DISPROPORTIONATION OF TOLUENE TO BENZENE AND XYLENES

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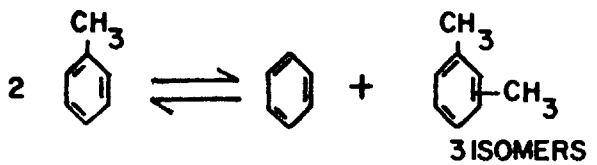
Disproportionation of toluene offers an attractive method for utilization of surplus toluene to produce benzene and xylenes. Earlier studies in liquid phase using Friedel-Crafts type catalysts did not show high conversion and selectivity, the corrosive nature and non-recoverability of such catalysts were additional disadvantages.

Disproportionation in vapour phase using metal exchanged molecular sieve catalysts have been reported in literature in recent years. Investigations on this using zeolite catalysts are reported in this paper. Equilibrium of the reaction at 500 — 1000°K, calculated from thermodynamic data, shows a conversion of 48.14 to 48.86 mole per cent of toluene. Dealkylation of toluene to benzene is thermodynamically more favourable and has been found to occur in various degrees in all cases as indicated by the benzene to xylenes ratio in the product. Acidity and degree of exchange of cations was found to considerably influence the activity of these catalysts. With Cadmium exchanged faujasite type zeolites of large pores, initial activity fell sharply as Cd sublimed out of the zeolites. Rare-earth-exchanged samples showed good activity, increasing with higher amount of exchanged cation. Presence of hydrogen and increasing pressures from 5 to 40 atm increased covnersion from 23.2 to 38.5 per cent at 500°C. Higher hydrogen partial pressure leads to more hydrodealkylation.

INTRODUCTION

Disproportionation of toluene to produce benzene and xylenes have received considerable attention in recent years due to the increasing demands for benzene and xylenes for production of plastics, synthetic rubber, synthetic fibres, detergents etc. and surplus toluene available from catalytic reforming and naphtha cracking plants.

In toluene disproportionation, two molecules react to form one each of benzene and xylene :



All the 3 isomers of xylene are formed; but it does not contain ethyl benzene which is always present in C_8 aromatics from catalytic reforming. The absence of

ethyl benzene is a distinct advantage since that makes the separation of isomers easier and significantly decreases the cost of recovery of *p*- and *o*-xylenes.

Early studies on this reaction were carried out in liquid phase using Friedel crafts catalysts (McCaulay 1962; CSIR 1965; and Schrie Sheim 1961) particularly proton donor lewis acids such as $AlCl_3$–HCl, HF–BF_3, $AlBr_3$–HBr. The main disadvantages with these catalysts are : (1) they are corrosive in nature; (2) these are continuously lost and cannot be economically recovered; (3) they are difficult to handle; and (4) these are generally used as slurries which increase mechanical problems.

Crystalline alumino-silicates (zeolites) have recently been found to be highly active solid acid catalysts for this disproportionation and related reactions which are supposed to proceed through the formation of carbonium ions as intermediates.

Studies on this process of disproportionation of toluene using modified 13 *x* zeolites are reported here.

Equilibrium and Enthalpy of Reaction

Equilibria of the toluene disproportionation reaction to equal moles of benzene and *m*-xylene were calculated at different temperatures from the free energy data and are given in Table I.

It can be seen from Table I that conversion between 47.40—48.86 mol. per cent is theoretically possible over the temperature range of 300–1000°K.

Since there is no increase or decrease in the number of moles in the reaction, equilibrium does not appear to be affected by pressure. However, use of hydrogen as carrier gas under pressure has been found to be helpful in controlling the partial pressure of toluene and in suppressing the highly undesirable deposition of carbon.

Heat of Reaction : The true disproportionation of toluene to benzene and xylenes is slightly endothermic. But in presence of hydrogen, the equilibrium of hydrodealkylation of toluene to benzene and methane is more favourable and has always been reported to occur (10). The extent of hydrodealkylation is indicated by the benzene to xylene molar ratio (*B*/*X*). Due to this hydrodealkylation, the overall reaction becomes exothermic. Table II shows the values of the overall heat of reaction at different B/X ratios in the product.

Experimental

Considering the equilibria, experimental studies were conducted to disproportionate toluene in vapour phase at the temperature range of 450–525°C in presence of hydrogen under pressure.

Catalyst : For use as catalysts, zeolites with large pores such as faujasite and mordenite have been found to be useful (Venuto & Landis 1968). The normal zeolites containing alkali are not active catalysts, but on replacement of the alkali cations with divalent or trivalent cations, the modified zeolites were reported to show good activity for reactions like isomerization, alkylation, disproportionation and others (Venuto & Landis 1968) which proceed through carboniumi on intermediates.

Linde molecular sieves 13 *X* and *Y* with pore size of about 10 Å and having silica-Alumina ratio upto 5.0 have been reported to be active catalysts for toluene disproportionation (Morita & Matsumoto 1968 *a*, *b*; and *vice-versa* 1968 *a*, *b*).

TABLE I

Free energy change, equilibrium constant and equilibrium conversions

Temperature °K	ΔF K cal/mole	K	Conversion mol. per cent	
			Benzene	*m*-xylene
300	0.938	0.206	23.70	23.70
400	1.236	0.211	23.90	23.90
500	1.526	0.215	24.07	24.07
600	1.808	0.220	24.19	24.19
800	2.372	0.225	24.34	24.34
1000	2.937	0.228	24.43	24.43

TABLE II

Enthalpy changes at different B/X molar ratios at various temperatures

Temperature °K	ΔH, K cal/mole at B/X mole ratio of				
	1.0	1.5	2.0	2.5	3.0
298.16	0.040	—3.9756	—6.5857	—8.5534	—10.0000
400	0.075	—4.1008	—6.8151	—8.8612	—10.3645
600	0.110	—4.3584	—7.2623	—9.4512	—11.0595
800	0.114	—4.5936	—7.6535	—9.9602	—11.6658
1000	0.123	—4.7720	—7.9537	—10.3522	—12.1145

For this study, molecular sieve 13 *X* with binder, in the pellet form (1/8″ size) was used. It was subjected to cation exchange with solutions of chloride/nitrates of Cadmium and Lanthanum. After exchange, the excess nitrates/chloride ions were removed by washing. The catalyst pellets were then dried at 120°C for 2 hours and calcined at 550°C for 3 hours. The degree of exchange with Cd or La was determined through analysis of sodium content by flame photometry.

Apparatus and Procedure: Figure-1 shows a sketch of the experimental unit. Toluene from a caliberated burette was fed by a microfeed pump to the top of the reactor along with measured stream of hydrogen from the cylinder at the required pressure. The feed mixture being preheated in the upper part of the reactor, flowed through the catalyst bed. The effluents were cooled and the gas was separated from the liquid in the pressure separator.

A stainless steel (18/8) tube of 15 mm internal diameter served as the reactor and was heated electrically. The catalyst bed was located at the constant temperature zone. Before the experiments, the catalyst was reduced by hydrogen.

Liquid and gaseous products were analysed by GLC and Orsat apparatus respectively. The catalyst was regenerated after every run and its level of activity checked by repeating a standardized experiment at fixed intervals.

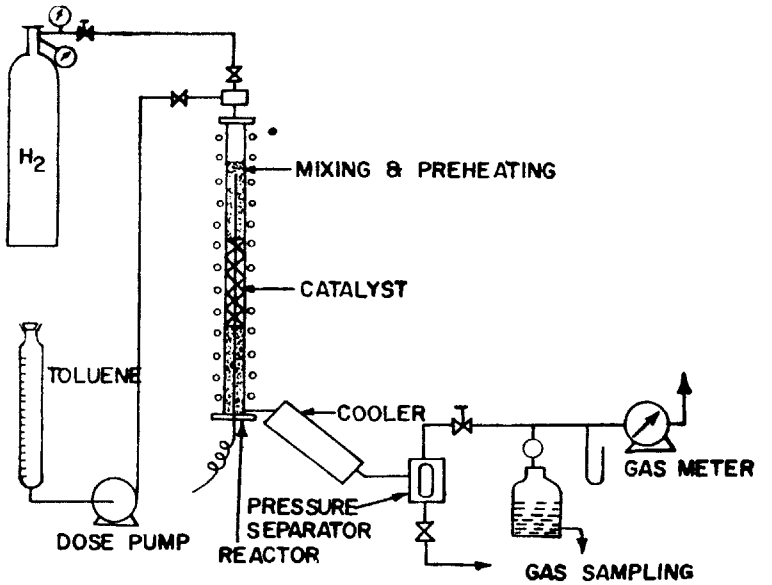


FIG. 1. Schematic diagram of disproportionation of toluene.

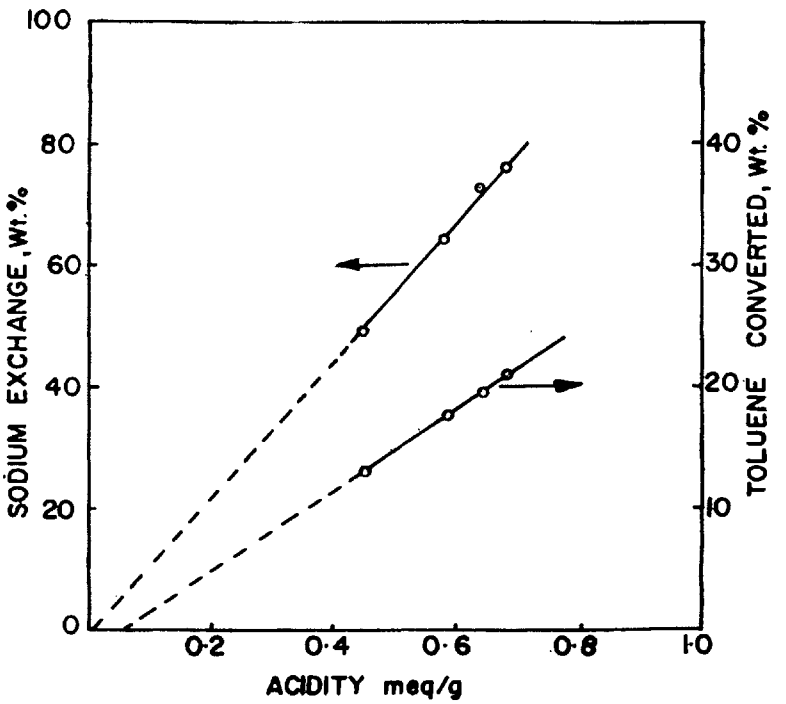


FIG. 2. Acidity of catalyst *vs.* sodium exchange and corresponding activity in toluene conversion at atmospheric pressure.

RESULTS AND DISCUSSION

With Cd-X Catalyst : Experimental work was carried out with Cd exchanged 13-X Catalyst (degree of exchange 70 per cent) in a silica reactor at atmospheric pressure and at 550°C. The average conversion for 2½ hours decreased from 11.2 to 1.1 per cent in three subsequent experiments. Some brownish yellow deposit was noticed at the exist of the reactor tube. The deposit was tested qualitatively and found to be that of Cadmium.

Some experiments were carried out at 7 Kg/cm² pressure, 500°C, LHSV of 0.86 g/g cat/hr and hydrogen to toluene molar ratio of 4.1 to see the influence of pressure. At pressure also, conversion of toluene decreased from 30 to 1.2 per cent in three subsequent experiments of one hour's duration. The results are shown in Table III (Expt. Nos. 1–3).

TABLE III

Disproportionation of toluene over Cd *and* La *exchanged* 13*X zeolite*

S. No.	Catalyst	Degree of exchange wt. % of Na	Pressure Kg/cm²	LHSV g/gat/hr.	Temp. °C	H²/ Tol. Molar	Duration hrs.	B+X wt. %	Calci-nation temperature °C
1.	Cd—X	70	7	0.86	500	4.10	1	30.0	550
2.	Cd—X	70	7	0.85	500	4.15	1	9.6	550
3.	Cd—X	70	7	0.86	500	4.10	1	1.2	550
4.	La—X	55	10	0.81	500	4.29	12	9.5	650
5.	La—X	55	10	0.82	500	4.25	12	15.2	550
6.	La—X	55	10	0.86	500	3.70	6	16.4	550
7.	La—X	85	10	0.85	500	3.85	6	26.8	550

The loss of activity seems to be due to the sublimation of Cadmium from the catalyst. It has been reported by Yates (1965) that reducible metals like Cd, Hg, Zn., diffuse out of the zeolite in presence of hydrogen because the formed atoms are held by weak van der Waal's forces in the lattice and the zeolites are not able to retain them.

With La-X Catalyst

(a) Effect of Degree of Exchange : Experiments were first carried out with different La-exchanged samples; results from 2 runs at 10 atm. pressure are given in Table III. The average conversion of toluene in 6 hours run was only 16.4 per cent with 55 per cent exchanged La-X catalyst at 500°C and 10 Kg/cm² pressure. On increasing the exchange of sodium with Lanthanum to 85 per cent, toluene conversion rose to 26.8 per cent.

The increased conversion at higher degree of exchange can be attributed mainly to increasing acidity of the catalyst and secondly the larger availability of the cations in accessible sites.

Acidity of the catalyst samples were measured by *n*-butylamine titration using neutral red indicator with p*Ka* value of +6.8. It can be seen from Figure 2 that

the acidity of the catalyst increased linearly with increasing level of exchange of sodium with lanthanum. With this increasing acidity, activity of the catalyst in toluene conversion also rose linearly. These results corroborate the observations of Matsumoto and Morita (1968 *b*) of increasing conversion with acidity level of such molecular sieve catalysts.

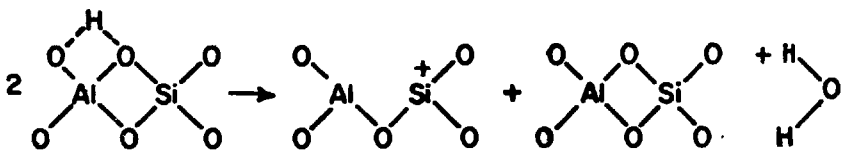
Extrapolation of the lines in Fig. 2 to lower acidities would indicate that this faujasite catalyst would show negligible activity for disproportionation at still lower exchange levels–only some dealkylation to benzene occurs. The cations introduced beyond this exchange contribute in toluene conversion. With increasing degree of exchange thereafter, their availability for the reaction rise linearly. This supports the view of Breck (1964) that there are three sites S_I, S_{II} and S_{III} where the cations are located. S_I sites are inaccessible to reacting molecules. S_{II} sites are the main source of activity and are located in α-cages which are formed by a tetrahedral arrangement of truncated octahedra and have internal dia of 12–13Å and aperture of 8–9 Å diameter. In the exchange of poly valent cations S_I sites are first filled (Pickert *et al.* 1964) and only then the cations occupy S_{II} sites.

In fact, the concentration of Bronsted acid sites in total acidity appears to be more important and this is affected by the calcination conditions and nature of the cation (4). To determine the proper calcination temperature, La–X (55 per cent exchanged) samples were calcined at 550°C and 650°C before use. Conversions of toluene with these two samples are given in Table III. In two runs of 12 hours duration, conversions were 15.2 per cent and 9.5 per cent respectively. This decrease in conversion at higher calcination temperature probably resulted from the transformation of some sites to inactive lewis acid.

Plank (1964) suggested that in such catalysts adsorbed water is polarized by the field associated with the cation, resulting in the formation of acidic hydroxyl groups :

$$M(OH_2)^{++} \longrightarrow MOH^{+} + H^{+}$$

The released proton attaches itself to the lattice oxygen to form an acidic hydroxyl group. These groups are the primary active sites for carbonium ion reactions. At temperatures, around 500°C and above, these protonic sites start getting converted into comparatively inactive lewis acid sites as follows :



(*b*) *Influence of Operating Variables*—The 85 per cent exchanged *La-X* catalyst was then used to study the conversion. The experiments were of six hours duration and the conversion is the average for that period at various operating conditions in the following range :

Temperature	—	475–525°C
Pressure	—	5–40 Kg/cm²
LHSV	—	0.5–1.18 g/g/hr.
H_2/Tol. molar	—	3.8–10.94

TABLE IV

Disproportionation of toluene over rare earth exchanged 13 X zeolite

SN.	Temperature °C	Pressure Kg/cm²	LHSV g/g cat/hr	H_2/Tol molar	B/X molar ratio	B+X wt. %
1.	500	5	0.85	3.8	3.08	23.2
2.	500	10	0.85	3.8	2.73	26.8
3.	500	20	0.85	3.8	2.40	30.9
4.	500	40	0.85	3.8	2.46	38.5
5.	475	20	0.85	3.8	1.73	26.8
6.	525	20	0.85	3.8	3.06	25.9
7.	500	20	0.512	3.8	2.88	30.0
8.	500	20	1.18	3.8	2.17	23.4
9.	500	30	0.85	3.99	2.14	30.3
10.	500	30	0.85	10.94	2.74	39.7

The results are given in Table IV.

The results showed that increase in pressure from 5–40 Kg/cm² was beneficial; toluene conversion increased from 23.2 to S8.5 wt. per cent at 500°C.

With increasing H_2 partial pressure, corresponding to H_2/Tol. molar ratio from 4 to 11, keeping all other parameters same, there was substantial increase of total $B+X$ yields, rising upto 40 per cent. But hydrodealkylation of toluene also rose at the same time as indicated by the increase of B/X ratio from 2.14 to 2.74.

The temperature of reaction seemed to have pronounced influence on conversion and selectivity with this catalyst. At 475°C the conversion to $B + X$ was 27 per cent which increased to 30.9 per cent but at 525°C, it fell to 26 per cent. On the others hand extent of hydrodealkylation increased linearly with temperature.

Increase of liquid hourly space velocity g/g/hr., in the range of 0.5–1.18, showed that conversion decreased from 30.9 to 23.4 wt. per cent. Molar ratio of B/X also decreased almost proportionally.

CONCLUSION

The equilibria of toluene disproportionation in vapour phase to benzene and xylenes shows that conversions of about 48.5 mol. per cent is possible at temperatures upto 550°C. Cation exchanged Linde 13—X molecular sieves showed good activity in this reaction. Among the cations tried, Cadmium was found unsuitable as it diffused out in presence of hydrogen. Lanthanum exchanged faujasites showed increasing activity with higher degree of exchange which could be attributed to increasing acidity of the catalyst. Calcination of the catalyst at higher temperature decreases its activity.

Good conversions were obtained within a narrow range of temperature and space velocity. At 500°C and LHSV of 0.85 g/g/hr around 40 per cent conversion of toluene was obtained at 30–40 atm. pressure in presence of hydrogen. Higher

hydrogen partial pressure improved conversion; but tended to increase also hydrodealkylation.

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