Catalytic Isomerization of Trimethylbenzenes over a Graphite-Sulfuric Acid

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Synopsis. The isomerization of 1,2,3- and 1,2,4-trimethylbenzene took place over a graphite–sulfuric acid to form 1,2,4- and 1,2,3-trimethylbenzene, respectively, but that of 1,3,5-trimethylbenzene was not observed.

Since Kondow et al.[1] found that the equilibration of protium–deuterium took place over a caesium–graphite intercalation compound (GIC), much attention has been paid to the characteristic properties of graphite intercalation compounds, and their catalytic properties have been investigated extensively in various reactions.[2,3] Watanabe et al.[4] reported a molecular-sieving-type physisorption of alkali metal graphites at 77 K.Tsuchiya et al.[5,6] have observed structure-selectivity in the hydrogenation and the isomerization of olefins over alkali metal graphites. The results have been explained on the basis of the molecular-sieving-like effect of the compound.

Because the molecular-sieving-like effect has been observed in the case that the intercalant of GIC is basic substances,[5,6] a similar effect would be expected in the case that the intercalant is an acidic substance. Trimethylbenzenes (1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene) are catalytically isomerized over an acid catalyst.[7] It can therefore be expected that a certain isomer of trimethylbenzene might be selectively formed over a graphite–acid with molecular-sieving effects. In this study interest was centered on a graphite–sulfuric acid.

A closed recirculation system using greaseless stopcocks was employed in order to follow the progress of the reaction; helium was used as the diluent. The reaction mixtures were occasionally analyzed by means of gas chromatography. The graphite–sulfuric acid used as the catalyst was prepared according to Takemoto et al.,[8] and identified by XRD. A bundle of glass-wool impregnated with sulfuric acid was used as "H_2SO_4-cat". Trimethylbenzenes were obtained from Tokyo Kasei Kogyo Co., Ltd., and their purity, more than 99%, was confirmed by gas chromatography.

Four kinds of reactions can be expected over an acid catalyst, as follows:

1) Disproportionation of trimethylbenzenes (1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene) to form dimethylbenzenes (1,2-, 1,3-, and 1,4-dimethylbenzene) and tetramethylbenzenes (1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetramethylbenzene).
2) Isomerization of trimethylbenzenes.
3) Isomerization of dimethylbenzenes.
4) Isomerization of tetramethylbenzenes.

Table 1 lists the equilibrium composition, assuming that these four kinds of reactions are in equilibrium. These values were calculated on the basis of reported API thermodynamic data.[9]

Figure 1 shows a typical result, when 1,2,3-trimethylbenzene was introduced over graphite-sulfuric acid at 373 K. 1,3,5-Trimethylbenzene was not observed. Neither dimethylbenzenes nor tetramethylbenzenes were detected. From a thermodynamic analysis the formation of 1,3,5-trimethylbenzene would be expected, if the interconversion of three isomers of

Table 1. Equilibrium Composition

Component	Composition C/mol%		
	300 K	400 K	500 K
1,2,3-Trimethylbenzene	1.38	2.13	2.71
1,2,4-Trimethylbenzene	29.27	29.31	28.74
1,3,5-Trimethylbenzene	19.56	15.59	13.11
1,2-Dimethylbenzene	4.06	5.02	5.86
1,3-Dimethylbenzene	14.89	15.05	15.18
1,4-Dimethylbenzene	5.94	6.42	6.69
1,2,3,4-Tetramethylbenzene	2.00	2.87	3.65
1,2,3,5-Tetramethylbenzene	13.15	13.82	14.28
1,2,4,5-Tetramethylbenzene	9.75	9.80	9.79

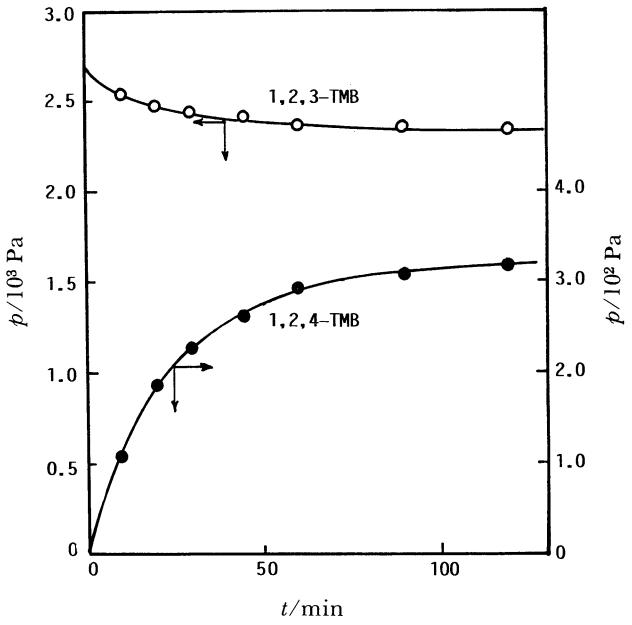

Fig. 1. Isomerization of 1,2,3-trimethylbenzene over a graphite–sulfuric acid at 373 K.

trimethylbenzenes take place. If the disproportionation of 1,2,3-trimethylbenzene takes place, dimethylbenzenes and tetramethylbenzenes might be expected. However, only 1,2,4-trimethylbenzene was selectively formed. This result suggests that only the isomerization of 1,2,3-trimethylbenzene to form 1,2,4-trimethylbenzene took place.

When 1,2,4-trimethylbenzene was the reactant, 1,2,3-trimethylbenzene was only observed as an aromatic compound. The formation of 1,3,5-trimethylbenzene, dimethylbenzenes, and tetramethylbenzenes was not detected. This result suggests that the isomerization of 1,2,4-trimethylbenzene to form 1,2,3-trimethylbenzene took place, and that the disproportionation of 1,2,4-trimethylbenzene did not take place. Another product observed was methane, the amount of which was less than 10% of the 1,2,3-trimethylbenzene formed. Methane might be formed by the decomposition of the reactant.

When 1,3,5-trimethylbenzene was the reactant, any hydrocarbon other than the reactant was observed at 373 K. This result suggests that 1,3,5-trimethylbenzene did not react under the present experimental conditions. Because neither dimethylbenzenes nor tetramethylbenzenes was observed, it is reasonably concluded that the disproportionation of trimethylbenzenes did not take place over the graphite–sulfuric acid under the present experimental conditions. At 413 K, methane was observed, the amount of which was ca. 20% of the reactant at 2 h. The methane might be formed by decomposition, as mentioned above. If the amount of methane is small, the formation of methane is an important problem, since carbon depositing on the catalyst surface might take place. In order to elucidate this point, further investigations are certainly necessary and should be carried out.

The widths of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene are 8.1, 7.6, and 8.6 Å, respectively. Since the interlayer distance of a graphite–sulfuric acid is 11.3 Å, wider molecules probably have more difficulty to penetrate into and move within the space between the graphite layers than do narrow molecules. Accordingly, the present experimental results, that the formation and conversion of 1,3,5-trimethylbenzene were not observed, are reasonably explained on the basis of a size effect of the molecules.

When 1,2,3-trimethylbenzene was introduced over H_2SO_4-cat, on the other hand, both dimethylbenzens and tetramethylbenzenes were observed. This result suggests that the disproportionation reaction took place over H_2SO_4-cat. Accordingly, the catalytic selectivity of H_2SO_4 was varied by forming such intercalation compounds as graphite–sulfuric acid.

In conclusion, graphite–sulfuric acid has shown high catalytic selectivity for the reaction of trimethylbenzenes.

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