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Catalytic Properties of BF_3-treated Aluminas

V. Vapor-phase Alkylation of Toluene with Ethylene Using BF_3-treated Aluminas

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Vapor-phase alkylation of toluene was studied under an atmospheric pressure using a series of the BF_3-treated aluminum oxides, ranging in precalcination temperatures up to 1000°C. It was found that these modified catalysts show considerable activity in the monoalkylation of toluene, in which the reaction proportion of *o*-ethyltoluene in the product mixtures was approximately 40–50% at a low conversion of ethylene. The selectivity for the isomeric ethyltoluenes was demonstrated to undergo a remarkable change depending on the experimental conditions such as temperature, time factor (W/F) and the reactant ratios in the feed; the total conversion to *o*- and *p*-ethyltoluene was approximately 80%. It was also demonstrated that the conversion of ethylene to ethyltoluenes under appropriate reaction conditions showed the most favorable correlation with the butylamine acidity of the catalysts.

It is suggested that the selectivity to certain isomeric ethyltoluenes appears to be more dependent on reaction conditions such as the temperature rather than the presence or absence of the Bronsted centers. Comparative results in batchwise reactions with aluminum chloride catalysts are also discussed.

INTRODUCTION

In recent years, alkylation of aromatic hydrocarbons using various acidic catalysts has been the center of considerable interest to industrial chemists from a view point of the synthesis of alkylbenzenes. Although many workers have reported the use of a silica–alumina and a crystalline aluminosilicate (zeolite) for alkylation reactions with olefins or alcohols (*1–5*), little work has been done in a follow-up of product distribution in a heterogeneous system. The isomeric composition of such alkylaromatic products over solid acids has generally been described to be dependent on the catalysts employed and to be nonpredictable by the simple rules of orientation. Kutz *et al.* (*2*), for example, showed that silica–alumina and aluminum chloride favored *m*-alkylation, whereas solid phosphoric acid and iron phosphate favored *o*-alkylation in the ethylation of toluene. Recently, Yashima *et al.* (*5*) also reported that *p*-xylene can be obtained selectively by using highly active zeolite, and this selectivity is due to the presence of Bronsted acidity. However, it appears to remain unsettled as to whether such a high selectivity in the alkylation resulted mainly from the difference in the nature of the catalysts employed, since simultaneous secondary side reactions are often observed in strongly acidic catalysts under usual experimental conditions. Besides, ethylation of toluene and benzene using rare earth X-type zeolite has been shown to follow the ortho–para orientation (*6*).

Boron trifluoride-treated aluminum oxides are now well known as effective catalysts for cracking, dehydration, isomerization and other acid-catalyzed reactions (*7–12*). The high activities in such hydrocarbon conversion reactions are reportedly described to be due to the Bronsted centers developed on the surface of aluminum oxides (*9*, *12*).

This paper describes direct vapor-phase alkylation of toluene with ethylene and alcohols using a series of BF_3-treated alumina catalysts ranging in precalcination temperature from 300 to 1000°C. Comparative isomer composition of alkylation products were examined over several acidic catalysts under a variety of experimental conditions. The results from batch operations using aluminum chloride are also discussed.

EXPERIMENTAL

Materials. The toluene was standard thiophene-free grade, indicating at least a 99.5% purity. It was dried over metallic sodium and then distilled just prior to use. The methanol and ethanol with a purity of over 99% were also used. The *o*-ethyltoluene used in the isomerization runs was prepared by Gabriel's procedure (*13*), and *p*-ethyltoluene by Adams' method (*14*). The ethylene supplied by Mitsui Sekiyu Kagaku Co. (Tokyo) was used after purification by distillation. Alumina (A) used in this work was obtained by thermal decomposition of bayerite at various temperatures for 3 hr in a stream of dry nitrogen. A series of the BF_3-treated aluminum oxides ranging in precalcination temperatures up to 1000°C were prepared from the following procedure; the adsorption of BF_3 was carried out at room temperature under atmospheric pressure by exposing the dehydrated aluminum oxides for 5 min or less and then immediate evacuation was done to remove residual vapors. The characteristics of the catalysts are summarized in Table 1. Other solid acids used for a comparative study were silica–alumina and ammonium type Y zeolite. Silica–alumina catalyst (SA) is an industrial spherical product of Nikki N-631(L) containing 13%-alumina and 30–60 mesh particles were used. The ammonium form of Y-type zeolite catalyst (NH_4Y) was prepared from NaY zeolite (Linde SK-40) by repeated exchange with 10% aqueous ammonium acetate solution at 80–90°C as described elsewhere (*15*). The degree of ion exchange was higher than 90%. Aluminum chloride was purified by sublimation before use.

Apparatus and procedure. The alkylation of toluene was carried out continuously over fixed-bed catalysts under an atmospheric pressure as described elsewhere (*3*). The catalyst bed was first heated for activation at 310°C for 2 hr in a stream of dry nitrogen and then brought to the desired temperature. The ethylene and toluene were charged into the catalyst bed in such a way as to bring it to the desired molar ratio. The sample of the products were collected periodically for analysis using an ice trap. When alcohols were used, the reaction products from the catalysis formed two layers, and the upper organic layers was analyzed after saturation with calcium carbonate. Ethylation in the presence of aluminum chloride was carried out batchwise at atmospheric pressure in glass equipment, with the ethylene passing into a

TABLE 1

SURFACE PROPERTIES OF BF_3-TREATED ALUMINAS

Precalctn. temperature (°C)	Surf. area (m^2/g)	Pore vol. (cc/g)	Avg. pore diam. (Å)	Amount of adsorbed BF_3 (mmol/g)	Total acidity at $H_0 \leq -5.6$ (meq/g)
300	200	0.22	25	4.1	0.49
400	192	0.23	22	3.2	0.69
450	190	0.30	31	2.6	—
500	158	0.29	35	2.2	0.70
600	134	0.29	43	2.1	0.55
700	130	—	—	—	0.54
800	119	0.25	41	1.9	0.63
900	111	—	—	—	0.48
1000	67	0.17	51	1.0	0.34

stirred mixture of aromatic hydrocarbon and 8% catalyst (*3*, *16*). The analyses were made by glpc, equipped with 6-m (Bentone-34 + DDP) copper tubing and flame ionization detector. The yield of ethyltoluene (ET) was defined as follows;

$$\text{Yield of ET (mol \%)} = \frac{\text{ET produced (moles)}}{\text{Ethylene or Ethanol fed (moles)}} \times 100$$

RESULTS AND DISCUSSION

Alkylation of toluene with ethylene. The comparative yields of reaction products were first examined by using a series of the BF_3-treated aluminas and silica–alumina catalysts. The results are summarized in Table 2. According to Minachev *et al.* (*4*), the alkylation does not readily proceed on a silica–alumina cracking catalyst at atmospheric pressure at any given temperature up to 500°C. However, it was found in the present work that the conversion of ethylene to the isomeric ethyltoluenes at 300°C with BF_3-treated aluminas is over 31% under some reaction conditions as indicated in Table 2, and therefore these modified catalysts are considered to have a relatively high activity in the alkylation reaction. On the other hand, as shown in the product compositions, there are a few products resulting from the side reactions of which the main one is the disproportionation of toluene to benzene and xylenes and alkylation of the benzene which are formed with ethylene, as revealed in Eq. (3). The side reactions appear to be especially noticeable at temperatures above 300°C, and their portion varies distinctly with the change in the reaction conditions as given in Table 2. Accordingly, it is concluded that BF_3-treated alumina catalysts give a higher activity for the monoalkylation of toluene under mild conditions at which the formation of by-products are considerably depressed. It also indicated that the composition of ethyltoluenes is relatively close to the thermodynamic equilibrium distribution which is shown in Table 3.

TABLE 2

VAPOR-PHASE ALKYLATION OF TOLUENE WITH ETHYLENE OVER ACIDIC CATALYSTS. REACTION CONDITIONS: TEMPERATURE = 300°C; C_7H_8/C_2H_4 = 10; W/F = 19 (g/mol/hr)

	Yield of ET[b]	Composition of reaction products (mol %)				Composition of ET (mol %)		
Catalyst[a]	(mol %)	B[c]	EB + X[d]	ET	PA[e]	*p*-	*m*-	*o*-
BA-350	31.2	2.2	6.2	88.2	3.4	26.8	51.8	21.4
BA-400	57.5	1.4	3.2	89.4	6.0	27.1	50.5	22.4
BA-500	62.9	0.9	2.4	90.0	6.7	26.0	55.4	18.6
BA-600	40.0	1.7	3.6	94.7	trace	26.0	55.6	18.4
BA-800	54.8	0.8	1.7	90.5	7.0	25.9	51.7	22.4
BA-1000	31.4	1.4	1.0	94.0	3.6	25.1	46.4	28.5
SA-500	14.6	4.5	5.7	89.8	trace	25.6	53.3	21.7
SA-500[f]	11.0	16.4	32.1	51.5	—	29.9	55.5	14.6
BA-400[f]	18.4	9.3	35.6	55.1	—	28.7	54.3	17.0

[a] BA = BF_3-treated alumina, SA = silica-alumina, [b] ET = ethyltoluene, [c] B = benzene, [d] EB = ethylbenzene, X = xylenes, [e] PA = polyalkylbenzenes.

[f] Reaction was carried out at the following conditions; temperature = 450°C, W/F = 125 (g/mol/hr), C_7H_8/C_2H_4 = 4.

Since alkylation of simple aromatics with olefins is generally assumed to follow the ortho–para substitution at the first stage of the reaction, a high composition of such initially formed isomers could be observed under appropriate reaction conditions at which the side reactions shown in Eqs. (2) and (3) are possibly depressed. Several reaction conditions including the temperature, the time factor (W/F),* and

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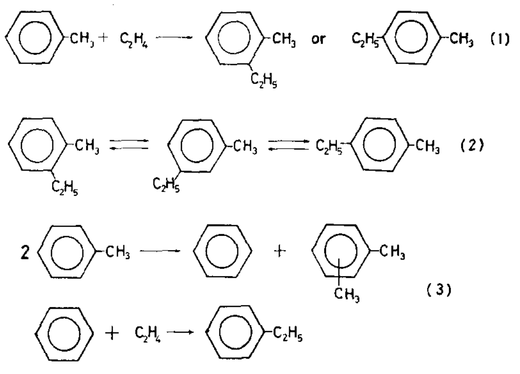
* The time factor was defined as follows: W/F (weight of catalyst)/(feed rate), g/mol/hr.



the molar ratio of the reactants were examined by using BF_3-treated aluminas and other solid acids. The results are presented in Table 4. It was found that under such experimental conditions isomeric ethyltoluenes were the main products and the by-products described above were only at a trace level. This would be consequently an optimum condition for selective monoethylation of toluene with ethylene and BF_3-treated alumina catalysts.

The composition of ethyltoluenes varied remarkably, depending upon the experimental conditions. Figure 1 shows a typical example in which the effect of the reaction temperature on the composition of isomeric ethyltoluenes is presented. While the reaction temperature decreases from 300 to 230°C, the conversion of ethylene to ethyltoluenes proportionally decreases by a factor of about 13. Of the distribution of monoalkylation products, *o*-ethyltoluene increases greatly from 25.8 to 46.3%, and in contrast, *m*-isomer decreases sharply from 48.8 to 27.9%. Such a change in the respective composition of the *o*- and *m*-isomer was also observed in the case of changes of the reactant molar ratio, and in changes of the time factor (*W/F*). Accordingly, it would be concluded that the composition of *o*- and *m*-alkylation products deviates remarkably from the thermodynamical equilibrium concentration under such mild conditions indicating the obedience to the

TABLE 3

VALUES OF THE EQUILIBRIUM CONCENTRATION OF ETHYLTOLUENES[a]

Ethyl-toluenes	Composition, in mole fraction		
	227°C	327°C	427°C
Ortho	13.9	16.3	18.3
Meta	50.3	50.3	50.2
Para	35.8	33.4	31.5
Ortho/Para	0.39	0.49	0.58

[a] Calculated from data of Taylor *et al.* (*17*).

TABLE 4

VAPOR-PHASE ALKYLATION OF TOLUENE WITH ETHYLENE OVER ACIDIC CATALYSTS UNDER VARIOUS CONDITIONS

Catalyst	React. temp. (°C)	Time factor (*W/F*)	C_7H_8/C_2H_4	Conv. (%)	Compostn of ET (mol %)		
					p-	*m*-	*o*-
BA-400	205	50	10	20.4	26.8	31.9	41.3
	255	50	10	32.2	25.8	48.4	25.8
	300	50	10	57.5	27.1	50.5	22.4
BA-600	300	5	10	1.8	26.4	35.9	37.7
	300	19	10	40.0	26.0	55.6	18.4
	300	50	10	70.0	26.8	52.7	20.5
BA-600	300	19	2	11.7	27.3	41.0	31.7
	300	19	5	16.4	24.1	42.6	33.3
	300	19	10	40.0	26.0	55.6	18.4
SA-500	300	50	10	14.6	25.0	53.5	21.7
BA-450	255	47.5	5	11.9	25.2	33.9	40.9
BA-800	255	47.5	5	10.4	23.4	33.2	43.4
SA-450	255	47.5	5	17.3	26.3	46.0	27.7
NH_4Y-500	255	47.5	5	20.5	27.7	57.0	15.3
	218	47.5	5	19.2	27.8	49.7	22.5
NH_4Y-700	255	47.5	5	12.5	26.9	47.4	22.7

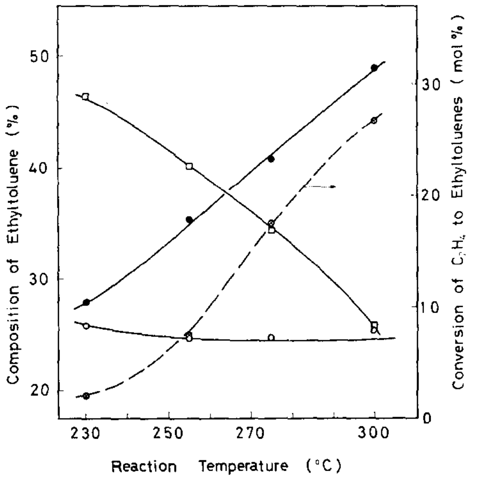


FIG. 1. Effect of reaction temperature. Conditions: catalyst BA-450; $W/F = 36.4$ (g/mol/hr); $C_7H_8/C_2H_4 = 5$. -□- *o*-ethyltoluene, -●- *m*-ethyltoluene, -○- *p*-ethyltoluene, -⊗- conversion of C_2H_4 to ethyltoluenes.

ortho–para orientation. The composition of *p*-ethyltoluene was constantly close to the thermodynamical concentration of 33.4% at 327°C, independently of such experimental conditions in this work.

The alkylation of toluene in the presence of aluminum chloride was carried out batchwise at atmospheric pressure and temperatures ranging from −20 to 80°C. The results are summarized in Table 5. It is indicated that the ratio of *o*- and *m*-ethyltoluenes produced at temperatures below 20°C is quite different from the thermodynamical ratio, as shown in the case of flow-type reactions. This clearly reveals that the composition depends to a certain degree upon the conversion of ethylene and gives a better coincidence with the results in the same alkylation reaction in the presence of aluminum chloride–nitroalkane catalyst, which has been interpreted not to give rise to a secondary conversion of the initial reaction products (*16*). The general orientation in the isomer composition of ethyltoluenes is in good accordance with that of Kutz *et al.* (*2*). Their results indicated that strong acidic catalysts favored *m*-alkylation indicating corresponding thermodynamical equilibrium concentrations, whereas relatively weak acids favored *o*-alkylation in the ethylation of toluene.

TABLE 5

LIQUID-PHASE ALKYLATION OF TOLUENE WITH ETHYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Reaction temperature (°C)	$AlCl_3$[a] (wt %)	C_2H_4 absorbed (vol %)	Composition of Ethyltoluenes (mol %)		
			o-	*m*-	*p*-
−20	8	25.0	51.4	25.6	23.0
20	8	58.7	51.8	25.4	22.8
50	8	80.5	31.2	41.4	27.4
80	8	97.5	11.1	64.9	24.0

[a] Based on the toluene used.

Recent results of Yashima *et al.* (*5*) described that in the alkylation of toluene with methanol, *p*-xylene can be selectively formed by using highly active zeolite catalysts and the selectivity is due to the presence of the strong Brønsted centers. Now, other comparative runs were carried out using several solid acids, which are believed to be generally of the Bronsted type. The result listed in Table 4 indicates clearly that *o*-ethyltoluene is obtained selectively at lower conversions with relatively weak acids, and the amount of the *m*-isomer increases in catalysts such as NH_4Y-500 that is known to be a strong acid. This would support the fact that the final composition of the product depends upon the degree of conversion resulting from the difference in acidic properties, especially in the number of strong acid centers of the catalysts. Since BF_3-treated aluminas (e.g., BA-400 or BA-800) and silica–alumina (SA-450) have pores of 18 to 77 Å (*7*), an in contrast, the ammonium type Y zeolite (NH_4Y-500) has entry pores of ca. 10 Å, it seems to be questionable as to whether the secondary isomerization reaction of the initially formed alkylaromatic products is depressed only in such a supercage of zeolite catalysts as discussed by Yashima *et al.* (*5*).

Alkylation of toluene with alcohols. Alkylation of toluene with methanol and ethanol was also studied in the same conventional steady-state reactor, principally to follow the isomer distribution of the

TABLE 6
VAPOR-PHASE ALKYLATION OF TOLUENE WITH ALCOHOLS
(CONDITIONS: W/F = 120 g/mol/hr; C_7H_8/ROH = 2)

Catalyst	Alcohol	React. temp. (°C)	Yield of xylene[a] (mol %)	Composition of xylene (mol %)		
				p-	*m*-	*o*-
BA-500	CH_3OH	225	1.9	25.4	20.3	54.3
	CH_3OH	310	7.7	26.9	23.0	50.1
	CH_3OH	380	13.9	26.7	36.4	36.9
NH_4Y-500	CH_3OH	225	26.5	43.3	37.0	19.7
	CH_3OH	310	45.3	26.7	50.4	22.9
BA-500	C_2H_5OH[b]	235	8.4	26.5	26.7	46.8
	C_2H_5OH[b]	330	16.1	25.3	55.5	19.2

[a] In the case of C_2H_5OH, yield of ethyltoluene.

[b] Reaction was carried out under the following conditions; W/F = 80 g/mol/hr, C_7H_8/C_2H_5OH = 2.

products. The results are presented in Table 6. It was shown again that *o*-ethyltoluene can be obtained selectively at a low conversion of ethanol, whereas the amount of *m*-isomer greatly increases with the increase in conversion, as described in the case of alkylation with ethylene. The comparative runs with methanol were carried out by using two catalysts, BA-500 and NH_4Y-500, which are of the Brønsted type, and the experimental conditions are similar to those in Ref. (*5*). As can be seen from the results presented in Table 6, high yields of *o*- or *p*-xylene are observed at relatively low conversions with both catalysts. However, the isomer distribution of the reaction products is appreciably closer to the corresponding thermodynamical equilibrium concentrations under more severe conditions. Although the selectivities to *o*- and/or *p*-xylenes differ over the two catalysts, it is clearly shown that the first stage reaction products are considerably left unchanged in their composition under appropriate conditions.

From the experimental results throughout the work, the following conclusions were obtained. A series of the BF_3-treated aluminum oxides indicated an excellent activity for selective monoalkylation of toluene as shown in Fig. 2, and this activity for ethylation showed a good correlation with the overall acid amount of the catalysts, as reported in certain other acid-catalyzed reactions (*7–9*). The composition of the alkylaromatic products greatly deviated from the corresponding thermodynamical equilibrium distribution, independent of the catalysts which are believed to be considerably different in nature depending upon their precalcination temperatures (*8*). There was no decisive evidence substantiating that the high selectivity to *o*-ethyltoluene in the product mixtures was strongly influenced by the presence of Brønsted acidity under a variety of experimental conditions in this work. This high selectivity may be actually observed at a

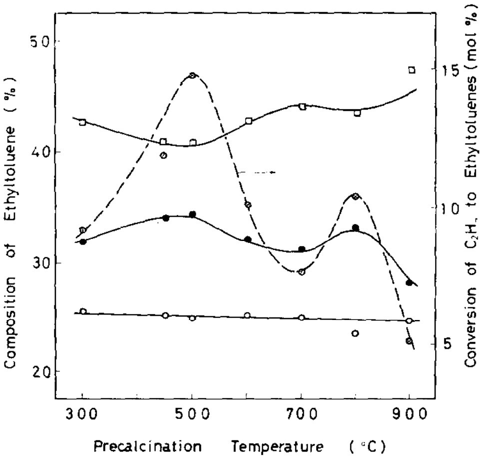


FIG. 2. Toluene-ethylene alkylation over a series of BF_3-treated aluminas. Conditions: Reaction temperature = 255°C; W/F = 47.5 (g/mol/hr); C_7H_8/C_2H_4 = 5. Symbols defined in Fig. 1.

TABLE 7

Isomerization of *o*- and *p*-Ethyltoluene over BA-500

Reactant	*o*-ET			*p*-ET		
Reaction temperature (°C)	240	300	325	240	300	325
W/*F* (g/mol/hr)	80	80	80	80	80	80
Composition of react. products (mol %)						
Toluene	8.7	10.3	16.9	4.5	8.4	16.3
Ethylbenzene	trace	1.1	1.9	trace	1.0	2.1
Xylenes	0	trace	1.1	0	trace	1.3
Ethyltoluenes	86.7	86.8	77.8	95.5	88.7	77.3
Polyalkylbenzenes	4.6	1.8	2.3	trace	1.9	3.0
Composition of ethyltoluene (mol %)						
Para	13.8	20.1	25.3	68.7	49.2	26.9
Meta	50.3	54.2	58.7	28.3	42.6	58.3
Ortho	35.9	25.7	16.0	3.0	8.2	14.8

lower conversion of reactants in which the overall rate of alkylation is generally slow, since simultaneous side reactions including isomerization and disproportionation reaction would be less significant under such conditions. Further, since the ortho/para ratios were considerably changed depending upon the experimental conditions and catalysts employed as shown in Tables 4 and 6, it was suggested that alkylation was not always in the operation of steric effects. An example of isomerization of pure ethyltoluene is given in Table 7. It is indicative of the relative composition of secondary side reaction products with the change in reaction temperature. The results by Yashima *et al.* (*5*), in fact, were those seen in relatively low conversions of methanol. Under such milder conditions, we could selectively obtain the monoalkylation products with high compositions of initially formed *o*- or *p*-isomer. Thus, one may consider that although the overall activities for alkylation reactions in a heterogeneous system are assumed to be even greater due to the number of the strong acid centers of the catalysts employed, the high selectivity to *o*- and/or *p*-isomer under milder conditions in this work does not result from a difficult occurrence of the secondary reactions within such a supercage but results from the obedience to the "normal" ortho–para substitution as demonstrated by Venuto (*6*). At more severe conditions, alkylation does not follow such a simple rule of orientation.

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