

Alkylation of Xylenes with Methanol on Alumina activated with Hydrofluoric Acid

MASAMI INOUE and SABURO ENOMOTO

Faculty of Pharmaceutical Sciences, Toyama University¹⁾

(Received December 23, 1974)

The catalytic alkylation of xylenes with methanol over alumina activated with hydrofluoric acid was examined using a flow reactor under the atmospheric pressure. The methylation takes place from 300° to 500° in the presence of an excess amount of methanol. At temperatures from 300° to 350° isomerization and disproportionation are not observed. The selectivity of the methylating position was correlated with the nature of the catalyst such as acidity, acid strength, and the structure of fluorinated alumina catalysts. The activity showed a maximum for 12.7% fluorinated alumina catalyst and conversion increased with the acidity of catalysts. The acid strength determined by the indicator method falls in the range of $+1.5 \leq H_0 \leq 3.3$, which suggests that the acid sites have a uniform structure on its surface. From the X-ray powder patterns of the catalysts used the active species were proposed to be $AlF(OH)_2$ and $AlF_2(OH)$.

Introduction

Tricarboxybenzenes, *e.g.*, trimellitic, trimesic, and hemimellitic acids, have been prepared from trimethylbenzenes by oxidation with potassium permanganate solution. In the C_9 aromatic compounds of the coal tar or petroleum cracking products, a mixture of mesitylene, pseudocumene, and hemimellitene is present. The separation of these isomers by physical and chemical methods is so laborious even at present. Trimethylbenzenes are also supplied by catalytic synthesis from xylenes, with methanol as an alkylating reagent.²⁾ In this method the products are composed of isomers closely reaching the equilibrium compositions at the reaction temperature. It has been difficult to control the orientation of alkyl groups in the methylation of xylene.

This paper describes the selective alkylation of xylenes with methanol on a series of the fluorinated alumina catalysts; *e.g.*, from *o*- and *m*-xylene to hemimellitene and pseudocumene, and from *p*-xylene to pseudocumene at 350°. Further, the catalytic activity of the isomerization and disproportionation was compared with methylation under the same reaction conditions. The purpose of this study is to determine the character of the acid sites of the catalysts and to elucidate the mechanism of the selective methylation.

Experimental

Apparatus and Procedure for Alkylation—The usual quartz reactor equipped with a preheater, injector, and a catalyst bed of 13 × 170 mm was used for the methylation, isomerization, and disproportionation. The temperature was measured with a thermocouple attached to the catalyst bed. A mixture of xylenes and MeOH (1:4), supplied from the injector at the rate of 3 ml/hr, was vaporized in the preheater held at 250°, and introduced over the catalyst with N_2 (3 liters/hr) as a carrier. The vapor products were condensed in the trap cooled in an ice bath.

Preparation of Catalysts—Alumina bead of 3 mm diameter (Mizusawa Chemical Co., Niigata) was impregnated with 10% aqueous HF solution for 3 hr at room temperature. The catalyst was dried at 120° and then calcined at 500° for 5 hr.

1) Location: 3190, Gofuku, Toyama.

2) P.B. Venuto, L.A. Hamilton, P.S. Landis, and J.J. Wice, *J. Catalysis*, **5**, 81 (1966); T. Yashima, H. Ahmad, K. Yamazaki, M. Katsuta, and N. Hara, *ibid.*, **16**, 273 (1970).

3) R.J. Rowley, J.G. Grier, and R.L. Parsons, *Anal. Chem.*, **25**, 1061 (1953).

Analysis of Products—Composition of the condensed oily products was analyzed with a gas-liquid chromatograph, Yanaco GCG-3DH, using Benton-34(5%) + Dinonylphthalate(5%) on silanized Celite (60—80 mesh) as a column (2 m) packing material and H_2 as a carrier at 120°.

Fluorine Content of Catalysts—According to the method by Rowley, *et al.*,³⁾ quantitative analysis of F of the catalyst was made. The fluorinated catalyst (0.1 g) and NaOH(0.1 g) were fused in a nickel crucible. The cruster was washed with 25 ml of $HClO_4$ into a roundbottomed vessel and HF was steam-distilled. NaOH solution was added to 500 ml of the distillate until the solution became alkaline. It was neutralized with HCl and the solution was adjusted with $ClCH_2COOH$ to pH 2.7—3.0. Then the solution was titrated with 0.1N $Th(NO_3)_4$ using sodium alizarinsulfonate as an indicator. The color changed from yellow to pink at the end-point.

Surface Area of Catalysts—The specific surface area of a series of alumina catalysts activated with HF was measured by the Brunauer, Emmett, and Teller (BET) method, using Ar as adsorbent at liquid N_2 temperature.

Acidity of Catalysts—The powdered catalyst (0.1 g) was dispersed in 10 ml of benzene, 1 or 2 drops of 1% benzene solution of Hammett indicator (pK_a , +4.8 to +0.8) were added, and the solution was titrated with 0.1N butylamine for 48 hr.

Result and Discussion

The catalytic alkylation of toluene and xylene using methanol as an alkylating reagent over zeolites and $SiO_2-Al_2O_3$ has been reported during recent years. The products methylated at 300° on these catalysts are composed of isomerized xylenes and trimethylbenzenes of equilibrium composition.^{2,4)} In contrast, alkylation over a hydrofluoric acid-mounted alumina catalyst yields hemimellitene and pseudocumene from *o*-xylene, and mesitylene is not detected in the products. When *m*-xylene is methylated at 350° over 12.7% fluorinated alumina, the predominant trimethylbenzene isomer is also hemimellitene and pseudocumene. From *p*-xylene, pseudocumene is obtained exclusively. These results are given in Table I.

TABLE I. Selective Methylation of Xylenes with Methanol on 12.7% Fluorine-containing Alumina Catalyst

Materials	Temp. (°C)	Conversion (mol%)	Products		
			Pseudocumene (%)	Hemimellitene (%)	Mesitylene (%)
<i>o</i> -Xylene	300	17.6	9.4	8.2	0
<i>m</i> -Xylene	350	13.7	11.9	1.8	0
<i>p</i> -Xylene	400	25.5	25.5	0	0

molar ratio of xylene to methanol, 1:4

If isomerization of trimethylbenzenes could be inhibited during the reaction, formation of mesitylene will be avoided. This relation can be seen in Chart 1.

In the present experiments, isomerization and disproportionation of *o*-xylene were performed to demonstrate the effect of temperature and flow rate. The composition of isomerized *o*-xylene over fluorinated alumina (F, 12.7%) from 300° to 500° is presented in Fig. 1.

At 350°, isomerization to *m*- and *p*-xylene takes place. The disproportionation of *o*-xylene occurs at 400° and produces toluene, trimethylbenzenes, and tetramethylbenzenes. At 500°, the highest temperature studied, a few percent of benzene is detected, by further complicated reactions including cracking.

Alkylation of *o*-xylene with excess of methanol begins at 300°. From 300° to 350°, trimethylbenzenes obtained are hemimellitene and pseudocumene, which are predicted from the *ortho*- and *para*-directing effects of an alkyl cation. Fig. 2 shows the results obtained for the experiments with methylation of *o*-xylene at various temperatures from 250° to 500° on

4) M. Inoue and S. Enomoto, *Sekiyu Gakkai Shi*, 15, 372 (1972).

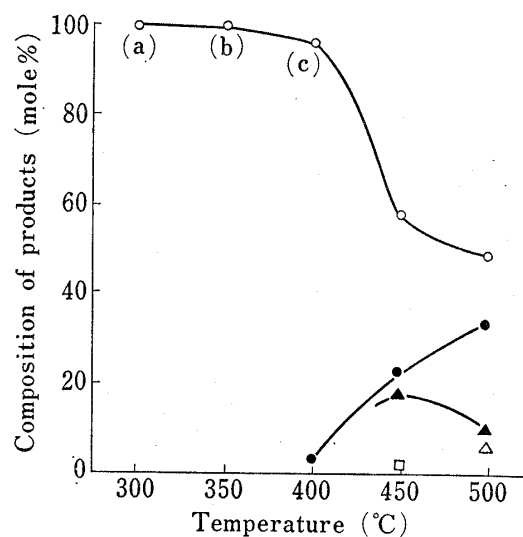
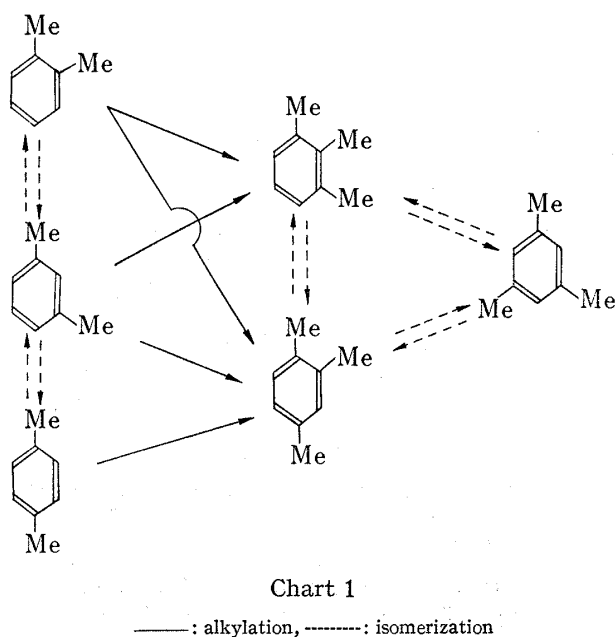


Fig. 1. Effect of Temperature in Isomerization and Disproportionation of *o*-Xylene on 9.9% Fluorine-mounted Alumina

(a) *o*:-97.4%, *m*:-2.6%, (b) *o*:-63.5%, *m*:-30.7%, *p*:-5.8%, (c) *o*:-43.0%, *m*:-45.4%, *p*:-11.6%
 —○—: *o*-xylene, —△—: benzene, —●—: toluene,
 —▲—: trimethylbenzenes, —□—: tetramethylbenzenes

fluorinated catalyst (F, 12.7%). At 350°, mesitylene, the isomerized component of hemimellitene and pseudocumene, appears in the reaction products. Prehnitene (1,2,3,4-tetramethylbenzene) was detected only at 300°. At a higher temperature the composition of trimethylbenzene isomers agrees closely with the equilibrium compositions as calculated from the thermodynamic constants by Mauras.⁵⁾ The results of alkylation at 300° and 450° are presented in Table II. At 300°, methylation of xylenes takes place at 2- or 4-position. In contrast, at higher temperatures (450°), isomerization is promoted. Fig. 3 shows the results of methylation of *p*-xylene at 450° over a series of fluorinated alumina catalysts. The catalytic activity of fluorinated alumina is much larger than Al_2O_3 or AlF_3 ; maximum activity has been observed with a composition of 12.7% fluorinated alumina. In the methylation of *p*-xylene, conversion reaches the maximum value of 52%.

As the cracking of the methyl groups from trimethylbenzenes at 450° is substantially negligible under our reaction conditions, the maximum in conversion is considered to be attributed to the properties of the catalysts such as acidity, acid strength, surface area, and the presence of some kind of specific chemical species on the catalyst.

Properties of the Catalysts

The BET surface area diminishes from 134 to 21 m^2/g as fluorine is incorporated (Table III). These results indicate that the collapse of alumina surface by hydrofluoric acid occurs during the preparation of the catalysts.

As can be seen from Fig. 4, the maximum acidity per unit surface area is observed at 12.7% fluorinated alumina and the maximum conversion is also seen at the same catalyst composition. The presence of strong acid sites ($H_0 = -8.2$) on fluorinated alumina has been reported.⁶⁾ In our experiments with fluorinated alumina catalysts, the acid site of $H_0 \geq +1.5$ were observed.

5) H. Mauras, *Bull. Soc. Chim. France*, **23**, 1642 (1956).

6) T.V. Antipina, O.V. Bulgakov, and V.V. Yushenko, *Kinet. Katal.*, **9**, 196 (1968); H.J. Reitsma and C. Boelhouer, *J. Catalysis*, **33**, 39 (1974).

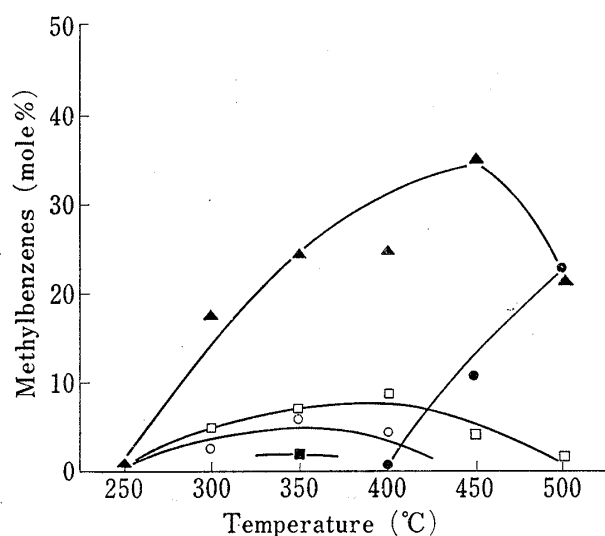


Fig. 2. Composition of Methylbenzenes vs. Temperature in Methylation of *o*-Xylene with Methanol on 12.7% Fluorine-mounted Alumina

molar ratio of xylene to methanol, 1 : 4, —▲—: trimethylbenzenes, —□—: tetramethylbenzenes, —○—: pentamethylbenzenes, —■—: hexamethylbenzene, —●—: toluene

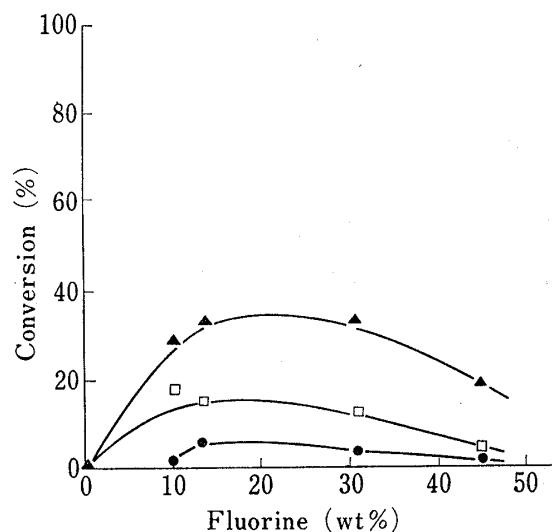


Fig. 3. Methylation of *p*-Xylene on a Series of Fluorine-containing Alumina Catalyst at 450°

molar ratio of *p*-xylene to methanol, 1 : 9, —▲—: trimethylbenzenes, —□—: tetramethylbenzenes, —●—: toluene

TABLE II. Tri- and Tetra-methylbenzene Fractions from Methylation of *o*-Xylene with Methanol at 300° and 450°

Temp. (°C)	Trimethylbenzene fraction			Tetramethylbenzene fraction	
	Pseudocumene	Hemimellitene	Mesitylene	Durene + isodurene	Prehnitene
	(%)	(%)	(%)	(%)	(%)
300	53.5	46.5	0	53.9	47.0
450	66.4	9.5	24.1	100	0

molar ratio of xylene to methanol, 1 : 4

TABLE III. Surface Area and Acidity of a Series of Fluorine-containing Alumina Catalyst

F/Al ₂ O ₃ (%)	0	9.9	12.7	20.4	30.8	56.0
Specific surface area (m ² /g)	134	106	79	64	45	21
Acidity; H ₀ ≤ +1.5 (meq/g)	0	0.55	0.60	0.30	0.20	0

Further, results of the acidity titration with Hammett indicator showed a narrow range distribution of acidity from +1.5 to +3.3; acid sites stronger than +1.5 is not found in all the catalysts.

The structure of the catalysts was assigned from the X-ray powder patterns. Results of the analysis of the catalysts used are summarized in Fig. 5. Another evidence for the structure of active species on the catalysts is represented in Fig. 5-(3); the peaks at 16.0° ($d=5.5345$), 30.8° ($d=2.9005$), 32.3° ($d=2.7691$), 46.2° ($d=1.9632$), 49.2° ($d=1.8503$), 53.8° ($d=1.7025$), 56.5° ($d=1.6273$), and 69.7° ($d=1.3479$) are attributed to $\text{AlF}_{1.96}(\text{OH})_{1.04}$.⁷⁾ In addition, the peaks of $\gamma\text{-AlF}_3$ (Fig. 5-(4)) and $\beta\text{-AlF}_3$ at 29.8° ($d=2.9955$) were observed. The

7) M.H. Read, "ASTM X-Ray Powder Data No. 11—631," Bell Telephone Laboratories, Murry Hill, 1958.

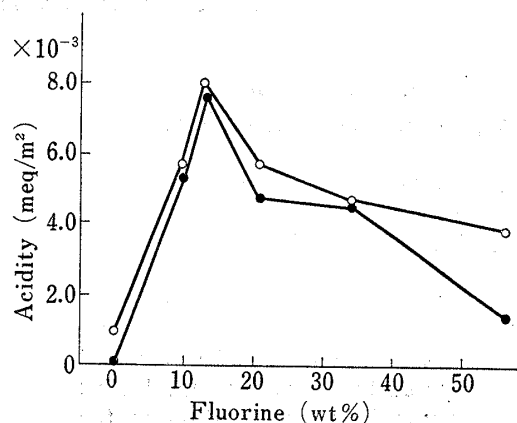
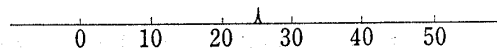


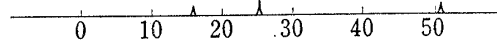
Fig. 4. Acidity of Fluorine-containing Alumina Catalyst

○..... $H_0 \leq +4.8$, ●..... $H_0 \leq +1.5$

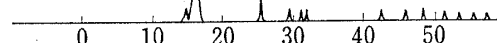
(1) F : 9.9%



(2) F : 12.7%



(3) F : 33.7%



(4) F : 56.0%

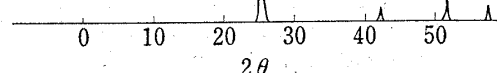


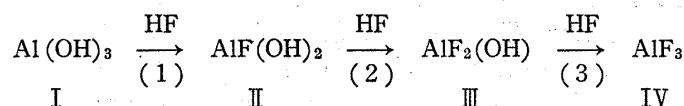
Fig. 5. X-Ray Diffraction Patterns of Hydrofluoric Acid-modified Alumina

Ni-filtered Cu $K\alpha$ -radiation was used.

intensity of $\text{AlF}_{1.96}(\text{OH})_{1.04}$ peaks increases until 33.7% of fluorine. When more fluorine is incorporated, it decreases. The intensity of the AlF_3 peaks increases until the amount of fluorine reaches 67.9%. This tendency also agrees with the conversion in the methylation of xylenes.

Active Sites on Fluorine-modified Alumina

Experiments on methylation of a series of fluorinated alumina catalysts (Fig. 3) showed that neither Al_2O_3 nor AlF_3 (F, 67.9%) is active and that intermediate fluorinated alumina catalysts are effective for methylation of xylenes. It might be possible that the active species are formed by the fluorination of Al_2O_3 according to the route from (1) to (3). Among them, II and III are expected to be active species,



and X-ray powder patterns suggest the structure III. The narrow range of H_0 value also supports the presence of a specific structure on the catalyst. It is well known that the solid acid catalyst like $\text{SiO}_2\text{-Al}_2\text{O}_3$ or zeolite has a wide range of H_0 value. It is therefore concluded from the present results that the acid sites are aluminum hydroxyfluorides with a moderate acid strength of $H_0 \geq +1.5$, explained by the electronegativity of fluorine.

Acknowledgement We are grateful to Mr. Kiyoshi Yamaoka for his technical assistance.