CHEMISTRY LETTERS, pp. 589-592, 1991

Effect of Surface Treatment with $CHClF_2$ on Catalytic Behavior of SiO_2-Al_2O_3 and Al_2O_3

Akito KUROSAKI and Susumu OKAZAKI *
Department of Industrial Chemistry, Faculty of Engineering,
Ibaraki University, Nakanarusawa-cho, Hitachi 316

$CHClF_2$ has been found to be effective as a surface treatment agent of SiO_2-Al_2O_3 and Al_2O_3, as well as chlorofluorocarbons (CFCs) such as CCl_2F_2 and $CClF_3$, to enhance its catalytic activity and/or activity maintenance for the alkylation of benzene with propene. The $CHClF_2$-treatment may be performed at temperatures considerably lower than those required for CFC-treatments.

In previous papers, the authors reported that the vapor-phase fluorination of some metal-oxide surfaces using chlorofluorocarbons (CFCs) such as CCl_3F, CCl_2F_2, and $CClF_3$ are effective for enhancements of the surface acidities and the catalytic activities and/or activity maintenance for some acid-catalyzed reactions.1) As is well known, however, the CFCs are claimed to be notorious on destruction of the ozone layer,2) and so they may be not used in the next century.

On the other hand, hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are reported to be less harmful than CFCs, because they may be decomposed without so much difficulty before they reach the ozone layer.3) Among HFCs, CHF_3,4-6) and $CHF_2CF_3$4) are known to be effective as a treatment agent for vapor-phase fluorination of Al_2O_3 and Al^{3+} exchanged Y-type zeolite, respectively, to enhance the catalytic activities for acid-catalyzed reactions. Regrettably, however, CHF_3, and CHF_2CF_3 are not produced on a large scale, and so necessarily expensive at the present stage. While, a simple and typical HCFC, $CHClF_2$, is less expensive since it is produced on a large scale as a common refriegerant ; furthermore it may be produced in larger quantities in the future as a raw material for syntheses of poly-tetrafluoroethylene and the related fluoropolymers. Thus, it is preferable to apply $CHClF_2$ as a surface treatment agent for preparation of solid acid catalysts. Nevertheless, to our knowledge, no studies have been carried out concerning such a use of $CHClF_2$.

Accordingly, we have examined the effects of $CHClF_2$ as a treatment agent for SiO_2-Al_2O_3 and Al_2O_3, and compared with those of $CClF_3$[1d)] and CHF_3, in this study. By considering the industrial significance, the alkylation of benzene with propene was selected as an acid-catalyzed reaction.

A commercial SiO_2-Al_2O_3 catalyst, N-631L (Nikki Chemical Co.,Si/Al=85/15), was used as a SiO_2-Al_2O_3 sample. Al_2O_3 was prepared by the hydrolysis of aluminum isopropoxide, followed by repeated washing of the precipitate. All of the catalyst oxides were heat-treated at 600 ℃ for 3 h immediately before a surface treatment with $CHClF_2$ or others. $CHClF_2$, $CClF_3$, and CHF_3, all of which were of purities higher than 99.9%, supplied by Mitsui-Dupont Fluorochemical Co., were directly used without further purification. Surface treatments were carried out in a conventional flow reactor using N_2 as a diluent at various temperatures ranging from 200 to 550 ℃ immediately before use as a catalyst. The other conditions of the treatment were as follows : treatment time, 0.5 h ; molar ratio of treatment agent / N_2= 1 ; total flow rate of gas, 100 mℓ min^{-1}. The F content in the surface layer of the fluorinated samples was determined by XPS. The vapor-phase alkylation of benzene with propene was carried out under ordinary pressure in a conventional flow reactor. The reaction conditions were as follows: reaction temperature, 350 ℃; W/F=17.8 g h mol^{-1}; C_3H_6 / C_6H_6 (molar ratio)= 2. The products were periodically analyzed by gas chromatography.

Figure 1 shows the effect of the treatment temperature on the F content in the surface layer of SiO_2-Al_2O_3. The order of the reactivity of the treatment agent toward SiO_2-Al_2O_3 was

$$CHClF_2 > CHF_3 > CClF_3.$$

Thus, $CHClF_2$ reacted with SiO_2-Al_2O_3 surface even at a fairly lower temperature of 200-300 ℃. In especial, the surface fluorination of SiO_2-Al_2O_3 was effectively performed at about 300 ℃, which is considerably lower than that required for the $CClF_3$-treatment[1d)] or CHF_3-treatment. For the treatment with $CHClF_2$ and $CClF_3$, the decrease in the F content found at higher than 350 ℃ and 550 ℃, respectively, was probably

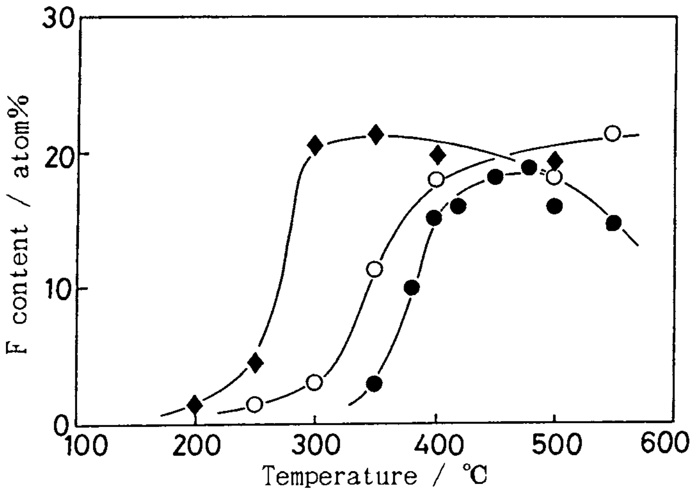

Fig.1. Effect of surface treatment temperature on F content in surface layer. ◆ : $CHClF_2$-, ● : $CClF_3$- (Data taken from Ref. 1d), ○ : CHF_3-treatment.

due to the formation of volatile compound such as SiF_4. The result of XPS analysis showed that there was no detectable amount of Cl component on the surface of SiO_2-Al_2O_3 treated with $CHClF_2$. The dependence of the catalytic activity of SiO_2-Al_2O_3 for the alkylation on the $CHClF_2$-treatment temperature is shown in Fig. 2. The catalytic activity represented by the conversion of benzene to cumene reached a maximum when the SiO_2-Al_2O_3 was treated with $CHClF_2$ at 300 ℃. This temperature coincided with the optimal temperature for the fluorination of SiO_2-Al_2O_3 shown in Fig. 1. However, when the treatment was carried out at a high temperature such as 500 ℃, the catalytic activity decreased drastically , nevertheless the F content decreased not so remarkably (Fig.1). This decrease is ascribable to the formation of inactive α-AlF_3.[1a,b)]

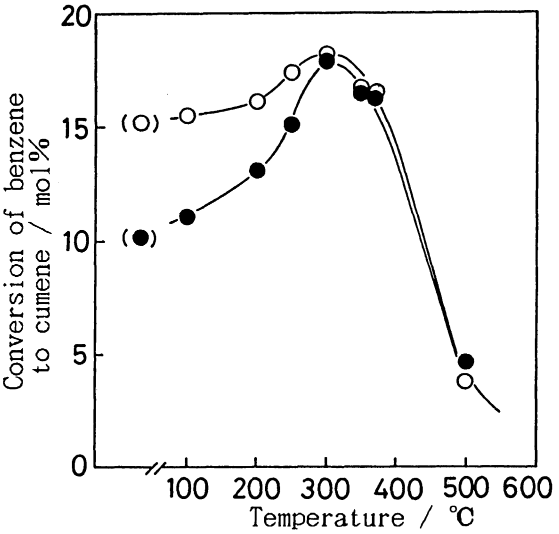

Fig.2. Dependence of catalytic activity on $CHClF_2$-treatment temperature. ○:time on stream 1 h, ●:time on stream 3 h. The symbols in parentheses indicate the conversion observed before the treatment.

The change of the catalytic activity with time on stream for the alkylation catalyzed by SiO_2-Al_2O_3 before and after treatment are shown in Fig. 3 together with those of Al_2O_3. As Fig. 3(A) shows, one of the constituent of the catalyst, Al_2O_3, exhibited only a slight catalytic activity for the alkylation, possibly because of absence or lack of the Brönsted acid sites. After surface fluorination with $CHClF_2$, Al_2O_3 exhibited a high catalytic activity for the alkylation, although the activity decreased gradually with time on stream. Such a effect of fluorination was found also for the treatment with CHF_3 or $CClF_3$. Nevertheless, the treatment effect with CHF_3 or $CClF_3$ was somewhat small compared to that with $CHClF_2$. Unlike Al_2O_3, SiO_2-Al_2O_3, which is a strong Brönsted acid, showed a high catalytic activity even before the treatment, as shown in Fig. 3(B). However, the activity decreased significantly with the process time. The marked lowering in the activity was pronouncedly depressed by the $CHClF_2$-treatment. The treatment with $CClF_3$ or CHF_3 exhibited a similar effect on the activity maintenance. Nevertheless, the high conversion at the stationary state suggested that $CHClF_2$ may be most suitable for the surface treatment of SiO_2-Al_2O_3 catalyst.

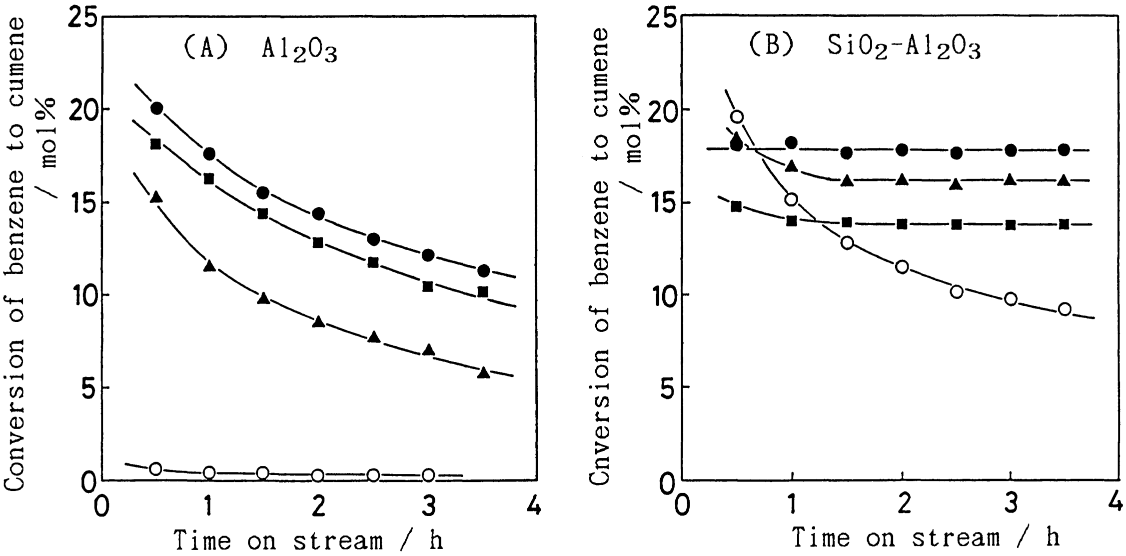

Fig.3. Change of catalytic activities with time on stream.
Conditions of surface treatment
(A) Al_2O_3: ●, $CHClF_2$ 300 °C; ■, CHF_3 350 °C; ▲, $CClF_3$ 350 °C; ○, before treatment; (B) SiO_2-Al_2O_3: ●, $CHClF_2$ 300 °C; ▲, $CClF_3$ 400 °C(Data taken from Ref. 1d); ■, CHF_3 400 °C; ○, before treatment.

It is prospective that the surface treatment using $CHClF_2$ and others is effective also for the enhancement of the catalytic activity and/or the activity maintenance of some other metal oxides. The effects may be ascertained in our coming studies.

The authors are grateful to Mitsui-Dupont Fluorochemical Co. for the finantical support for this study.

References

1) a) A.Kurosaki and S.Okazaki, Chem.Lett., 1983, 1741 ; b) A.Kurosaki and S. Okazaki, Bull.Chem.Soc.Jpn., 56, 1279(1983) ; c) S.Okazaki, A.Kurosaki, and S.Suzaki, ibid., 57, 1046(1984) ; d) A.Kurosaki and S.Okazaki, ibid., 63, 2363(1990).
2) M.J.Molina and F.S.Rowland, Nature, 249, 810(1974); C.J.Farman, B.G. Gardinar, and J.D.Shanklin, ibid., 315, 207(1985).
3) T.Ibusuki, Shokubai, 31, 552(1989).
4) R.I.Hegde and M.A.Barteau, J.Catal., 120, 387(1989).
5) G.B.McVicker, C.J.Kim, and J.J.Eggert, J.Catal., 80, 315(1983).
6) S.Kowalak, J.Chem.Soc., Faraday Trans.1, 84, 2035(1988).

(Received December 21, 1990)