Catalytic Isomerization of Xylenes over Aluminium Bromide Supported on Carbon

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The reactions of xylenes over AlBr_3 and AlBr_3/C were studied with a continuous flow reactor. Xylenes and small amounts of toluene were observed mainly in the flow downstream from the reactor. The relative rate constants and the activation energies of the reactions have been measured. The reaction profile of isomerization of xylenes is of a *meta*-convex type. When AlBr_3 was supported on graphite and molecular-sieving carbon, the reaction profiles were varied. The ratio, *para*-xylene/*ortho*-xylene formed from *meta*-xylene was in equilibrium in the low conversion region over AlBr_3 , but over AlBr_3/C , the amount of *para*-xylene found was greater than that at equilibrium. The results suggest the structure effect of xylene isomer molecules. *meta*-Xylene was more predominantly formed from both *ortho*-xylene and *para*-xylene. The product ratios, *meta*/*ortho* and *meta*/*para*, were, respectively, higher than those at equilibrium. The results are consistent with the simple consecutive, proposed 1,2-methyl shift mechanism.

1. Introduction

Much attention has been paid to the characteristic properties of graphite intercalation compounds, and their catalytic properties have been investigated extensively in various reactions.^{1),2)}

Watanabe et al.³⁾ reported a molecular-sieving type physisorption of alkali metal graphite at 77 K. Tsuchiya et al.^{4),5)} have observed structure-selectivity in hydrogenation and isomerization of olefins over KC_{24} . The results have been explained on the basis of the molecular-sieving-like effect of the compound.

Xylenes (1,2-, 1,3- and 1,4-dimethylbenzene) are catalytically isomerized over some acid catalysts. It can therefore be expected that a certain isomer of xylenes is selectively formed over some acid catalysts with molecular-sieving effects.

Having the isomerization of xylenes investigated, the interest in the present study has been centered on AlBr_3/C , where graphite and molecular sieving carbon were employed as the carbon.

2. Experimental

A usual flow type system with a by-pass at at-

mospheric pressure was employed to follow the progress of reaction, and nitrogen was used as the diluent. AlBr_3 supplied from Katayama Chemical Co., Ltd., was purified by sublimation. Graphite used was Union Carbide's spectroscopic-grade powder and molecular-sieving carbon (MSC) was supplied by Takeda Chemical Industry, Ltd.

The AlBr_3 /graphite samples used as catalysts were prepared in vacuo in a manner similar to that employed previously.⁶⁾ The method is illustrated in **Fig. 1**. The apparatus consisting of an upper and a lower vessel was evacuated after AlBr_3 had been introduced. The lower vessel was then heated at 385 K to sublime AlBr_3 onto the cold center pole in the upper vessel for purification. After the lower vessel was sealed off, argon was introduced into the upper vessel. The AlBr_3 sublimed was scraped off in the argon atmosphere (**Fig. 1b**) and removed into another vessel (**Fig. 1c**).

The purified AlBr_3 and dried graphite were mixed (**Fig. 1d**) and heated at 488 K for 30 min to prepare AlBr_3 /graphite (**Fig. 1e**). For the preparation of AlBr_3/MSC , MSC was used instead of graphite.

The catalyst prepared beforehand was fixed in

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Fig. 1 Preparation of AlBr_3 /Graphite

- (a) : AlBr_3 in the lower vessel was sublimed onto the cold center pole in the upper vessel, and the lower vessel was sealed off
 (b) : AlBr_3 sublimed was scraped off in Ar atmosphere
 (c) : AlBr_3 scraped off was removed into another vessel
 (d) : Purified AlBr_3 and dried graphite were mixed
 (e) : The mixture was heated to form AlBr_3 /graphite

a flow system. In the meantime, a nitrogen stream with the reactant was flowing only through the by-pass; then the stream was diverted to flow through the reactor. For each run the rate of nitrogen flow was ca. $25 \text{ cm}^3/\text{min.}$, and the amount of catalyst used was $0.3\sim 0.8 \text{ g.}$ The reaction mixtures were analysed by gas chromatography.

Xylenes were obtained from Tokyo Kasei Kogyo Co., Ltd., and purified by distillation. Their purity, more than 99%, was confirmed by gas chromatography. Before each run, the catalyst was treated with a nitrogen stream at 373 K for 2 h.

3. Results

Figure 2 shows how the composition of the vent stream except the diluent, from the reactor changed with time on stream over AlBr_3 /graphite at 358 K when *meta*-xylene (1,3-dimethylbenzene) was the reactant. The reaction is seemed to reach a steady state after 100 min. on stream. *ortho*-Xylene (1,2-dimethylbenzene) and *para*-xylene (1,4-dimethylbenzene) as well as toluene were observed. No isomers of trimethylbenzenes were observed.

Figure 3 shows the results when *para*-xylene was introduced over AlBr_3 /MSC at 332 K. The reac-

Fig. 2 Composition Change of Gas Phase with Time on Stream

tion seemed to be in a steady state after 200 min. on stream. *meta*-Xylene and *ortho*-xylene as well as toluene were observed, but no isomers of trimethylbenzenes were observed. In all cases in which the reactant was an isomer of xylenes and the catalyst was AlBr_3 /graphite, AlBr_3 /MSC, or AlBr_3 alone, toluene was observed. Trace amounts (less than 0.5%) of trimethylbenzenes were observed when *ortho*- and *para*-xylene were passed over

Reactant: *para*-xylene, Reaction temp.: 332 K, Catalyst: AlBr_3/MSC

Fig. 3 Composition Change of Gas Phase with Time on Stream

AlBr_3 . The individual isomers of trimethylbenzenes, however, could not be identified.

No isomer of trimethylbenzenes was observed in the reaction over $\text{AlBr}_3/\text{graphite}$ and over AlBr_3/MSC .

The isomerization of xylenes was almost first-order with respect to the pressures of the reactants. From the rates of reaction and the selectivity ratios, e. g. *ortho/para*, all six of the rate constants,

Scheme 1

k_r , expressed by Scheme 1, and the activation energies, E_r , of reaction were determined, where $r = om, mo, mp, pm, po$, and op . The rate constants at 343 K and the activation energies are shown in **Tables 1** and **2**, respectively.

The rate constant of isomerization of *ortho*-xylene was the largest when AlBr_3 alone was the catalyst. On the other hand, when AlBr_3 was

Table 1 Rate Constants of Isomerization of Xylenes at 343 K

Catalyst	AlBr_3	$\text{AlBr}_3/\text{Graphite}$	AlBr_3/MSC
	$(10^6 \text{ k/mol} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$		
k_{om}	9.0	10.2	4.5
k_{op}	1.9	3.1	0.9
$k_{om} + k_{op}$	10.9	13.3	5.4
k_{mp}	2.4	11.7	4.4
k_{mo}	2.8	3.2	1.4
$k_{mp} + k_{mo}$	5.2	14.9	5.8
k_{po}	1.4	2.2	0.6
k_{pm}	5.9	28.5	10.7
$k_{po} + k_{pm}$	7.3	30.7	11.3

Table 2 Activation Energies of Isomerization of Xylenes

Catalyst	AlBr_3	$\text{AlBr}_3/\text{Graphite}$	AlBr_3/MSC
	$E/\text{kJ mol}^{-1}$	$E/\text{kJ mol}^{-1}$	$E/\text{kJ mol}^{-1}$
E_{om}	8.3	32.8	21.5
E_{op}	32.7	52.0	23.4
E_{mp}	58.5	38.0	41.6
E_{mo}	51.5	44.6	26.9
E_{po}	34.0	59.5	24.8
E_{pm}	21.1	32.1	40.9

fixed on graphite and MSC, the isomerization of *para*-xylene proceeded at the highest rate.

4. Discussion

Figure 4 shows the reaction profiles of isomerization of xylenes over AlBr_3/MSC (solid lines) and over AlBr_3 alone (dotted lines) at 353 K. Since the formation of toluene could be considered to be

Fig. 4 Reaction Profiles of Isomerization of Xylenes over AlBr_3/MSC (Solid Lines) and over AlBr_3 alone (Dotted Lines) at 353 K

Fig. 5 Reaction Profiles of Isomerization of Xylenes over $\text{AlBr}_3/\text{Graphite}$ (Solid Lines) and over AlBr_3 alone (Dotted Lines) at 323 K

Fig. 6 Molecular Dimensions of *ortho*-, *meta*- and *para*-Xylene

the side reaction, the reaction profiles were consisted of only xylene isomers. These profiles have been obtained from the rate constants in a manner similar to that described previously.⁸⁾ A *meta*-convex type profile was obtained.

When *meta*-xylene was the reactant, *para*-xylene and *ortho*-xylene were formed over AlBr_3 in the equilibrium ratio at the low conversion region as shown with the dotted lines. Over AlBr_3/MSC , on the other hand, *para*-xylene was formed more selectively than the equilibrium value at the low conversion region as shown with the solid lines.

Figure 5 shows the reaction profiles of isomerization of xylenes over $\text{AlBr}_3/\text{graphite}$ (solid lines) and AlBr_3 alone (dotted lines) at 323 K. A *meta*-convex type profile was also obtained. *para*-Xylene was formed from *meta*-xylene over $\text{AlBr}_3/\text{graphite}$ more selectively than the equilibrium value indicated. These results shown in **Figs. 4** and **5** suggest the structure effects of xylene isomer molecules. The profiles seemed not to vary with the amount of AlBr_3 supported on carbon.

The molecular dimensions widths of *ortho*-, *meta*- and *para*-xylene are 7.46, 7.41 and 6.68 Å, respectively, as shown in **Fig. 6**. It has been suggested that the isomerization of xylenes should take place by the 1,2-methyl shift mechanism.^{9),10)} If most of the reaction takes place on the AlBr_3 held in the layer structure of graphite and in the slit structure of molecular sieving carbon, the dimension of space in the layer and the slit structure will be important. The layer distance of graphite increases from 5.35 Å to 10.0 Å by intercalation of AlBr_3 ¹¹⁾, and three kinds of xylene isomer molecules can be held in the layer of graphite. The slit width of molecular sieving carbon is about 5 Å, and the thickness of benzene ring is 3.2 Å.¹²⁾ Accordingly, xylene molecules can also be held in the slit structure. In the narrow space, however, a smaller molecule may be more favorably activated for reaction. Therefore, *para*-xylene may be more readily formed than *ortho*-xylene from

meta-xylene, since the direction from *meta*-xylene to *para*-xylene decreases the molecular dimension. The results are consistent with the 1,2-methyl shift mechanism. *meta*-Xylene was more predominantly formed from *ortho*-xylene over both $\text{AlBr}_3/\text{graphite}$ and AlBr_3/MSC as shown in **Figs. 4** and **5**. These results can not be explained on the basis of the molecular dimension, but they can be by the 1,2-methyl shift mechanism; *para*-xylene is formed by the subsequent isomerization of the beforehand-formed *meta*-xylene. One more step is necessary for *para*-xylene than for *meta*-xylene. The product ratio, *meta/para*, accordingly, became higher than that at equilibrium. In the case of *para*-xylene, the result can also be explained by the 1,2-methyl shift mechanism.

For the formation of toluene, two possibilities could be considered: (1) disproportionation of xylenes and (2) demethylation of xylenes. If toluene was formed by disproportionation of xylenes as shown by Eq. (1), equal molar amounts of trimethylbenzenes would have been observed.

Figure 7 shows the equilibrium composition of a xylenes-toluene-trimethylbenzenes system calculated on the basis of thermodynamic data⁷⁾, where isomerization of xylenes, disproportionation of xylenes and isomerization of trimethylbenzenes were considered. The details of calculation are described in the Appendix. Among the trimeth-

Fig. 7 Equilibrium Composition of Xylenes-Toluene-Trimethylbenzenes System

ylbenzenes, 1,2,4-trimethylbenzen would thermodynamically be predominantly formed. The fact that the formation of trimethylbenzenes could not be observed might suggest that toluene was not predominantly formed by disproportionation of xylenes, instead demethylation of xylenes might have taken place. To elucidate the point, the material balance of benzene rings was calculated in some cases. About 70% of the benzene rings introduced were recovered in the reaction. The amount of the benzene rings recovered was estimated from the amount of toluene formed and from the amounts of xylenes formed and unreacted. Since trimethylbenzenes may be more strongly chemisorbed than toluene and xylenes on the catalyst, the possibility that trimethylbenzenes formed had hardly desorbed from the catalyst cannot be dismissed.

The chemisorbed species may be more readily oxidized than graphite. When the feeding of the reactant into the carrier gas was stopped, no hydrocarbon was detected in the downstream from the reactor. Air was then introduced, and carbon dioxide was observed in the downstream. The fact can be explained on the basis that the surface species formed from xylenes was oxidized to form carbon dioxide. A likely candidate for the surface species may be the CH_3 group demethylated from xylenes, trimethylbenzenes, and others, but it has not yet been identified; it awaits further investigation.

5. Conclusion

$\text{AlBr}_3/\text{graphite}$ and AlBr_3/MSC show structure selectivity in the isomerization of xylenes in which 1,2-methyl shift mechanism has been considered.

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Appendix

The calculation of such bimolecular reaction shown as Scheme 1 is rather complicated. Two

mols of reactant, X_1 , react to form one mol of product, Q , and one mol of a mixture of isomers, Y_i , without changing the total amounts of sub-

stances of X_i , Q and Y_i , where X_1 isomerizes to a mixture of isomers, X_i .

The mol fractions of the individual components at equilibrium are as follows;

$$X_i : x_{ie} = \frac{x_i}{2} \quad (\text{A.1})$$

$$Q : q_e = \frac{q}{2} \quad (\text{A.2})$$

$$Y_i : y_{ie} = \frac{y_i}{2} \quad (\text{A.3})$$

The equilibrium constant, K_1 , is

$$K_1 = \frac{\frac{q}{2} \cdot \frac{y_1}{2}}{\left(\frac{x_1}{2}\right)^2} = \frac{q y_1}{x_1^2} \quad (\text{A.4})$$

Since

$$y_2 = K_{y_2} \cdot y_1 \quad (\text{A.5.1})$$

$$y_3 = K_{y_3} \cdot y_2 = K_{y_3} \cdot K_{y_2} \cdot y_1 \quad (\text{A.5.2})$$

$$y_i = K_{y_i} \cdot \dots \cdot K_{y_3} \cdot K_{y_2} \cdot y_1 \quad (\text{A.5.3})$$

and

$$y_1 + y_2 + y_3 + \dots + y_i = q \quad (\text{A.6})$$

By definition

$$(1 + K_{y_2} + K_{y_2} \cdot K_{y_3} + K_{y_2} \cdot K_{y_3} \cdot K_{y_4} + \dots) = K_y \quad (\text{A.7})$$

$$q = K_y \cdot y_1 \quad (\text{A.8})$$

Similarly

$$x_2 = K_{x_2} \cdot x_1 \quad (\text{A.9.1})$$

$$x_3 = K_{x_3} \cdot x_2 = K_{x_3} \cdot K_{x_2} \cdot x_1 \quad (\text{A.9.2})$$

$$x_i = K_{x_i} \cdot \dots \cdot K_{x_3} \cdot K_{x_2} \cdot x_1 \quad (\text{A.9.3})$$

By definition

$$K_{x_2} + K_{x_2} \cdot K_{x_3} + K_{x_2} \cdot K_{x_3} \cdot K_{x_4} + \dots = K_x \quad (\text{A.10})$$

When the reaction proceeds

$$x_1 = 2 - (q + x_2 + x_3 + \dots) - (y_1 + y_2 + \dots) \quad (\text{A.11})$$

By proper substitution

$$x_1 = 2 - \left(\frac{2\sqrt{K_1} \cdot K_y + \sqrt{K_y} \cdot K_x}{\sqrt{K_1}} \right) y_1 \quad (\text{A.12})$$

From (A.4) and (A.12)

$$y_1 = \frac{2\sqrt{K_1}}{K} \quad (\text{A.13})$$

$$x_1 = \frac{2\sqrt{K_y}}{K} \quad (\text{A.14})$$

where

$$K = \sqrt{K_y} + 2\sqrt{K_1} \cdot K_y + \sqrt{K_y} \cdot K_x \quad (\text{A.15})$$

From (A.5) and (A.13)

$$y_i = \frac{2\sqrt{\bar{K}_1} \cdot K_{yi}}{K} \quad (i \geq 2) \quad (\text{A.16})$$

From (A. 9) and (A. 14)

$$x_i = \frac{2\sqrt{\bar{K}_y} \cdot K_{xi}}{K} \quad (i \geq 2) \quad (\text{A.17})$$

x_{ie} , y_{ie} and q_e , can be accordingly calculated.

Nomenclature

$K_i (i=1, 2, \dots)$:

Equilibrium constant

x_i : Content of component X_i at equilibrium

y_i : Content of component Y_i at equilibrium

q : Content of component Q at equilibrium

$r_e (r=Q, X_i \text{ and } Y_i)$:

Concentration of Component R ($R=Q, X_i$ and Y_i) at equilibrium

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要 旨

グラファイト担持臭化アルミニウム触媒によるキシレンの反応

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グラファイト-アルカリ金属層間化合物は気体の吸収に対して分子ふるい作用を示す。そのうちのひとつ KC_{24} は、オレフィンの異性化反応、水素化反応において分子ふるい選択性を示す。キシレンは酸触媒で異性化される。したがって、適当な酸とグラファイトまたはモレキュラーシービングカーボン(MSC)とを組み合わせると、キシレンの異性化に対して、反応分子の構造に由来する選択性を示す触媒の調製が期待される。本報文は酸として臭化アルミニウムを用いた結果の報告である。

$AlBr_3$ /グラファイト触媒(調製法 Fig. 1)により *m*-キシレンを反応させると、*o*-キシレンと *p*-キシレンのほかにトルエンが生成したが、トリメチルベンゼンは認められなかった(Fig. 2)。 $AlBr_3$ /MSC 触媒により *p*-キシレンを反応させると、*m*-キシレン、*o*-キシレンのほかトルエンが生成したが、トリメチルベンゼンは認められなかった(Fig. 3)。

キシレン類の異性化は一次反応で進行した。そこで、キシレン異性体間の相互変換の反応速度定数および活性化エネルギーを求めた(Tables 1, 2)。

これらの速度定数をもとにして、キシレン異性化反応のネットワーク解析を行い、メタ凸型プロフィールを得た。これからわかるように、 $AlBr_3$ /MSC、 $AlBr_3$ /グラファイトのいずれの場合も、 $AlBr_3$ 単独(点線で表示)を触媒とした場合とは著しくプロフィールが異なる。特に *m*-キシレンを出発原料とした場合に注目すると、 $AlBr_3$ 単独を触媒とした場合は生成する *o*-キシレンと *p*-キシレンの比は平衡組成の比であるが、 $AlBr_3$ /

グラファイト触媒および $AlBr_3$ /MSC 触媒の場合は、平衡値よりも *p*-キシレンが *o*-キシレンよりも多く生成する。これは *m*-キシレンから *p*-キシレンになる方が、*o*-キシレンになるよりも分子の大きさが小さくなるためと考えれば、従来提案されている 1,2-メチル基移動機構で説明できる(Fig. 6)。

p-キシレンおよび *o*-キシレンを出発原料としたとき、*m*-キシレンが多く生成し、*m/o* 比および *m/p* 比は、それぞれ $AlBr_3$ /グラファイトおよび $AlBr_3$ /MSC いずれの場合でも平衡値より大きかった。この結果も、1,2-メチル基移動機構と矛盾しない。

トルエンの生成には、キシレンの不均化と脱メチル化が考えられる。キシレンを不均化すると、トルエンとトリメチルベンゼンが生成するので、キシレンの不均化、キシレンの異性化、トリメチルベンゼンの異性化の三種類の反応を考えて、トルエン-キシレン類-トリメチルベンゼン類系の平衡組成図を求めた(Fig. 7)。これからわかるように、トルエンがキシレンの不均化により生成したとすれば、トリメチルベンゼン類も同時に生成しなければならない。したがって、一見不均化により生成したものではないように思われる。

しかし、出発原料中のベンゼン環の物質収支を計算すると、約 70% しか回収されていない。したがって、もし生成トリメチルベンゼン類が強く吸着したため気相に脱離して出て来ないものとすれば、不均化の可能性も除外はできない。反応中の吸着種の同定については、今後研究すべき課題である。

Keywords

Aluminium bromide catalyst, Graphite, Isomerization, Molecular sieving carbon, Shape selective, Xylene