# The Effects of Higher-boiling Compounds on the Liquid-phase Isomerization of *m*-Xylene over a Silica-Alumina Catalyst under Pressure

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The liquid-phase isomerization of *m*-xylene was studied over a silica-alumina catalyst under pressure on the additions of 2% of 8 higher-boiling compounds and 20—50% of benzene to reactant *m*-xylene. The catalyst activity in the isomerization was not greatly affected by hexamethylbenzene, naphthalene, α-methylnaphthalene, diphenyl, or *s*-dibenzyl. On the other hand, the activity was greatly lowered by 1,6-dimethylnaphthalene, diphenylmethane, and anthracene. Moreover, a very rapid exchange reaction occurred between an aromatic ring of diphenylmethane and a reactant xylene molecule, while the content of the isomerization product decreased linearly with an increase in the amount of benzene. From these results, the chemisorption states of xylene were discussed as follows. Most xylene molecules may be deduced to be chemisorbed on acid sites by those benzene rings. On the other hand, the fact that diphenylmethane inhibits the isomerization implies the existence of such a chemisorption state of xylene as a methylbenzylcarbonium ion, which may be an intermediate in the disproportionation reaction of xylene. The acid sites available for the chemisorption of diphenylmethane and for the disproportionation were speculated to be common and to have both acidic characters, protonic and Lewis.

In an earlier paper[1] the present authors reported that a silica-alumina catalyst revealed high activity in the isomerization of *m*-xylene in a liquid-phase reaction under pressure and that no practical decline in activity was observed even after 20 days at a temperature below 380°C. The enhanced activity in the liquid-phase reaction may be ascribed to the cleaning effects of the reactant: the higher-boiling by-products, which are inhibitors, are successively dissolved in the liquid reactant. The dissolution effect suggests the possibility of experiments using higher-boiling compounds in the liquid-phase reaction.

The components of the higher-boiling by-product were studied by the mass spectrometry.[1] However, they could not be identified precisely, since several probable components have the same mass number. This problem may be solved by comparing the effects of pure higher-boiling compounds on the isomerization of *m*-xylene with those of the higher-boiling by-products.

The first purpose of this paper is to study the effects of the pure higher-boiling compounds on the isomerization of *m*-xylene and to discuss the above problem. The second is to examine the pure higher-boiling compounds for the relative intensity of chemisorption on the acid site available for the reactions of xylene and to discuss the chemisorption state of xylene.

## Experimental

The equipment used was the same as that described in previous papers.[1,2] The catalytic activity was measured by 4 hr's operations at a feed rate of 24 g/h under a pressure of 300 kg/cm$^2$, with using pure *m*-xylene or *m*-xylene solutions containing 2 weight per cent of the higher-boiling compounds. Between these measurements, pure *m*-xylene was fed into the reactor at a rate of 6 g/h in order to desorb the higher-boiling compounds from the catalyst surface or to keep the catalytic activity constant.[1] A temperature as low as 280°C was selected as the reaction temperature, because the change in catalytic activity could be observed sensitively at a low concentration of the isomerization product.

The catalyst used (2.5 g) was powdered Nikki N633L silica-alumina; it was calcined at a temperature of 500°C for 20 hr. The purity of *m*-xylene (produced by Mitsubishi Gas Chemical Co., Inc.) was 99.6%, and it contained 100—130 ppm of water. The other reagents were commercial grade and were used for the experiments without any further purification.

The product was analyzed by gas chromatography at 57°C. The column used for this measurement was 4 m in length, 1 mm in dia., and packed with 5% bentone 34+5% DIDP on diasolid L (100—200 mesh). The higher-boiling compounds were analyzed by means of a Hitachi double-beam mass spectrometer. The mass spectra were obtained at an ionization voltage as low as 15 V in order to allow only the parent peaks of the compounds to appear.

## Results

The higher-boiling compounds used were hexamethylbenzene, naphthalene, α-methylnaphthalene, 1,6-dimethylnaphthalene, diphenyl, diphenylmethane, *s*-dibenzyl(1,2-diphenylethane), and anthracene; the results are shown in Figs. 1—5. In these figures, the arrow signs designate the results of 4 hrs' operations using *m*-xylene solutions containing 2 weight per cent of high-boiling compounds. The other points show results when pure *m*-xylene was used as the reactant. The figures show that hexamethylbenzene, naphthalene, α-methylnaphthalene, diphenyl, and *s*-dibenzyl did not greatly affect the activity in the isomerization of *m*-xylene. On the other hand, 1,6-dimethylnaphthalene, diphenylmethane, and anthracene lowered the activity greatly. However, when reactants were changed from the *m*-xylene solutions to pure *m*-xylene, different behavior was observed in the recovery of the activity among

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[1] H. Takaya, N. Todo, T. Hosoya, T. Minegishi, M. Yoneoka, and H. Oshio, This Bulletin, **44**, 2296 (1971).

[2] H. Takaya, N. Todo, T. Hosoya, T. Minegishi, and M. Yoneoka, *Kogyo Kagaku Zasshi*, **73**, 1831 (1970).

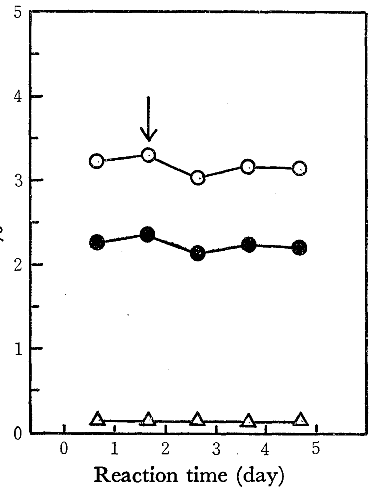

Fig. 1. Effects of hexamethylbenzene on the isomerization of *m*-xylene.
The arrow sign designates the results of four hours operation with using the *m*-xylene containing 2 wt% of hexamethylbenzene.
○: *p*-Xylene. ●: *o*-Xylene. △: Toluene.

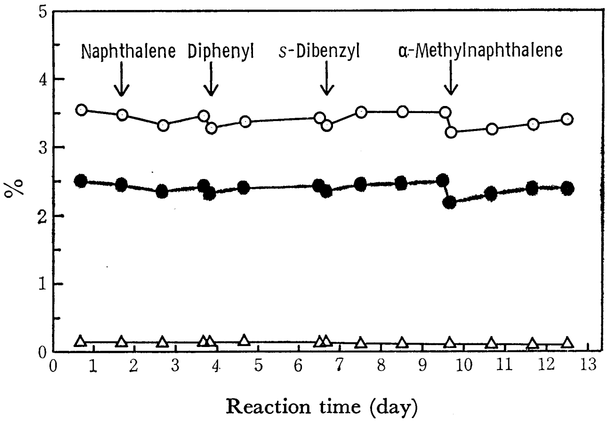

Fig. 2. Effects of naphthalene, diphenyl, *s*-dibenzyl and α-methylnaphthalene on the isomerization of *m*-xylene.
○: *p*-Xylene, ●: *o*-Xylene, △: Toluene.

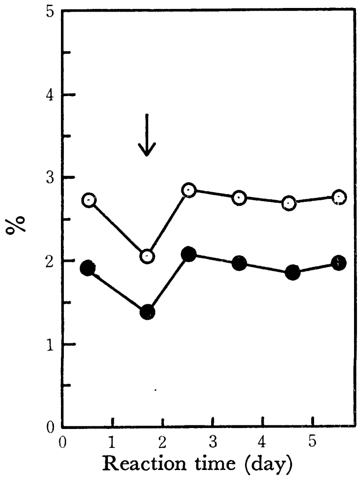

Fig. 3. Effects of 1,6-dimethylnaphthalene on the isomerization of *m*-xylene.
○: *p*-Xylene, ●: *o*-Xylene.

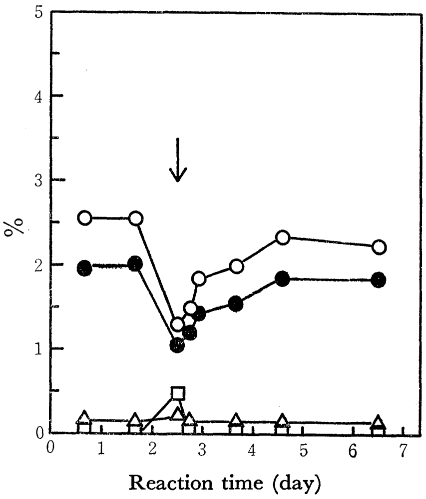

Fig. 4. Effects of diphenylmethane on the isomerization of *m*-xylene.
○: *p*-Xylene, ●: *o*-Xylene, △: Toluene, □: Benzene.

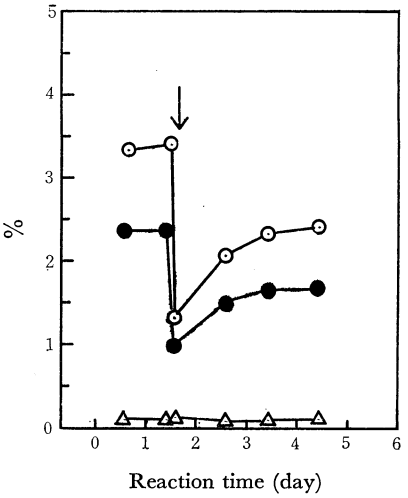

Fig. 5. Effects of anthracene on the isomerization of *m*-xylene
○: *p*-Xylene, ●: *o*-Xylene, △: Toluene.

the three cases: in the case of dimethylnaphthalene, the recovery was 100%; in the case of diphenylmethane, it was 90%, and in the case of anthracene, it was only 60%. It was noted that the addition of diphenylmethane to the *m*-xylene reactant resulted in the production of 0.5% of benzene.

An experiment was carried out using dried *m*-xylene and a dried *m*-xylene solution containing 2 weight per cent of diphenylmethane; we intended to examine the effects of water on the chemisorption of diphenylmethane with reference to the results in Fig. 4. However, when a catalyst was packed in the reactor in a dried box, the catalyst was moistened by *m*-xylene containing a small amount of water in order to obtain a high activity.[3] This reaction was carried out at a temperature of 290°C and at a feed rate of 13 g/h. The *m*-xylene solution was fed into the reactor for

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3) H. Takaya, N. Todo, T. Hosoya, H. Oshio, and T. Minegishi, This Bulletin, **45**, 2337 (1972).

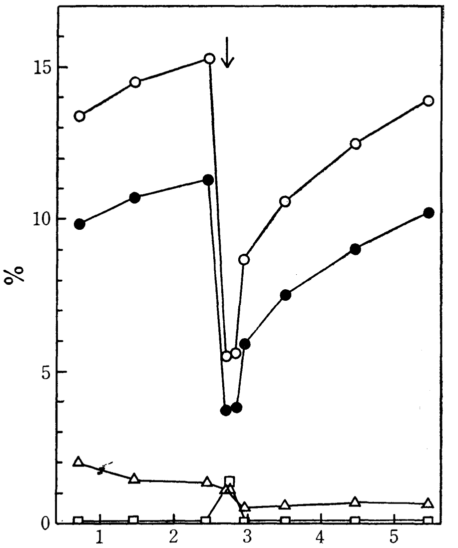


Fig. 6. Effects of diphenylmethane on the isomerization of *m*-xylene. This experiment was carried out with using dried *m*-xylene.

○: *p*-Xylene, ●: *o*-Xylene, △: Toluene, □: Benzene.

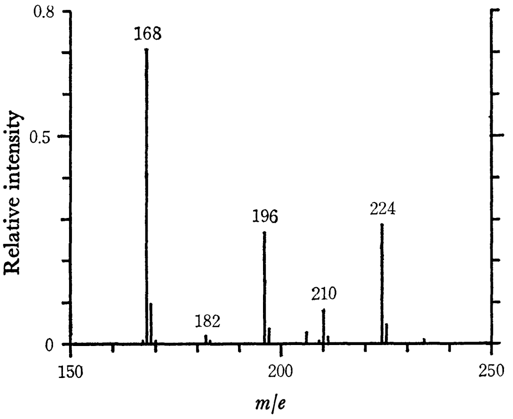


Fig. 7. Mass spectra of the higher-boiling products at the time designated by the arrow sign in Fig. 4.

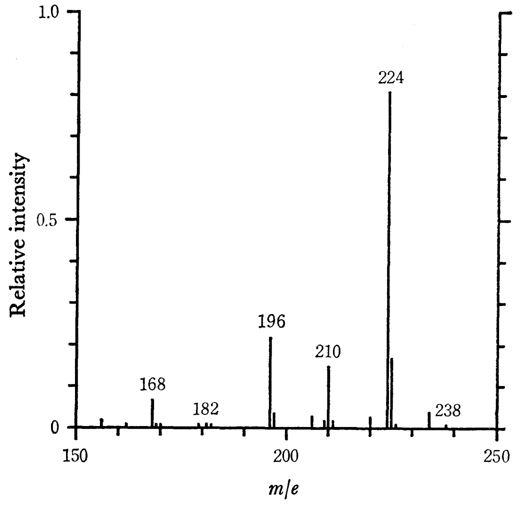


Fig. 8. Mass spectra of the higher-boiling products at the time designated by the arrow sign in Fig. 7.

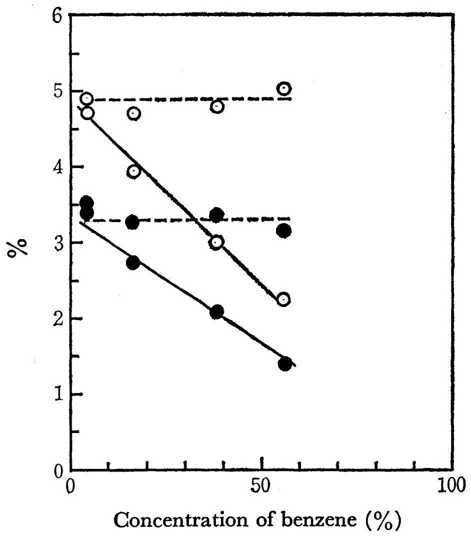


Fig. 9. Effects of benzene on the isomerization of *m*-xylene. —○—: content of *p*-xylene in a product. —●—: content of *o*-xylene in a product. —○—: *p*-xylene content / total xylene content. —●—: *o*-xylene content / total xylene content.

6 hr at the time designated by the arrow sign in Fig. 6. Also, diphenylmethane lowered the activity in the isomerization in this case, and 1.3% of benzene was produced. When the reactant was changed from the solution to pure and dried *m*-xylene, there was a gradual recovery of activity.

Fugures 7 and 8 show the mass spectra of higher-boiling compounds at the times designated by the arrow signs in Figs. 4 and 6 respectively. The compositions of the higher-boiling compounds were obtained from the spectra; they are tabulated in Table 1. The results show that diphenylmethane was converted mainly to di and tetramethyldiphenylmethane.

The influence of benzene on the activity in the isomerization of *m*-xylene was also studied in order to compare the intensity of the chemisorption of benzene on the acid sites available for the reaction with that of xylene. Figure 9 shows a linear decrease in the contents of *p*- and *o*-xylene with an increase in the amount of benzene.

Table 1. The yields of higher-boiling compounds (wt %)

| Mass number | 168 | 182 | 196 | 210 | 224 |
|---|---|---|---|---|---|
| Number of methyl group | 0 | 1 | 2 | 3 | 4 |
| Sample of Fig. 7[a)] | 0.97 | 0.03 | 0.43 | 0.14 | 0.53 |
| Sample of Fig. 8[b)] | 0.07 | 0.00 | 0.35 | 0.27 | 1.75 |

a) The concentration of diphenylemthane in the *m*-xylene reactant was 2.22%.

b) The concentration of diphenylmethane in the *m*-xylene reactant was 1.98%.

## Discussion

*1. The Main Compounds of the Higher-boiling By-product in the Isomerization of* m-*Xylene.* As was shown in earlier papers,[1,3)] the mass numbers of the main compounds of the higher-boiling by-products were 182, 196, 210, 224, and 238 in the isomerization and the disproportionation of *m*-xylene over a silica-alumina catalyst.

Furthermore, the addition of 2% of the main compounds to the *m*-xylene reactant resulted in a decrease in activity in the isomerization and the production of about 1% of toluene.

Considering only the mass numbers, the main compounds may be polymethyldiphenyl, polymethyldiphenylmethane, or polymethyl-*s*-dibenzyl. However, only diphenylmethane exhibited the behavior shown in Fig. 4, where the activity for the isomerization decreased greatly and about 0.5% of benzene was produced. This was the same behavior as shown by the main compounds in an earlier paper.[1] The production of benzene seemed to correspond to that of toluene on the addition of the main compounds to the *m*-xylene reactant, since the main compounds were polymethyl-ones. On the other hand, the addition of 2% of diphenyl or 2% of dibenzyl to the *m*-xylene reactant did not greatly decrease the catalytic activity and resulted in the production of neither benzene nor toluene. Therefore, it can be concluded that polymethyldiphenylmethanes are the main compounds. This conclusion is consistent with the NMR data in the earlier paper.[1]

2. *Effects of Benzene on the Isomerization.* As is shown in Fig. 9, the addition of a large amount of benzene to the *m*-xylene reactant resulted in a decrease in the yields of both *p*- and *o*-xylene. However, the ratio of the *p*-xylene yield to the total xylene content as well as that of the *o*-xylene yield to the total xylene content was constant, independent of the benzene concentration, as is shown in Fig. 9. Since the coverage of the active site is 1 under these reaction conditions,[2] this means that the ratio of the number of molecules of benzene adsorbed on the sites available for the isomerization to that of *m*-xylene is equal to the ratio in the reactant. Therefore, the intensity of the adsorptivity of benzene on the sites is equivalent to that of *m*-xylene. Furthermore, this conclusion implies that most molecules of *m*-xylene adsorb on the sites by the benzene rings, not by the methyl groups, since a benzene molecule has no methyl group. This is supported by the fact that the addition of 2% hexamethylbenzene to the *m*-xylene reactant did not greatly affect the activity in the isomerization, as is shown in Fig. 1; the intensity of the adsorptivity of *m*-xylene is approximately equivalent to that of hexamethylbenzene.

3. *Chemisorption of Diphenylmethane.* It has been well known electronic-spectrally that a triphenylmethylcarbonium ion is formed from triphenylmethane over a silica-alumina.[4–6] The high stability of the ion can be ascribed partly to its character as a resonating structure because of the presence of three phenyl groups. Hence, it may be expected that a stable diphenylmethylcarbonium ion is formed from diphenylmethane on an acid site, since the ion has two phenyl groups, as is shown in Fig. 10. The stable ion may result in a strong chemisorption of diphenylmethane and may be responsible for the relatively larger influence of diphenylmethane on the activity in the isomerization in comparison with the influences of diphenyl or *s*-dibenzyl. In addition, the fact that most of the diphenylmethane added to *m*-xylene was recovered as polymethyldiphenylmethane seems to support the formation of the diphenylmethylcarbonium ion.

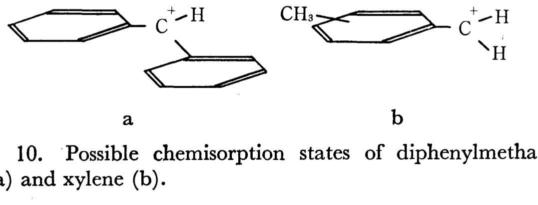
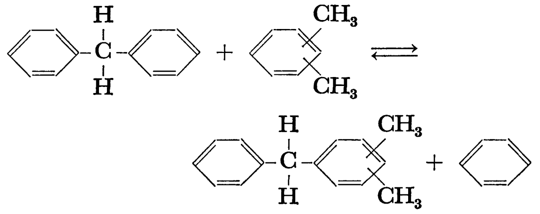


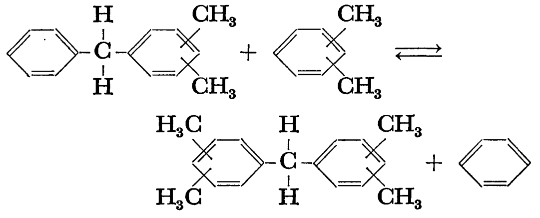
Fig. 10. Possible chemisorption states of diphenylmethane (a) and xylene (b).

Diphenylmethane is considered to be chemisorbed by its methylene group on an acid site. If one of the two phenyl groups in a diphenylmethylcarbonium ion (Fig. 10a) is formally replaced by a hydrogen atom, the ion is converted to a benzylcarbonium ion (Fig. 10b). The benzylcarbonium ion suggests the possibility that xylene chemisorbs on an acid site by means of its methyl group.

4. *Exchange Reaction between the Aromatic Ring of Diphenylmethane and Reactant* m-*Xylene.* In Table 1, the order of increasing yield is: tetra$\geq$di$>$trimethyldiphenylmethane, while the yield of monomethyldiphenylmethane is zero. When considering that 0.5—1.3% of benzene was produced in Figs. 4 and 6, this order suggests the occurrence of a rapid exchange reaction between an aromatic ring of diphenylmethane and a reactant *m*-xylene molecule, as is shown in Eqs. (1) and (2). When considering the chemisorption state of diphenylmethane (Fig. 10a) and the nucleophilic property of aromatic compounds,[7] Fig. 11a is a possible intermediate for the exchange reaction. Hamanaka *et al.*[8] studied the same kind of reaction catalyzed by aluminum chloride at room temperature using methylbenzylbenzene and *p*-xylene, and suggested a benzylcarbonium ion as the intermediate. In the present paper, however, the benzylcarbonium ion can be excluded as the intermediate since the stability of the benzylcarbonium ion is lower than that of the diphenylmethylcarbonium ion. The low stability of the benzylcarbonium ion is confirmed by the fact that most xylene molecules chemisorb on acid sites



(1)



(2)

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4) H. P. Leftin, *J. Phys. Chem.*, **64**, 1714 (1960).

5) R. P. Porter and W. K. Hall, *J. Catal.*, **5**, 366 (1966).

6) A. E. Hirschler and J. O. Hudson, *ibid.*, **3**, 239 (1964).

7) Y. Ogata, "Yuki Han-noron", Maruzen, Tokyo (1962), p. 232.

8) S. Hamanaka, S. Saigan, K. Itoh, and M. Ogawa, *Kogyo Kagaku Zasshi*, **70**, 695 (1967).

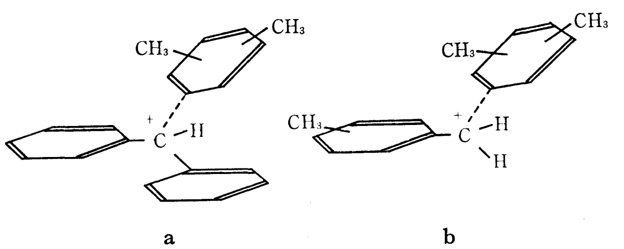
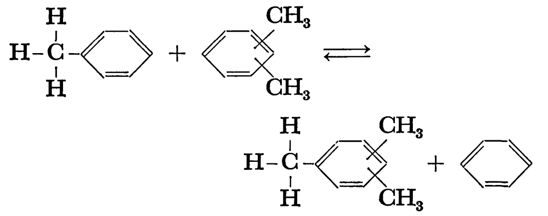


Fig. 11. Possible intermediates for the exchange reaction between an aromatic ring of diphenylmethane and a xylene molecule and for the disproportionation reaction of xylene. a: for the exchange reaction, b: for the disproportionation reaction.

by means of the benzene rings, not the methyl groups, under the present reaction conditions.

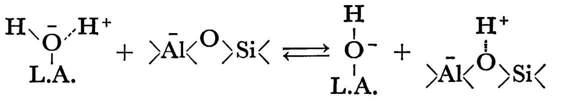
The exchange reaction is similar to the transalkylation reaction which includes the disproportionation of xylene. When an aromatic ring of diphenylmethane is formally replaced by a hydrogen atom in Eq. (1), we obtain Eq. (3), which corresponds to a transmethylation reaction. Figure 11b is a possible intermediate for the transmethylation (or the disproportionation) reaction. This model is consistent with the results reported in an earlier paper.[3)]



(3)

*5. The Acid Site Available for the Chemisorption of Diphenylmethane.* On the basis of the discussion in the preceding sections, a common acid site may be available for the formation of a triphenylmethylcarbonium ion, a diphenylmethylcarbonium ion, and a benzylcarbonium ion, and for both the exchange and disproportionation reactions. The reaction of triphenylmethane with a silica-alumina catalyst to form a chemisorbed triphenylmethylcarbonium ion has been interpreted by Leftin and Hall as a hydride abstraction by Lewis-acid sites on the surface.[4)] Following this interpretation, the decrease in the catalytic activity for the isomerization on the addition of diphenylmethane to the *m*-xylene reactant indicates that the chemisorption of diphenylmethane on Lewis-acid sites decreases the protonic acidity of the catalyst, since it has been generally accepted that the isomerization is catalyzed by a protonic acid site.[3,9–12)] Hence, the acid site available for the chemisorption of diphenylmethane may be considered to have both acidic characters, protonic and Lewis. Figure 12 shows a possible model of such an acid site, which was proposed by Uytterhoeven over H–Y zeolite[13)]; (a) is a protonic acid state and (b) is a Lewis acid state. When diphenylmethane is chemisorbed on the b state, the protonic acidity of the site disappears.

It has been reported that the presence of a small amount of water is preferable for the disproportionation of xylene[3)] and for carbonium-ion formation from triphenylmethane.[14)] On the basis of the above consideration of the acid site, this fact may be interpreted as follows. In a reaction system containing a small amount of water, the chemisorption of water on free Lewis-acid sites may be considered to generate the acid site of Fig. 12, as is shown in Eq. (4). Here, the words "free Lewis-acid sites" mean all the Lewis-acid sites except for the type of Fig. 12b.



$$\underset{\text{L.A.}}{\overset{\text{H}\diagdown\ \diagup\text{H}^+}{\bar{\text{O}}}} + \rangle\bar{\text{Al}}\langle{}^{\text{O}}\rangle\text{Si}\langle \rightleftarrows \underset{\text{L.A.}}{\overset{\text{H}}{\text{O}^-}} + \overset{\text{H}^+}{\overset{\vdots}{\rangle\bar{\text{Al}}\langle{}^{\text{O}}\rangle\text{Si}\langle}} \quad (4)$$

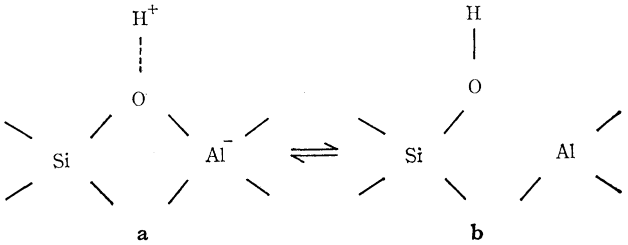


Fig. 12. A model for the acid site which has both acidic characters protonic and Lewis one.
a: a protonic acid state, b: a Lewis acid state.

In view of the fact that only a strong acid such as concentrated sulfuric acid above 85% converts triphenylmethane to the carbonium ion, the strength of the Lewis acid of Fig. 12b has to be stronger than that of a free Lewis acid, since it has been proposed that only the Lewis acid of Fig. 12b is available for the chemisorption of triphenylmethane and for the disproportionation. The consideration that the strength of the binding of an oxygen atom or a hydroxyl group to a Lewis acid increases with an increase in the strength of the Lewis acid supports the above consideration of the acid site of Fig. 12b—that an oxygen atom is still bound to an aluminum atom in the second term in Eq. (4). The aluminum atom is a Lewis acid site in Fig. 12b. Therefore, Eq. (4) indicates the possibility that the adsorption of water on a weak Lewis-acid site may generate a strong Lewis-acid site in a reaction system containing a small amount of water.

There is a different interpretation possible in the case of the chemisorption of diphenylmethane on Lewis-acid sites. It may be considered that the adsorption of water on a Lewis-acid site generates a protonic acid, and that the reverse reaction generates a Lewis one. Hence, the chemisorption of diphenylmethane on a Lewis-acid site results in a decrease in the protonic acidity. However, this interpretation does not seem to be reasonable in view of the results in Fig. 6. In the experiment of Fig. 6, the dried *m*-xylene was used with the intention of preventing a Lewis-acid site from being converted to a protonic acid by the adsorp-

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[9)] V. C. F. Holm and A. Clark, *J. Catal.*, **2**, 16 (1963).

[10)] H. Matsumoto and Y. Morita, *Bull. Japan Petr. Inst.*, **11**, 40 (1969).

[11)] S. M. Csicsery and D. A. Hickson, *J. Catal.*, **19**, 386(1970).

[12)] J. W. Ward, *ibid.*, **17**, 355 (1970).

[13)] B. Uytterhoeven, L. G. Christener, and W. K. Hall, *J. Phys. Chem.*, **69**, 2117 (1965).

[14)] F. D. Dollish and W. K. Hall, *ibid.*, **71**, 1005 (1967).

tion of water. Therefore, the adsorption of diphenylmethane on a Lewis-acid site does not affect a protonic one directly. However, the isomerization activity was greatly lowered by diphenylmethane.

Hirshler⁶⁾ showed the possibility of the chemisorption of triphenylmethane on a protonic-acid site. He found that triphenylmethane is oxidized by chemisorbed oxygen to triphenylcarbinol, followed by the reaction with a protonic acid to generate the triphenylmethylcarbonium ion, and that 90% or more of the chemisorbed triphenylmethylcarbonium ion was recovered as triphenylcarbinol. On the other hand, Porter⁵⁾ reported that it is not necessary to oxidize triphenylmethane to triphenylcarbinol preliminary to carbonium-ion formation. Furthermore, most of the diphenylmethane was recovered as polymethyldiphenylmethane in the present experiment. Therefore, the chemisorption mechanism proposed by Hirschler may be excluded under the reaction conditions of the present paper.

Our and others results do not seem to exclude the possibility of the chemisorption of diphenylmethane on strong protonic-acid sites. However, the interpretation seems to suffer from the defect that the chemisorption state can not be drawn easily. Further investigations will be necessary to solve this problem.