Disproportionation of Toluene on Synthetic Mordenites*

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Summary: Disproportionation of toluene was studied over several cation exchanged synthetic mordenites. H-mordenite was used for choosing the reaction conditions, i.e. catalyst calcination temperature, reaction temperature and contact time. It was found that toluene was converted with a high yield to benzene and xylene, and the reaction equilibrium was almost attained at 300–400°C over H-mordenite, accompanied with a small amount of dealkylation and cracking.

With the exception of Be which had an ionic radius of only 0.3 Å, divalent cation exchanged mordenites showed no activity for disproportionation of toluene. This result suggested that the exchanged cation stuck out of the mordenite channel walls, thus hindering the diffusion of reactants into the channel and to the active sites. Ce, which had a rather large ionic radius of about 1.1 Å, showed a very small activity. It could be explained that Ce was a trivalent cation, so its number of atoms was less in the mordenite frame; therefore, the hindrance effect was less.

The plot of logarithmic rate constant (k) against $1/T$ showed that the apparent activation energy decreased at a higher reaction temperature, where the diffusion of toluene was the main rate determining step. At a lower temperature, the reaction rate was apparently of a zero order for toluene, owing to strong adsorption of toluene on the catalyst.

1 Introduction

Aromatic hydrocarbons, especially benzene, toluene and xylene, are the most important raw materials for the organic chemical industry. Recently demands for them have increased very rapidly, and they are being supplied from naphtha by catalytic reforming and steam cracking.

Toluene, however, has a tendency to be over-produced, because there is a smaller demand for it than for benzene and xylene. It is, therefore, profitable for the chemical industry to convert toluene to benzene and xylene by a disproportionation reaction. It is well known that the disproportionation reaction of toluene to benzene and xylene occurs over some solid acid catalysts, but the usual solid acid catalysts give only a very small yield.

The disproportionation of toluene means that one molecule of benzene and one molecule of xylene are produced from two molecules of toluene as shown in Eq. 1, and xylene is always formed as an equilibrium mixture of *o*-, *m*- and *p*-isomers. In this reaction, the calculated equilibrium conversion of toluene is about 55% at a wide range of reaction temperature (250–500°C).

Crystalline aluminosilicates are shown to be highly active solid acid catalysts, and are expected to show a greater activity for the disproportionation of toluene. Matsumoto and Morita¹⁾ reported that CdX and LaX showed the highest activity for the disproportionation of toluene in the cation exchanged X type faujasites, and the addition of HCl showed a promoting effect for this reaction. Under the conditions they used, the toluene conversion obtained was about 50% at 550°C, but dealkylation of toluene became the main reaction in place of disproportionation; therefore, much more benzene was produced than xylene, i.e. the benzene/xylene ratio was 4.0–7.5 (mol/mol).

Venuto²⁾ reported that disproportionation of toluene occurred over REX faujasites, giving a low yield at 264°C and 400 psig in the liquid phase. On the cation exchanged Y type faujasites, Isakov³⁾ reported that the yield of xylene was 12.4% at 450°C on CaY catalyst and the benzene yield was the same as that of xylene under the conditions he employed. The authors⁴⁾ found, in the alkylation reaction of toluene with methanol over various cation exchanged zeolite catalysts, that synthetic H-mordenite was rather effective for disproportionation of toluene, and under a condition without methanol, conversion of toluene came up to the equilibrium values

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(about 55%), yielding almost the same amounts of benzene and xylene at 400°C. Benesi³⁾ used the toluene disproportionation reaction as one of the model reactions for the comparison of the catalytic activity of several types of synthetic zeolites, and concluded also that the synthetic mordenite showed a higher activity for this reaction than Y type faujasites.

The present investigation was undertaken to study the disproportionation reaction of toluene in more detail and to present the kinetic discussion of this reaction on the cation exchanged mordenite catalysts.

2 Experimental

2.1 Catalyst

Two kinds of synthetic mordenite were used as basic materials. One was the commercial synthetic Na- and H-mordenite (NaZ and HZ) manufactured by Norton Co. The other was the synthetic Na-mordenite (NaM) prepared by Nihon Kagaku Kogyo Co. The analytical data of these mordenite were shown in Table 1.

Table 1 Chemical Composition of Synthetic Mordenites (wt%)

	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	H ₂ O
NaZ	68.84	11.68	7.10	—	12.37
NaM	68.91	10.50	5.51	0.37	14.71

The cationic and H forms of mordenite were prepared by conventional cation exchange procedures. NaZ or NaM was brought into contact with an aqueous solution (0.5~1N) of the cations (as sulfate, chloride or acetate) at 75°C for 16~24 hours. The degree of cation exchange was determined by flame photometry.

All catalysts were pelleted with no binder, crushed and sized to 8/14 mesh before use.

2.2 Reactants

Toluene, having a purity of 99.8%, was obtained from a commercial source.

2.3 Analysis

The reaction mixture was analyzed by gas chromatography, using a 4 meter stainless steel column which had a diameter of 3 mm and contained a stationary phase Celite-545 (60/80 mesh) impregnated with 7 parts of Bentone-34 and 5 parts of DNP with respect to 100 parts of solid support. The carrier gas was H₂ (0.8 kg/cm² input pressure) and the analysis temperature was 95°C.

2.4 Apparatus and Procedure

The experiment was carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure.

The catalyst was placed in the electrically heated quartz reactor and the air was replaced with nitrogen. The calcination was carried out for one hour at a selected temperature, and then it was brought to the reaction temperature in situ. Toluene was fed into the catalyst bed by a micro feeder. The product was cooled with an ice trap, and the samples for analysis were collected periodically.

The effect of N₂ or H₂ gas as a diluent agent, necessary to keep the catalyst activity for a longer time, seemed alike at least under atmospheric pressure, so N₂ was used throughout the experiments. The result was independent from this effect when N₂ was more than 5 times as much as the toluene feed, therefore, in the further experiments 1/5 molar ratio of toluene/N₂ was used.

3 Results and Discussion

In order to choose the appropriate reaction conditions, the effects of calcination temperature,

Catalyst: HZ calcined at 700°C for one hour
 Reaction condition;
 reaction temperature: 400°C
 W/F: 15 (g/mol/hr)
 N₂/toluene: 5/1 (mol/mol)

Fig. 1 The Activity Change with Streaming Time

reaction temperature and contact time were studied, using an HZ catalyst. The activity of the catalyst changed considerably with the progress of the reaction, as shown in Fig. 1. The products were mainly benzene and xylenes, a small amount of trimethylbenzenes and a trace of ethylbenzene as well as ethyltoluenes as a by-product. Moreover, a small amount of C_2 - C_5 olefin rich aliphatic hydrocarbons was produced as a gaseous product. The xylene isomers obtained always corresponded closely to thermodynamical equilibrium values. At the initial stage, cracking of toluene occurred; therefore, less benzene and xylenes were produced. Later, the yield of benzene and xylenes decreased with the streaming time, perhaps because the active sites of the catalyst were poisoned by carbon deposits. The data of toluene disproportionation experiments were taken at the highest activity which usually occurred between 30 and 45 minutes in the streaming time.

The yields of benzene and xylenes would be used as the maximum value. The yield of products and W/F as parameter of contact time were defined as follows:

$$\text{yield} = \frac{\text{mole of products}}{1/2 \text{ mole of fed toluene}} \times 100 \text{ (mol\%)}$$

$$W/F = \frac{\text{catalyst weight (g)}}{\text{feed rate of toluene and } N_2 \text{ (mol/hr)}}$$

3.1 Effect of Calcination Temperature of Catalyst

The effect of the calcination temperature on the catalyst activity was shown in Fig. 2, when the

Catalyst: HZ
Reaction condition;
reaction temperature: 300°C
 W/F : 10 (g/mol/hr)
 N_2 /toluene: 5/1 (mol/mol)

Fig. 2 Effect of Calcination Temperature

calcination temperature was changed from 500°C to 800°C over HZ under the following conditions; reaction temperature: 300°C, W/F : 10 (g/mol/hr), N_2 /toluene: 5/1 (mol/mol). Both yields of benzene and xylenes reached the maxi-

Catalyst: HZ calcined at 700°C for one hour
Reaction condition;
 W/F : 10 (g/mol/hr)
 N_2 /toluene: 5/1 (mol/mol)

Fig. 3-1 Effect of Reaction Temperature

Catalyst: HZ calcined at 700°C for one hour
Reaction condition;
 W/F : 15 (g/mol/hr)
 N_2 /toluene: 5/1 (mol/mol)

Fig. 3-2 Effect of Reaction Temperature

imum values at 600~700°C; however, toluene was converted to benzene and xylenes more selectively at 700°C than at 600°C. These results agreed with the results of Benesi⁵⁾, and suggested that the suitable amount of adsorbed water on mordenite was strongly related to the catalytic activity.

All cation exchanged mordenites were calcined at 700°C for one hour, as the standard treatment before use. However, the optimum calcination

temperature for some cations seemed to be different. This phenomenon will be discussed later.

3.2 Effect of Reaction Temperature and Contact Time

The results obtained with an HZ catalyst were shown in Fig. 3-1 and 3-2, when the reaction temperatures were changed from 300°C to 400°C at 10 and 15 g/mol/hr of W/F . The scope of the effect of contact time (W/F) was shown in Figs. 4-1 and 4-2 at 300°C and 400°C, respectively. It was thought that disproportionation of toluene almost reached a state of equilibrium, accompanied by a little dealkylation and cracking. Under a more severe condition, more dealkylation and cracking occurred; therefore, benzene and gaseous products increased.

At 250°C and below the reaction scarcely occurred, and at 450°C and over the yield of xylenes decreased, such side reactions as dealkylation and cracking increased.

3.3 Activity of Cation Exchanged Mordenites

The activity of cation exchanged mordenites and Y type faujasites was shown in Table 2, the following conditions being applied; reaction temperature: 400°C, W/F : 15 (g/mol/hr) N_2 /toluene: 5/1 (mol/mol). The table showed that only H-mordenite had a high activity for disproportionation of toluene. Ce exchanged faujasite showed the highest activity for many carbonium ion type reactions, but Ce exchanged mordenite had shown only a small activity for this reaction. Divalent cation exchanged mordenites had almost no activity, with the exception of Be which has an ionic radius of only 0.3 Å. It seemed, therefore, that the exchanged cations in the mordenite framework stuck out from the channel walls, thus hindering the diffusion of the hydrocarbons, such as toluene, into the channels and to the active sites. However, Ce, which has a rather large ionic radius of about 1.1 Å, showed some activity, although it was very small. This result could be explained by the fact that Ce was a trivalent cation and so the number of its atoms would be less in the mordenite frame; therefore, a part of toluene could be in contact with the active sites.

Z mordenite and M mordenite both showed similar activity, but BeM and CeM showed less activity than BeZ and CeZ. The small activity of BeM and CeM could be explained by the lower degree of exchange.

Catalyst: HZ calcined at 700°C for one hour
Reaction condition;
reaction temperature: 300°C
 N_2 /toluene: 5/1 (mol/mol)

Fig. 4-1 Effect of Contact Time

Catalyst: HZ calcined at 700°C for one hour
Reaction condition;
reaction temperature: 400°C
 N_2 /toluene: 5/1 (mol/mol)

Fig. 4-2 Effect of Contact Time

Table 2 Activity of Cation Exchanged Mordenite Catalysts

Catalyst	Ion Exchange (%)	Calcination Temperature (°C)	Toluene Conversion (mol%)	Yield (mol%)			Composition (mol%)			
				B	X	3MeB	B	T	X	3MeB
HZ	93	700	57	43	42	5	24	49	24	3
HZ (NH ₄)	95	700	55	42	39	6	22	55	20	3
BeZ	72	700	21	8	9	0	5	90	5	0
BeZ	72	500	28	20	21	1	11	77	11	1
MgZ	84	700	trace	trace	trace	0	—	—	—	—
MgZ	84	500	trace	trace	trace	0	—	—	—	—
CaZ	65	700	0	0	0	0	—	—	—	—
CdZ	73	700	0	0	0	0	—	—	—	—
CeZ	79	700	15	4	4	0	2	95	2	0
HM (HCl)	88	700	52	36	37	4	21	55	21	2
HM (NH ₄)	93	700	52	39	40	4	22	54	22	2
CeM	43	700	trace	trace	trace	0	—	—	—	—
BeM	55	700	5	1	1	0	1	98	1	0
CeY	74	300	29	15	17	0	9	82	10	0
HY (NH ₄)	81	500	35	28	31	2	14	69	15	1
SiO ₂ -Al ₂ O ₃	—	550	1	0.3	0.4	0	—	—	—	—

Reaction condition; reaction temperature: 400°C, W/F : 15 (g/mol/hr), N_2 /toluene: 5/1 (mol/mol)

On BeZ, the catalytic activity was higher when it was calcined at 500°C than when calcined at 700°C. It was suggested that the optimum calcination temperature for BeZ was lower than that for HZ. This phenomenon was consistent with that for the faujasites.

For this reaction, HY and CeY showed an induction period similar to the alkylation reaction of toluene with methanol^{(6),(7)}.

3.4 Kinetic Discussion

The reaction is kinetically discussed by using an HZ catalyst. The initial activity derived by extrapolating the streaming time to zero is used in this discussion.

At 275, 300, 325, 350, 375, 400 and 425°C, each reaction rate constant (k) was calculated for the conversion of toluene at 1~5 g/mol/hr of W/F . An Arrhenius plot was given in Fig. 5. It was shown that an Arrhenius plot could be divided into two sections. At the higher temperature range, the apparent activation energy decreased and was about 11.8 kcal/mol. It seemed that the diffusion of toluene was the main rate determining step. While, at the lower

Catalyst: HZ calcined at 700°C for one hour
Reaction condition;

N_2 /toluene: 5/1 (mol/mol)

E : apparent activation energy

Fig. 5 Arrhenius Plot

temperature range the apparent activation energy was about 18.8 kcal/mol and the adsorption of toluene on the catalyst was very strong; therefore, the reaction rate was apparently of zero order for toluene.

4 Conclusion

1) Disproportionation of toluene proceeded to almost a state of equilibrium over H-mordenite, accompanied by a little dealkylation and cracking.

2) Only H-mordenite, among the cation exchanged mordenites, showed high activity for the discussed reaction. The exchanged cation stuck out from the mordenite channel walls, thus metallic ions hindering the diffusion of the reactants.

3) At the higher reaction temperature range, the apparent activation energy decreased, because

the diffusion of toluene was effective on the rate determining step. At the lower temperature range, the adsorption of toluene on the catalyst was very strong, and therefore the reaction rate was apparently of zero order for toluene.

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