

Effect of Surface Fluorination with CClF_3 on Catalytic Activity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ for Alkylation of Benzene with Propene

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(Received March 12, 1990)

For surface modification, the vapor-phase fluorination of $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 carried 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⁾ $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$,⁵⁾ $\text{TiO}_2\text{-Al}_2\text{O}_3$,¹⁾ and $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ ¹⁾ using such chlorofluorocarbons (CFCs) as CCl_3F , CClF_3 , and $\text{CCl}_2\text{FCClF}_2$ 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 $\text{SiO}_2/\text{Al}_2\text{O}_3=19$).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, $\text{SiO}_2\text{-Al}_2\text{O}_3$ shows a remarkably large surface acidity compared to both SiO_2 and Al_2O_3 . As is well known, $\text{SiO}_2\text{-Al}_2\text{O}_3$ is a typical solid acid that is useful as an industrial catalyst. It would be favorable if the surface acidity of $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ has been only little reported in the literature.

Experimental

Materials. A commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst, N-631L

(Nikki Chemical Co., Si/Al (atomic ratio)=85/15), was used as a $\text{SiO}_2\text{-Al}_2\text{O}_3$ sample. For a comparison, a protonated Y-type zeolite, HY (Toso Co., TSZ-320HOA, $\text{SiO}_2/\text{Al}_2\text{O}_3$ (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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 cm²).⁸⁾

Determinations of Surface Properties. The acidity change of $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ due to surface fluorination was examined by the vapor-phase adsorption of water, hexane, propene, benzene, and cumene on $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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

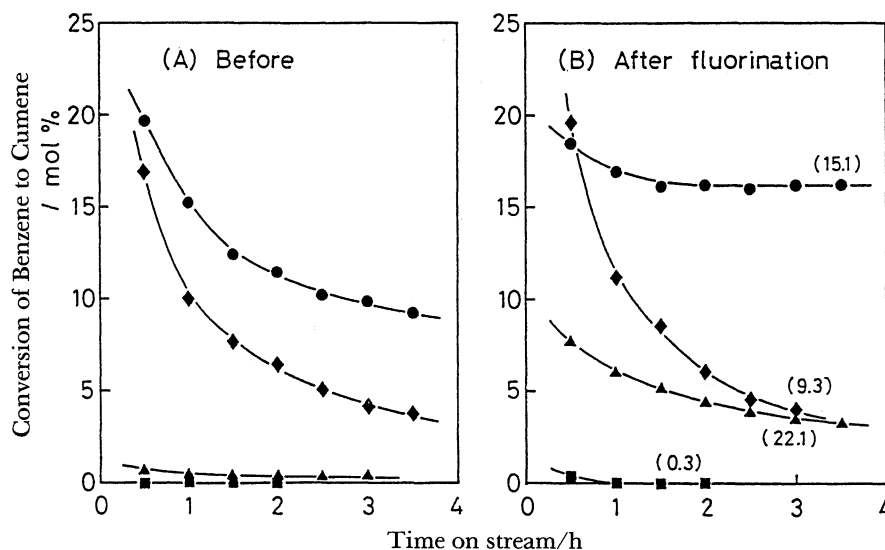


Fig. 1. Catalytic activities for alkylation of benzene with propene of metal oxides before and after fluorination. ●: SiO₂-Al₂O₃(N-631L), ▲: Al₂O₃, ■: SiO₂, ◆: HY. Fluorination temperature: 400 °C. The numbers in parentheses indicate the F content of respective samples.

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 Unipor HP.

Results and Discussion

Comparisons of Catalytic Activity. Figure 1 shows the results of the alkylation of benzene with propene catalyzed by SiO₂, Al₂O₃, SiO₂-Al₂O₃ and HY before and after the CClF₃-treatment.

As Fig. 1(A) shows, the single oxides, Al₂O₃ and SiO₂, 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 Al₂O₃^{10,11)} and SiO₂¹¹⁾ surfaces. In fact, SiO₂-Al₂O₃ 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 CClF₃ (Fig. 1(B)), Al₂O₃ showed a high catalytic activity for the alkylation, even though the activity gradually decreased with the process time. On the other hand, the SiO₂ surface was still catalytically inactive, even after the CClF₃-treatment. Fluorinated SiO₂-Al₂O₃, 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 CClF₃-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 SiO₂-Al₂O₃. Thus, the effects of the surface-treatment of SiO₂-Al₂O₃ 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 CClF₃-

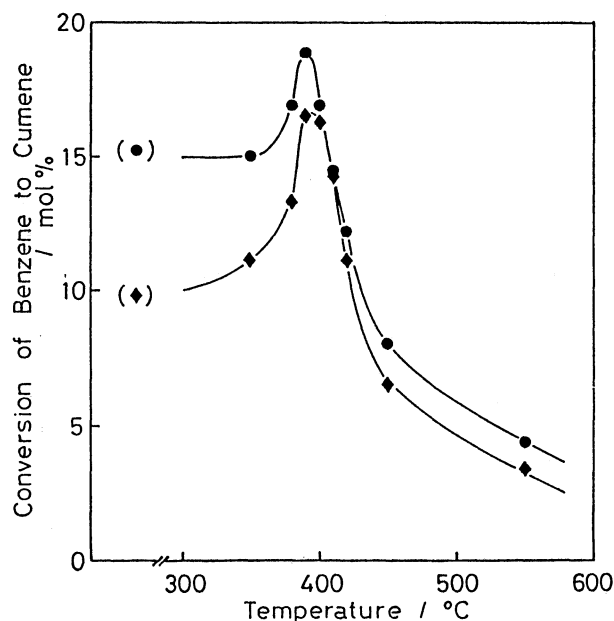


Fig. 2. Effect of fluorination temperature on catalytic activity. ●: time on stream 1 h, ◆: time on stream 3 h. The symbols in parentheses indicate the conversion for unfluorinated SiO₂-Al₂O₃.

treatment on the catalytic activity for alkylation, reactions were carried out in the presence of SiO₂-Al₂O₃ either treated or fluorinated with CClF₃ 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 SiO₂-Al₂O₃ was fluorinated at 400 °C. When SiO₂-Al₂O₃ was fluorinated at such high temperatures

Table 1. Specific Surface Area of Al₂O₃ and SiO₂-Al₂O₃ Fluorinated at Various Temperatures

Oxide	Temperature / °C	Specific surface area / m ² g ⁻¹
Al ₂ O ₃	—	226 ^{a)}
	350	161
SiO ₂ -Al ₂ O ₃	—	480 ^{a)}
	400	473
	450	447
	500	439
	550	424

a) Value of before fluorination.

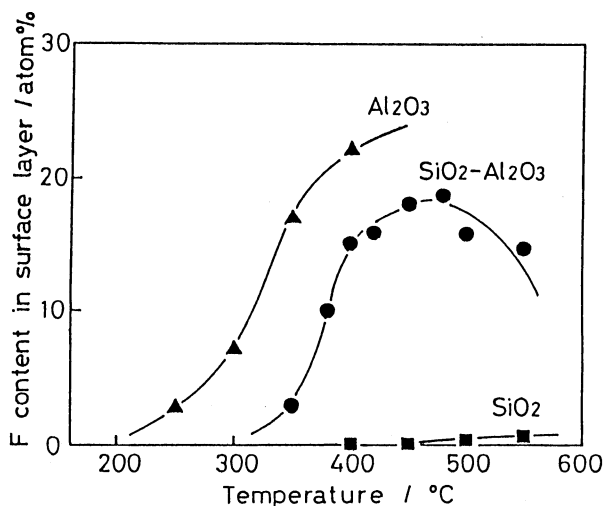
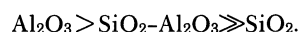


Fig. 3. Effect of Fluorination temperature on F content in surface layer.

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 diminished by the replacement with F atoms during the CClF₃-treatment at higher temperatures.⁷⁾

Effects of Fluorination on Surface Area and Structures. As shown in Table 1, the specific surface area of Al₂O₃ was significantly decreased by fluorination at 350 °C, possibly due to the formation of stable or crystalline AlF₃.⁵⁾ On the other hand, the surface area of SiO₂-Al₂O₃ was little decreased by the fluorination carried out even at higher temperatures. The XRD analyses revealed that SiO₂-Al₂O₃ 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 CClF₃ was



Concerning the surface fluorination of SiO₂-Al₂O₃, 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 SiF₄.⁷⁾

The peak due to F1s in XPS spectra for SiO₂-Al₂O₃ fluorinated at around 400 °C was found at 687.3–687.6 eV. The peak position is close to that for AlF₃ (687.3 eV)⁴⁾ or Al₂O₃ fluorinated with CClF₃ (687.5 eV),⁴⁾ while it is far from that of SiO₂ fluorinated with chlorofluoromethanes (688.3–688.7 eV).⁷⁾ This fact indicated that the F atoms introduced by CClF₃ molecules preferentially bound to the Al atoms in the SiO₂-Al₂O₃ surface layer.

Acidity of Fluorinated Surface. In order to examine the acidity changes of SiO₂-Al₂O₃ during surface fluorination, and its use as a catalyst, NH₃-TPD was attempted using modified gas chromatography at

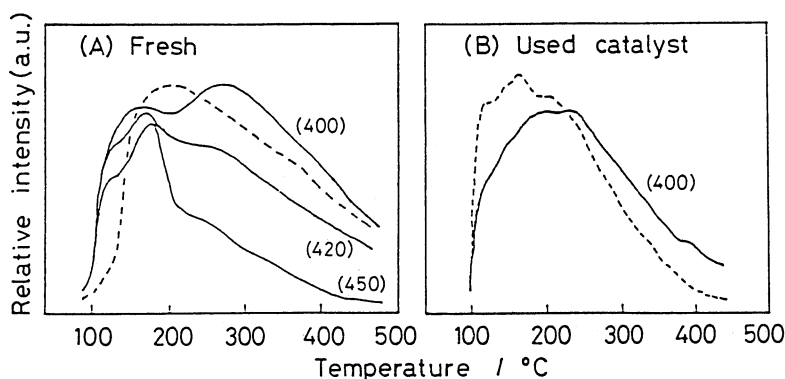


Fig. 4. NH₃-TPD spectra for fresh and used catalyst. Dotted line: SiO₂-Al₂O₃, solid line: SiO₂-Al₂O₃ fluorinated with CClF₃. The numbers in parentheses indicate the fluorination temperature.

temperatures ranging from 100 to 500 °C.

As shown in Fig. 4(A), the NH_3 -TPD spectra of $\text{SiO}_2\text{-Al}_2\text{O}_3$ before use as a catalyst varied remarkably with the fluorination temperature. Especially, the peak position of $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ was reduced to a certain extent by a use as a catalyst. However, a reduction of the strong surface acidity observed for fluorinated $\text{SiO}_2\text{-Al}_2\text{O}_3$ was slight compared to that observed for $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$.

Adsorptive Activities of Fluorinated Surface for Various Gases. Figures 5 and 6 show Freundlich plots for the vapor-phase adsorption of water, hexane, pro-

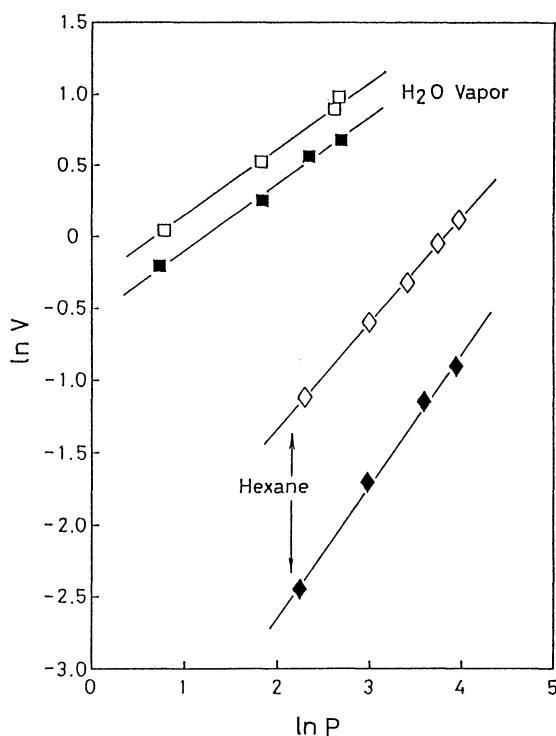


Fig. 5. Application of Freundlich equation for gaseous adsorption of water and hexane.

P: Vapor pressure/Torr (1 Torr=133.322 Pa), V: Adsorbed amount/ $\mu\text{mol m}^{-2}$. $\square, \diamond$: $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\blacksquare, \blacklozenge$: $\text{SiO}_2\text{-Al}_2\text{O}_3$ fluorinated at 400 °C. $\square$: $V=7.26 \times 10^{-1} P^{0.47}$, $\blacksquare$: $V=5.64 \times 10^{-1} P^{0.47}$, $\diamond$: $V=6.11 \times 10^{-2} P^{0.73}$, $\blacklozenge$: $V=1.12 \times 10^{-2} P^{0.92}$.

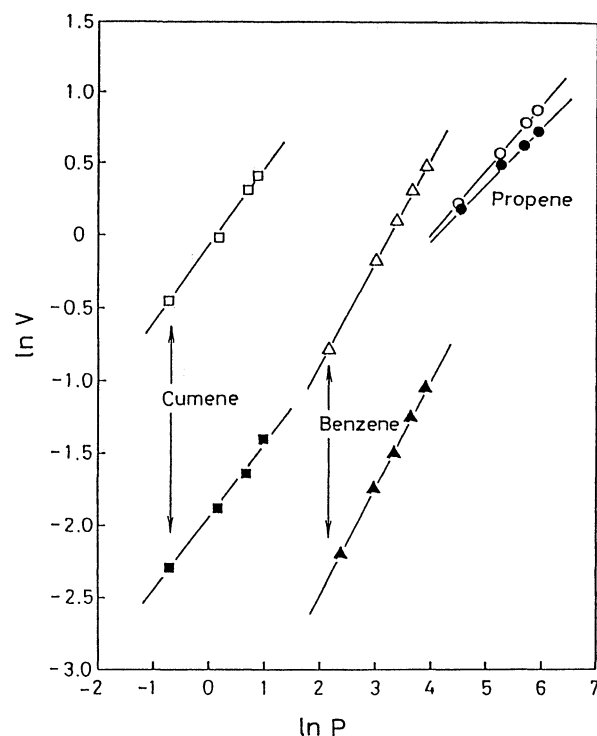


Fig. 6. Application of Freundlich equation for gaseous adsorption of propene, benzene, and cumene.

P: Vapor pressure/Torr, V: Adsorbed amount/ $\mu\text{mol m}^{-2}$. $\circ, \triangle, \square$: $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\bullet, \blacktriangle, \blacksquare$: $\text{SiO}_2\text{-Al}_2\text{O}_3$ fluorinated at 400 °C. $\circ$: $V=1.39 \times 10^{-1} P^{0.48}$, $\bullet$: $V=2.04 \times 10^{-1} P^{0.38}$, $\triangle$: $V=8.87 \times 10^{-2} P^{0.75}$, $\blacktriangle$: $V=1.85 \times 10^{-2} P^{0.75}$, $\square$: $V=1.38 \times 10^{-1} P^{0.53}$.

ene, benzene, and cumene on $\text{SiO}_2\text{-Al}_2\text{O}_3$ before and after fluorination. The equilibrium adsorption amounts per unit surface area of $\text{SiO}_2\text{-Al}_2\text{O}_3$ were all decreased by fluorination. Thus, $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ surface, which is well-covered by F atoms. A similar characteristic surface was also obtained for chloro-fluoromethane-treated SiO_2 .⁷⁾

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 $\text{SiO}_2\text{-Al}_2\text{O}_3$ 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 accumulation

of the less volatile reaction products or carbonaceous deposits on the SiO₂-Al₂O₃ catalyst surface. In addition, the decrease in the adsorptive activity of the SiO₂-Al₂O₃ 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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