CHEMISTRY LETTERS, pp. 1089-1090, 1986. © 1986 The Chemical Society of Japan

ALKYLATION OF CHLOROBENZENE WITH CH_3OH OVER H-MORDENITE TREATED WITH CHLOROFLUOROBENZENE

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

The vapor phase alkylation of chlorobenzene was promoted by H-mordenite treated with chlorofluoromethane. Ortho alkylation was preferentially promoted in the catalytic reaction after process times of 1 h.

Except for propyl alcohol,[1)] there are no other reported alkylations of chlorobenzene(CB) using alcohols. Thus, the vapor phase alkylation of CB with CH_3OH in the presence of some solid acid catalysts was attempted in this study. The reactions were carried out in a conventional continuous flow reactor under atomospheric pressure at room temperature ranging from 250 to 450 °C. A mixture of CB and CH_3OH at a molar ratio of 1, was supplied to the reactor containing 1 g of catalyst at a rate of 2.5 mmol h^{-1} by using N_2 as a carrier gas. The reaction products were analyzed by gas chromatography using a column(3 mm x 7 m) packed with Azoxydianisol SG/Uniport HP.

The HM used as a catalyst in this work was prepared by heat-treatment of NH_4-mordenite at 500 °C for 3 h. The NH_4-mordenite was prepared from commercial Na-mordenite(Toyo Soda Co., TSZ, SiO_2/Al_2O_3 molar ratio=19) by ion exchange with NH_4Cl solution. The ZSM-5 used here was prepared according to the method reported in literature.[2)] The HY(protonated Y type zeolite) was obtained by heat-treatment at 500 °C of NH_4Y, which was prepared by ion exchange of commercial NaY. As SiO_2-Al_2O_3 catalyst, the commercialy available product(Nikki Chemical Co., N 631, SiO_2/Al_2O_3 molar ratio=85/15) was used. By reference to the fact that the catalytic activity of HM for isomerization of chlorotoluene was remarkably enhanced by pretreatment with $CClF_3$,[3)] the effect of $CClF_3$-treatment on the catalytic activity for the alkylation was examined at first.

Table 1 shows the conversions of the alkylation carried out at 300 °C in the presence of various solid acid catalysts before and after $CClF_3$-treatment. Although HM, like other solid acid catalysts, did not promote the alkylation very much, it became more catalytically active after pretreatment with $CClF_3$.

As is shown in Fig.1, the catalytic activity of untreated HM was low and completely lost after use as a catalyst for 1 h. On the other hand, the decrease in catalytic activity of the $CClF_3$-treated HM was not so pronounced after the same time. Such a noticeable effect of the $CClF_3$-treatment on the activity maintenance may be due to the pore size enlargement resulting from the reaction of $CClF_3$ with the HM. Pore size enlargement due to $CClF_3$-treatment has already been ascertained

Table 1. Alkylation of chlorobenzene over various catalysts

Catalyst	Conversion of chlorobenzene to chlorotoluene(mol%)[a]	
	Before $CClF_3$-treatment	After $CClF_3$-treatment[b]
HM	2.0	22.5
H ZSM-5	3.6	8.2
HY	2.1	1.8
SiO_2-Al_2O_3	2.1	3.6

a) The conversions were measured for samples collected during the first 30 minutes of reaction.

b) The $CClF_3$-treatments were carried out at 450 °C for 8 min by using gaseous $CClF_3$ diluted with an equal amount of N_2.

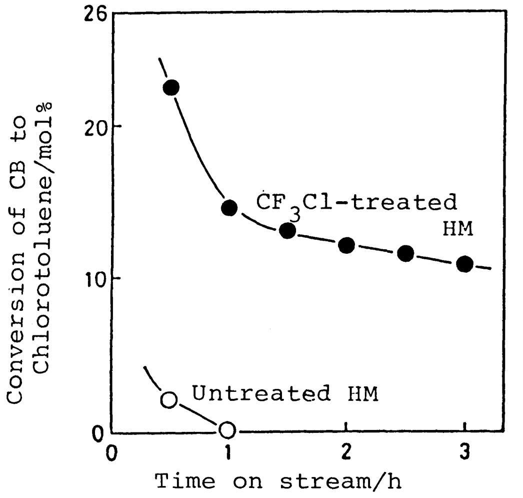

Fig.1. Change of conversion with time on stream.

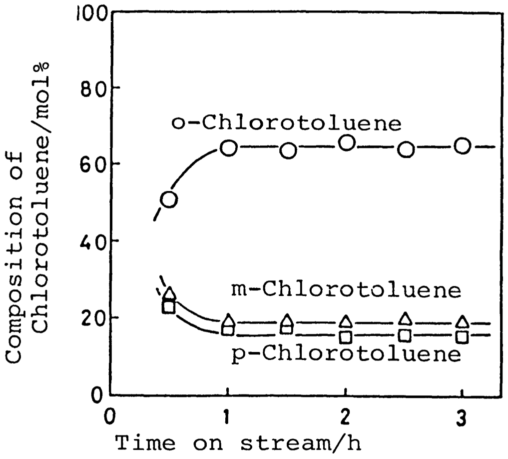

Fig.2. Change of selectivity with time on stream.

reaction temp: 300 °C, W/F=78.7 g h mol^{-1}(for Figs. 1 and 2)

by a previous study of adsorptions of several compounds having different molecular cross-sectional areas.[3] As is shown in Fig.2, ortho alkylation proceeded more favorably than meta and para alkylations, and the ratio of the ortho isomer to other isomers remained constant after process time of 1 h.

The enhancements of the catalytic activity and activity maintenance also performed by the CCl_2F_2- or CCl_3F-treatment. Since CCl_4- and CF_4-treatments were less or not effective for the enhancement, chlorination followed by successive fluorination seems essential for the effective treatment of HM catalyst.

References

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(Received Aril 11, 1986)