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DISPROPORTIONATION OF XYLENE OVER PARTIALLY METAL EXCHANGED H-MORDENITE

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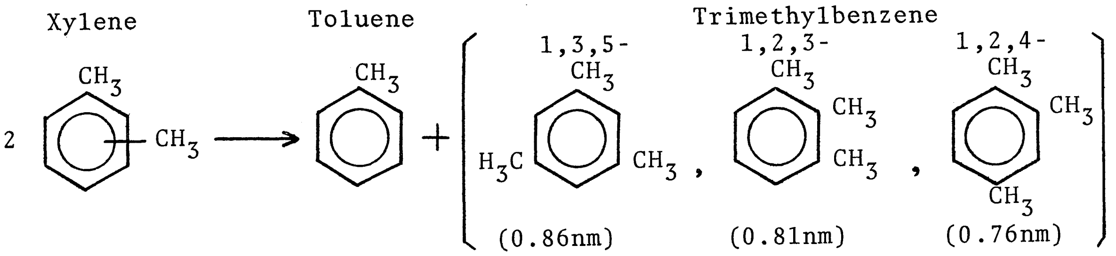
It was found that the shape-selective disproportionation of xylene effectively proceeded over the partially exchanged H-mordenite catalyst by the cations with a suitable ionic radius(ca. 0.07nm), and produced 1,2,4-trimethylbenzene in a high selectivity(84%).

We have reported that the H-mordenite catalyst effectively accelerates the disproportionation of toluene with a high selectivity, and the produced xylene is a mixture of three isomers in a thermodynamic equilibrium state(1). Therefore, it is expected that the H-mordenite catalyst also accelerates the disproportionation of xylene(see eq. 1). And the produced trimethylbenzene is also a mixture of three isomers in equilibrium.



-----(eq. 1)

On the other hand, the effective pore dimension of the mordenite can be controlled by selecting the exchanged-cation of the catalyst, because the pore structure of mordenite is composed of two dimensional channels and the cations stick out from the channel walls. H-mordenite has a large pore dimension, that is about 0.9nm, and can absorb some simple aromatic compounds in it. However, the mordenites exchanged by multi valent cations, except Be, can hardly absorb such aromatic compounds(2).

Thus, when the disproportionation of xylene proceeds over the mordenite catalyst exchanged by the cation with a suitable radius, the smallest isomer in trimethylbenzenes is predominantly produced. The molecular dimension of trimethylbenzene isomers is shown in eq. 1. The smallest is 1,2,4-isomer and the largest is 1,3,5-isomer. So as we expected, a high selectivity for 1,2,4-isomer can be obtained using this kind of catalyst. And 1,2,4-trimethylbenzene is the precursor of trimellitic acid which is a raw material of the heat-resisting polymers.

The experiments were carried out in a fixed bed type apparatus with a continuous flow system under atmospheric pressure. Nitrogen was used as a carrier gas. The liquid product was cooled with an ice-water trap. The sample for gas-chromatography was collected periodically. Both the yield and the composition of the trimethylbenzenes produced did not depend on the kind of xylene isomers used. So, we used meta-xylene in this study.

The effective pore dimension of mordenite can be controlled by the partial exchange of the cation, because the pore structure of mordenite is a two dimensional tubular system. H-mordenite is the best catalyst for the disproportionation of xylene. We prepared the partially exchanged H-mordenite catalysts by several kinds of cations. Table 1 shows the ionic radius of cations.

It was found that on the H-mordenite catalysts partially exchanged by alkaline earth metal cation, the Be-H-mordenite catalyst had a high selectivity, while Ca, Sr, and Ba-H-mordenite catalysts had a low activity, and by these catalysts the composition of produced trimethylbenzenes was similar to that by the pure H-mordenite catalyst. The Mg-H-mordenite catalyst had a considerable activity and a higher selectivity for 1,2,4-trimethylbenzene than the pure H-mordenite catalyst. These results suggest that the suitable ionic radius is nearly 0.07nm. We expected that Ni, Co, Cu, and Zn would be the suitable ions for this reaction.

Figure 1 shows that over the H-mordenite catalyst, the fraction of 1,2,4-isomer in total trimethylbenzenes is higher than the thermodynamic equilibrium value, when the conversion is low. And over Mg, Co, Ni, Zn, and Cu-H-mordenite catalysts, the fraction of 1,2,4-isomer has a much higher value. On the other hand, the fraction of

Table 1. Ionic Radius

Cation	Na^+	Be^{++}	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}	Ni^{++}	Co^{++}	Cu^{++}	Zn^{++}
Radius(nm)	0.097	0.033	0.066	0.099	0.116	0.136	0.069	0.072	0.072	0.074

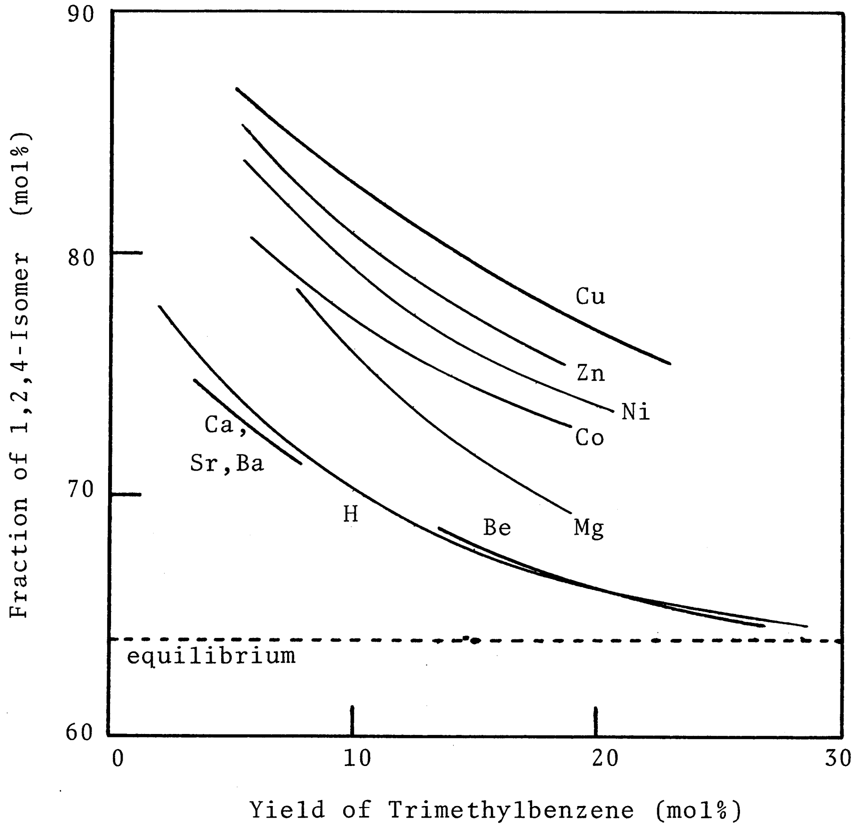


Fig. 1. Effect of Cation Added to H-Mordenite.

Reaction conditions:
Temperature=300°C,
catalyst=cation(20%)-H-mordenite, pre-calcined at 600°C for 2hr in nitrogen.

1,3,5-isomer decreases with the increase of 1,2,4-isomer fraction. But the fraction of 1,2,3-isomer is always 8%, and this value is equal to that in equilibrium state.

In the case of H-mordenite catalyst partially exchanged by a small cation, such as Be, its effective pore dimension is large enough to freely desorb any trimethylbenzenes. So, these catalysts have the similar activity and selectivity to that of H-mordenite catalyst. While, in the cases exchanged by large cations, xylene or produced trimethylbenzenes are disturbed in sorbing into or desorbing from the channel. These catalysts have a low activity. However, the similar selectivity is obtained, probably because a small part of the channels in these catalysts contains only protons.

Figure 2 shows the effect of the fraction of Cu ion in Cu-H-mordenite on the yield of trimethylbenzenes and the fraction of 1,2,4-isomer. The yield of trimethylbenzenes decreases with the increase of Cu ion in the H-mordenite catalyst. This result shows that the Cu ion reduces the active sites for the disproportionation of xylene. And also from the geometrical point of view, in such a narrow channel of Cu-mordenite, the disproportionation, that is a bimolecular reaction, hardly proceeds.

On the other hand, the fraction of 1,2,4-isomer is leveled at about 75% over the H-mordenite occupied by Cu ion more than 20%. This result suggests that a small part of Cu cation, which is perhaps near the pore mouth, effects on the shape-selectivity of trimethylbenzenes. The optimum catalyst is, therefore, the H-mordenite 20% exchanged by Cu cation.

Figure 3 shows the effect of reaction temperature on H-mordenite 20% exchanged by

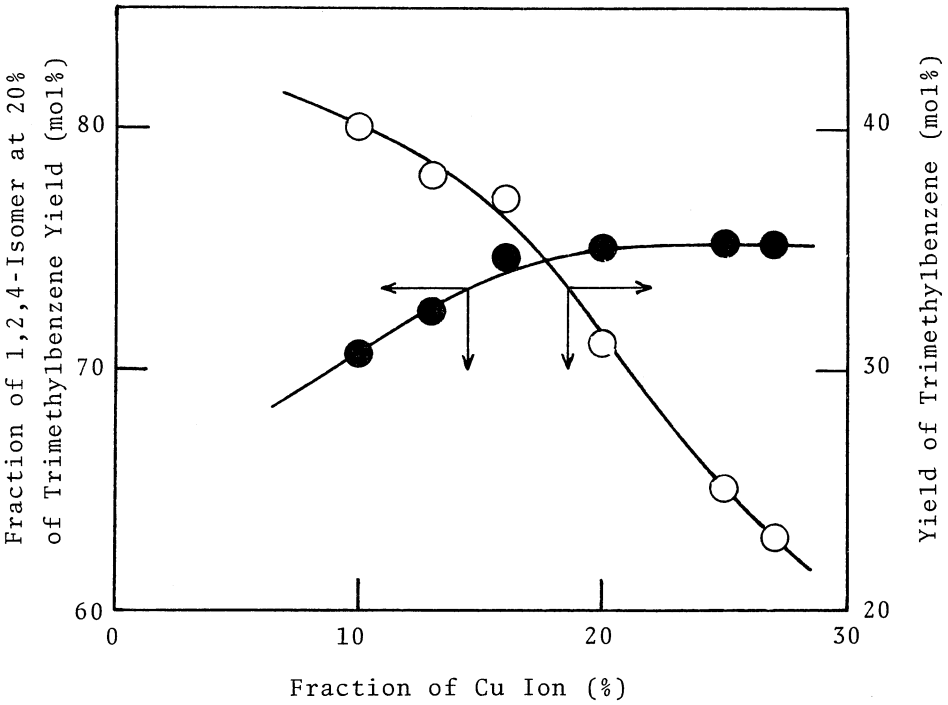


Fig. 2. Effect of Fraction of Cu Ion in Cu-H-Mordenite.

Reaction conditions: Temperature=300°C, catalyst=Cu-H-mordenite, pre-calcined at 600°C for 2 hr in nitrogen.

Cu cation. In a temperature range more than 350°C, the fraction of 1,2,4-trimethylbenzene decreases with the increase of reaction temperature. These results are explained in terms of the great thermal vibration of cations and oxygen atoms surrounding the apertures and the great mobility of the reaction products. These thermal behavior of molecules prevents the molecular sieving effect of the catalyst at a high temperature. However, the fraction of 1,2,4-isomer is still higher than that in equilibrium state even at 500°C. At a temperature up to 300°C, the effect of reaction temperature on the composition of the produced trimethylbenzene isomers is scarcely observed.

As a conclusion, the shape-selective disproportionation of xylene effectively proceeds over the partially exchanged H-mordenite catalysts by the cations with a suitable ionic radius, and produces 1,2,4-trimethylbenzene in a high selectivity. The suitable ionic radius is nearly 0.07nm and the most proper catalyst is the H-mordenite 20% exchanged by Cu cation. Under the optimum reaction conditions, the fraction of 1,2,4-trimethylbenzene is 84% at 10% of total yield of trimethylbenzenes.

References

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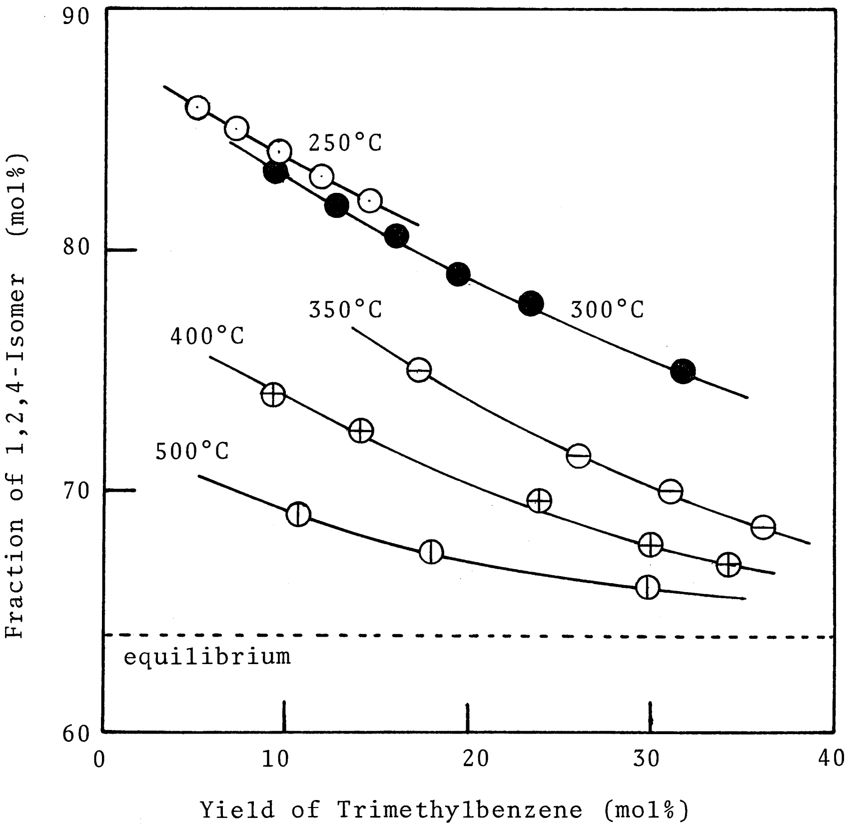

Fig. 3. Effect of Reaction Temperature.

Reaction conditions: Catalyst=Cu(20%)-H-mordenite, pre-calcined at 600°C for 2hr in nitrogen.

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