_2-Al_2O_3 with $CClF_3$ was carried out at various temperatures ranging from 350 to 550 °C in a conventional flow reactor. It was found that surface fluorination at about 400 °C was especially effective for the enhancement of both the catalytic activity and the maintenance of the catalytic activity for the vapor-phase alkylation of benzene with propene. Ammonia-TPD revealed that the surface acidity of SiO_2-Al_2O_3 could be somewhat increased by surface fluorination at about 400 °C. The vapor-phase adsorption of water, hexane, propene, benzene, and cumene showed that the SiO_2-Al_2O_3 surface became hydro- and lipo-phobic after surface fluorination. Thus, an enhancement of catalytic activity maintenance was assignable to a decrease in the affinity of the catalyst surface to reaction products.

It is known that the surface acidities of some metal oxides are enhanced by surface fluorination. Hitherto, surface fluorination has generally been carrid out by using aqueous solutions of HF,[1] NH_4F,[2] and NH_4HF_2.[3] Recently, the authors have found that the vapor-phase fluorination of Al_2O_3,[4] Al_2O_3-Cr_2O_3,[5] TiO_2-Al_2O_3,[1] and TiO_2-SiO_2-Al_2O_3[1] using such chlorofluorocarbons(CFCs) as CCl_3F, $CClF_3$, and CCl_2FCClF_2 are effective for increasing the surface acidities and the catalytic activities for some acid-catalyzed reactions. In addition, treatment using $CClF_3$ at temperatures lower than 600 °C was also effective for the surface fluorination of H-mordenite (molar ratio of SiO_2/Al_2O_3=19).[6] Furthermore, this treatment was found to be available not only for increasing the catalytic activity, but also for enhancing the stability of the activity.

In general, the surface properties of mixed oxides are fairly different from those of their component oxides. Thus, SiO_2-Al_2O_3 shows a remarkably large surface acidity compared to both SiO_2 and Al_2O_3. As is well known, SiO_2-Al_2O_3 is a typical solid acid that is useful as an industrial catalyst. It would be favorable if the surface acidity of SiO_2-Al_2O_3 could be further enhanced by chlorofluorocarbon(CFC)-treatments similarly to those of SiO_2[7] and Al_2O_3.[4] However, the CFC-treatment of SiO_2-Al_2O_3 may be not necessarily effective for such an enhancement, since the CFC-treatment of H-mordenite, which is mainly composed of SiO_2 and Al_2O_3, on the contrary, decreased its surface acidity.[6] Hence, the effect of the CFC-treatment on both the surface acidity and the catalytic activity for a certain acid-catalyzed reaction, the alkylation of benzene with propene, was studied due to the fact that the CFC-treatment of SiO_2-Al_2O_3 has been only little reported in the literature.

Experimental

Materials. A commercial SiO_2-Al_2O_3 catalyst, N-631L (Nikki Chemical Co., Si/Al(atomic ratio)=85/15), was used as a SiO_2-Al_2O_3 sample. For a comparison, a protonated Y-type zeoliye, HY(Toso Co., TSZ-320HOA, SiO_2/Al_2O_3 (molar ratio)=5.7), was used as another sample. Single oxides, SiO_2 and Al_2O_3, were prepared by the hydrolysis of ethyl silicate and aluminum isopropoxide, respectively. All of the catalyst oxides other than HY, were heat-treated at 600 °C for 3 h immediately before use as a catalyst or for surface fluorination. Exceptionally, HY was heat-treated at a lower temperature, such as 500 °C, since HY partly decomposes upon heating at 600 °C or above.

The fluorination agent, $CClF_3$, having a purity of higher than 99.9%, was supplied by Mitsui-Dupont Fluorochemical Co., and used without further purification.

Fluorination Procedure. Fluorination with $CClF_3$ was carried out in a conventional flow reactor using N_2 as a diluent at various temperatures ranging from 250 to 550 °C immediately before use as a catalyst. The other conditions of the fluorination were as follows: fluorination time, 0.5 h; $CClF_3/N_2$ (molar ratio)=1; flow rate of gas($CClF_3+N_2$), 100 ml min^{-1}.

Determinations of Structure and F Content. The structure of SiO_2-Al_2O_3 was determined by XRD. The F content in the surface layer was measured by XPS employing Mg $K\alpha$ radiation. The content was calculated from the areas of the spectral peaks on the basis of the photo-ionization cross section at 1245 eV in units of the C 1s cross section, 22200 barns (1 barn=10^{-24} cm^2).[8]

Determinations of Surface Properties. The acidity change of SiO_2-Al_2O_3 due to surface fluorination was determined by using NH_3-TPD under the following conditions: pretreatment, evacuation at 400 °C for 1 h; adsorption temperature of NH_3, 100 °C; increasing rate of the bed temperature, 20 °C per minutes. The surface areas were determined by applying the BET equation for the adsorption isotherm of N_2 at −196 °C. The change in the adsorptive activity of SiO_2-Al_2O_3 due to surface fluorination was examined by the vapor-phase adsorption of water, hexane, propene, benzene, and cumene on SiO_2-Al_2O_3 at 50 °C, before and after surface fluorination.

Reaction Procedure. The vapor-phase alkylation of benzene with propene was carried out under ordinary pressure in a conventional flow reactor. Unless otherwise noted, the

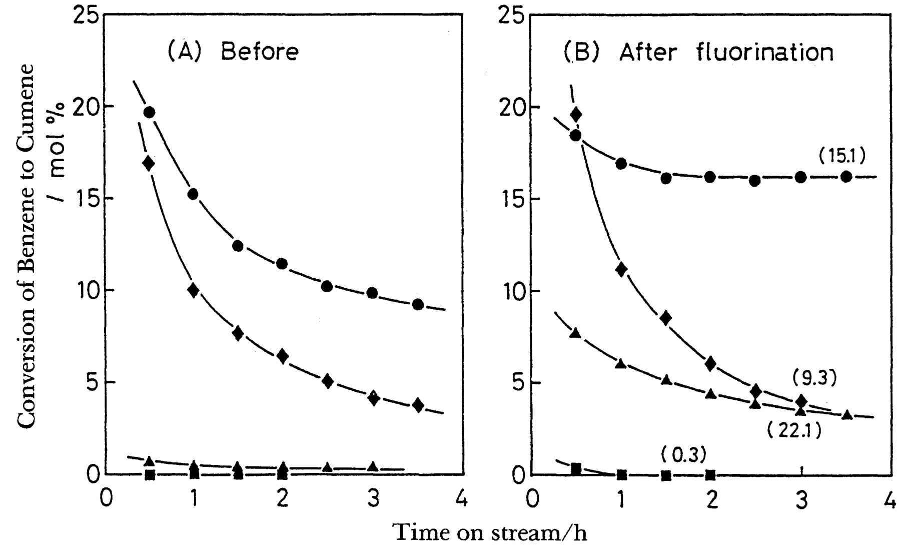

Fig. 1. Catalytic activities for alkylation of benzene with propene of metal oxides before and after fluorination. ●: SiO_2-Al_2O_3(N-631L), ▲: Al_2O_3, ■: SiO_2, ◆: HY. Fluorination temperature: 400 °C. The numbers in parentheses indicate the F content of respective samples.

reaction conditions were as follows: reaction temperature, 350 °C; W/F=17.8 g h mol^{-1}; propene/benzene (molar ratio)=2. The products were analyzed by gas chromatography using a column packed with Bentone 34(5%) and DIDP(5%) supported on Uniport HP.

Results and Discussion

Comparisons of Catalytic Activity. Figure 1 shows the results of the alkylation of benzene with propene catalyzed by SiO_2, Al_2O_3, SiO_2-Al_2O_3 and HY before and after the $CClF_3$-treatment.

As Fig. 1(A) shows, the single oxides, Al_2O_3 and SiO_2, exhibited only slight catalytic activities for the alkylation. Since alkylation is known to be catalyzed by Brönsted acid sites,[9] the lower catalytic activities are ascribable to the absence or lack of the Brönsted acid sites on Al_2O_3[10,11] and SiO_2[11] surfaces. In fact, SiO_2-Al_2O_3 and HY, which are known to be strong Brönsted acids, showed high catalytic activities, even though the catalytic activities decreased significantly with time on stream. This decrease may have resulted from the deposition of carbonaceous product on the active sites of the catalyst surfaces.

After surface fluorination with $CClF_3$ (Fig. 1(B)), Al_2O_3 showed a high catalytic activity for the alkylation, even though the activity gradually decreased with the process time. On the other hand, the SiO_2 surface was still catalytically inactive, even after the $CClF_3$-treatment. Fluorinated SiO_2-Al_2O_3, having a high Si/Al atomic ratio (such as 85/15), exhibited a high catalytic activity. In addition, the activity was well maintained during its use as a catalyst for alkylation. Thus, the decrease in the conversion was very slight after a process time of about 90 min, in contrast to that found for the $CClF_3$-treated HY. As is well known, metal fluorides are less volatile than the corresponding metal chlorides, and are far more stable towards water vapor or moisture in air. The stability of metal fluoride or M–F bond on a CFC-treated surface should be one reason for the excellent maintenance of the catalytic activity of CFC-treated SiO_2-Al_2O_3. Thus, the effects of the surface-treatment of SiO_2-Al_2O_3 on the catalytic activity and the surface properties were examined in further detail as follows.

Effect of Fluorination Temperature on Catalytic Activity. To determine the effect of a $CClF_3$-

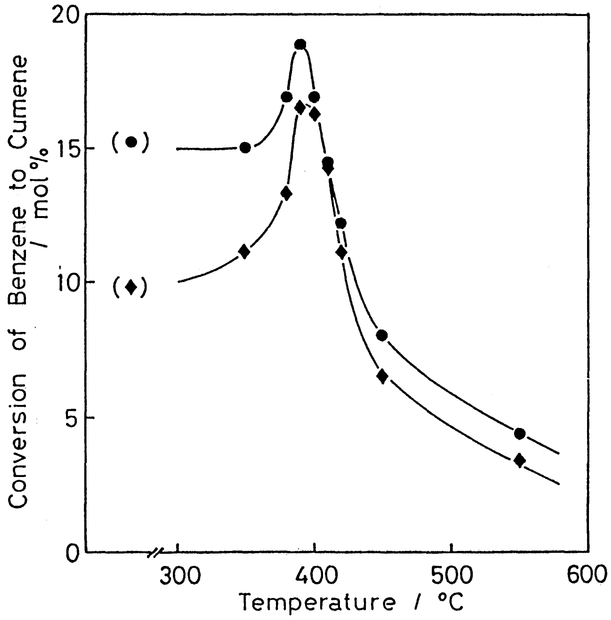

Fig. 2. Effect of fluorination temperature on catalytic activity. ●: time on stream 1 h, ◆: time on stream 3 h. The symbols in parentheses indicate the conversion for unfluorinated SiO_2-Al_2O_3.

treatment on the catalytic activity for alkylation, reactions were carried out in the presence of SiO_2-Al_2O_3 either treated or fluorinated with $CClF_3$ at various temperatures ranging from 350 to 550 °C. As shown in Fig. 2, the catalytic activity shown by the conversion of benzene to cumene reached a maximum when the SiO_2-Al_2O_3 was fluorinated at 400 °C. When SiO_2-Al_2O_3 was fluorinated at such high temperatures as 450 °C or above, the catalytic activity abruptly decreased and became lower than that of the untreated one. This decrease was ascribable as being due to either the surface OH groups, or to the Brönsted acid sites on the surface being fully dimnished by the replacement with F atoms during the $CClF_3$-treatment at higher temperatures.[7]

Table 1. Specific Surface Area of Al_2O_3 and SiO_2-Al_2O_3 Fluorinated at Various Temperatures

Oxide	Temperature / °C	Specific surface area/$m^2\,g^{-1}$
Al_2O_3	—	226[a)]
	350	161
SiO_2-Al_2O_3	—	480[a)]
	400	473
	450	447
	500	439
	550	424

a) Value of before fluorination.

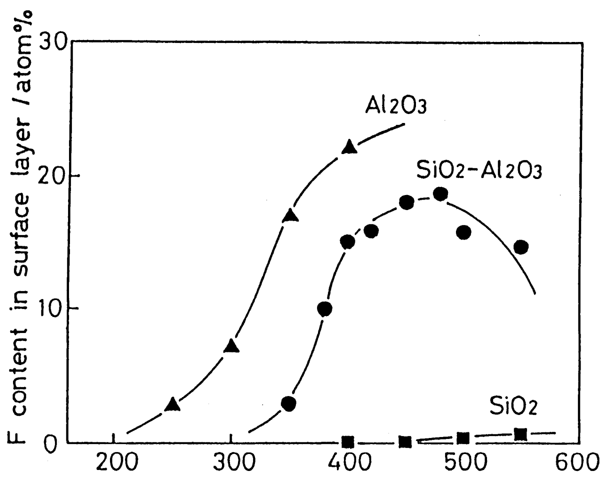

Fig. 3. Effect of Fluorination temperature on F content in surface layer.

Effects of Fluorination on Surface Area and Structures. As shown in Table 1, the specific surface area of Al_2O_3 was significantly decreased by fluorination at 350 °C, possibly due to the formation of stable or crystalline AlF_3.[5] On the other hand, the surface area of SiO_2-Al_2O_3 was little decreased by the fluorination carried out even at higher temperatures. The XRD analyses revealed that SiO_2-Al_2O_3 was still amorphous, even after fluorination at such high temperatures as 550 °C.

Content and Bonding of F Atoms in the Fluorinated Surface Layer. As Fig. 3 shows, the order of the reactivity of the metal oxides toward $CClF_3$ was

$$Al_2O_3 > SiO_2\text{-}Al_2O_3 \gg SiO_2.$$

Concerning the surface fluorination of SiO_2-Al_2O_3, there was an optimal temperature at about 450 °C for increasing the F content in the fluorinated surface layer. The decrease in F content at temperatures higher than 500 °C was due to the formation of volatile SiF_4.[7]

The peak due to Fls in XPS spectra for SiO_2-Al_2O_3 fluorinated at around 400 °C was found at 687.3—687.6 eV. The peak position is close to that for AlF_3(687.3 eV)[4] or Al_2O_3 fluorinated with $CClF_3$ (687.5 eV),[4] while it is far from that of SiO_2 fluorinated with chlorofluoromethanes (688.3—688.7 eV).[7] This fact indicated that the F atoms introduced by $CClF_3$ molecules preferentially bound to the Al atoms in the SiO_2-Al_2O_3 surface layer.

Acidity of Fluorinated Surface. In order to examine the acidity changes of SiO_2-Al_2O_3 during surface fluorination, and its use as a catalyst, NH_3-TPD was attempted using modified gas chromatography at

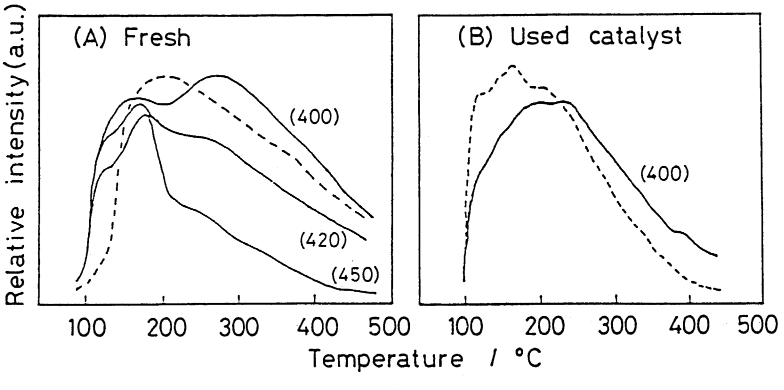

Fig. 4. NH_3-TPD spectra for fresh and used catalyst. Dotted line: SiO_2-Al_2O_3, solid line: SiO_2-Al_2O_3 fluorinated with $CClF_3$. The numbers in parentheses indicate the fluorination temperature.

temperatures ranging from 100 to 500 °C.

As shown in Fig.4(A), the NH_3-TPD spectra of SiO_2-Al_2O_3 before use as a catalyst varied remarkably with the fluorination temperature. Especially, the peak position of SiO_2-Al_2O_3 was markedly shifted from 200 to 300 °C by fluorination at 400 °C, indicating a strengthening of the surface acidity. This peak, however, was significantly lowered by surface fluorination above 420 °C. These results indicate a weakening of the surface acidity by fluorination at temperatures higher than 400 °C. The fact that maximum surface acidity was obtained at a fluorination temperature of 400 °C is consistent with the fact that the maximum activity was found for a sample fluorinated at the same temperature, as shown in Fig. 2.

As shown in Fig. 4(B), the strong surface acidity of SiO_2-Al_2O_3 was reduced to a certain extent by a use as a catalyst. However, a reduction of the strong surface acidity observed for fluorinated SiO_2-Al_2O_3 was slight compared to that observed for SiO_2-Al_2O_3 without surface fluorination. The superior retention of strong surface acidity may be the main reason for the preferable enhancement of the activity maintenance observed for fluorinated SiO_2-Al_2O_3.

Adsorptive Activities of Fluorinated Surface for Various Gases. Figures 5 and 6 show Freundlich plots for the vapor-phase adsorption of water, hexane, propene, benzene, and cumene on SiO_2-Al_2O_3 before and after fluorination. The equilibrium adsorption amounts per unit surface area of SiO_2-Al_2O_3 were all decreased by fluorination. Thus, SiO_2-Al_2O_3 became hydro- and lipo-phobic after surface fluorination. The characteristic property supplied by the $CClF_3$-treatment should have resulted from the remarkably low surface energy of the fluorinated SiO_2-Al_2O_3 surface, which is well-covered by F atoms. A similar characteristic surface was also obtained for chlorofluoromethane-treated SiO_2.7)

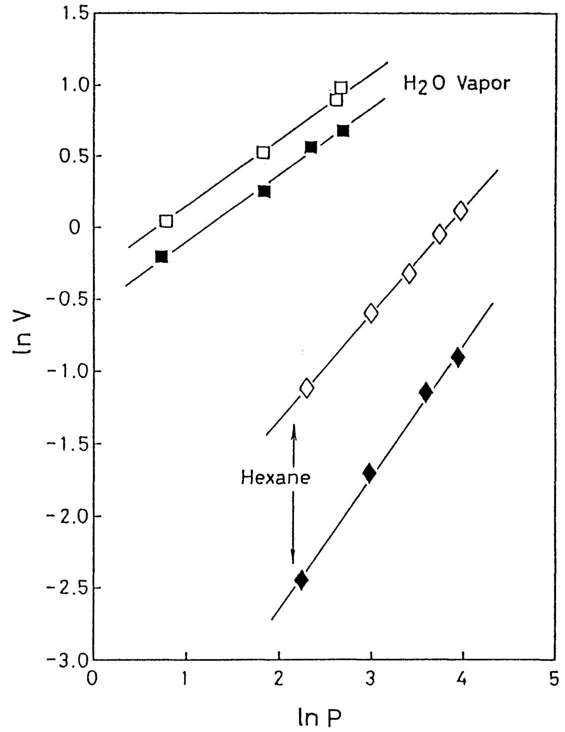

Fig. 5. Application of Freundlich equation for gaseous adsorption of water and hexane.
P: Vapor pressure/Torr (1 Torr=133.322 Pa), V: Adsorbed amount/μ mol m^{-2}. □, ◇: SiO_2-Al_2O_3, ■, ◆: SiO_2-Al_2O_3 fluorinated at 400 °C. □: $V=7.26\times10^{-1}\,P^{0.47}$, ■: $V=5.64\times10^{-1}\,P^{0.47}$, ◇: $V=6.11\times10^{-2}\,P^{0.73}$, ◆: $V=1.12\times10^{-2}\,P^{0.92}$.

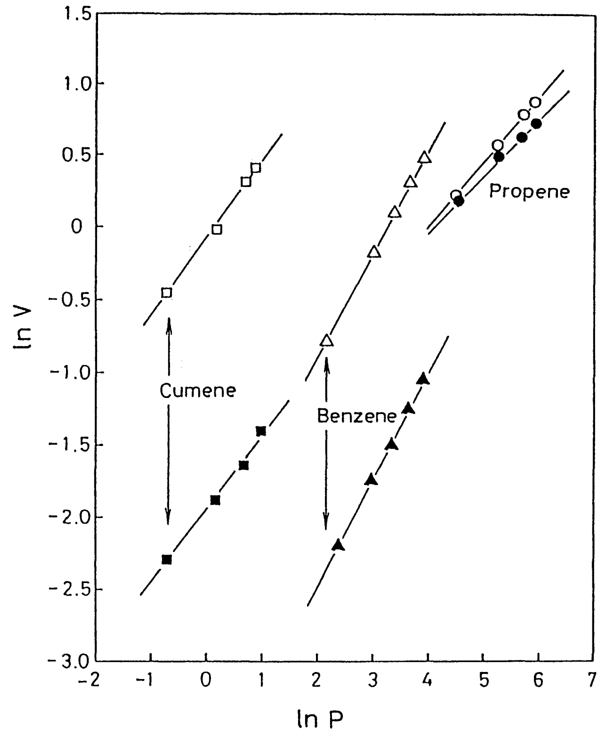

Fig. 6. Application of Freundlich equation for gaseous adsorption of propene, benzene, and cumene.
P: Vapor pressure/Torr, V: Adsorbed amount/μ mol m^{-2}. ○, △, □: SiO_2-Al_2O_3, ●, ▲, ■: SiO_2-Al_2O_3 fluorinated at 400 °C. ○: $V=1.39\times10^{-1}\,P^{0.48}$, ●: $V=2.04\times10^{-1}\,P^{0.38}$, △: $V=8.87\times10^{-2}\,P^{0.75}$, ▲: $V=1.85\times10^{-2}\,P^{0.75}$, □: $V=1.38\times10^{-1}\,P^{0.53}$.

As shown in Figs. 5 and 6, the decrease in the adsorption amount of polar or nucleophilic compounds, such as water and propene, was not so remarkable compared to that observed for non- or less polar compounds such as hexane, benzene and cumene. It is well known that the catalytic alkylation of benzene with olefins and alcohols proceeds via carbonium ions formed by the protonation of the alkylation agent.12) Hence, it seems very favorable for maintaining the catalytic activity that the affinity of SiO_2-Al_2O_3 for propene is not changed so remarkably by surface fluorination.

Thus, the results suggested that the effect of surface fluorination on the enhancement of the stability of the activity was ascribable to decreasing the acumulation of the less volatile reaction products or carbonaceous deposits on the SiO_2-Al_2O_3 catalyst surface. In addition, the decrease in the adsorptive activity of the SiO_2-Al_2O_3 catalyst surface for the desired product, cumene, may also be favorable for promoting product desorption and for a more frequent use of the active site for alkylation.

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