

TOLUENE AND XYLENE DISPROPORTIONATION OVER HZSM-5 CRYSTALS OF DIFFERENT SIZE

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ABSTRACT

Toluene, xylene (isomer equilibrium mixture) or 1,2,4-trimethylbenzene (1,2,4-TMB) were fed to a fixed-bed reactor in a flow of H₂ or N₂, at 300 to 360°C. The catalyst was HZSM-5, employed as mixed crystals or one of three separate fractions from 2.5 to 7.5 μm average size. A few runs were also carried out after poisoning the catalyst outer surface with 4-methylquinoline.

The catalyst crystal size showed no effect on the disproportionation of toluene and a slight effect on that of xylene. Xylene gave also demethylation, which was the main reaction of 1,2,4-TMB. Poisoning showed a marked effect on selectivity in the case of toluene and on fractional conversion for xylene disproportionation, and deeply affected the reactions of 1,2,4-TMB.

INTRODUCTION

Toluene disproportionation on unmodified HZSM-5 catalysts proceeds usually to an equilibrium mixture of xylene isomers [1]. The para-selectivity could be increased up to 35% by reaction over "large crystals" of catalyst (3 μm size) at 550°C [2]. More impressive results were achieved by using ZSM-5 catalysts modified with Mg, P or B [1,3], or partially deactivated by coking [4].

Xylene reactions over HZSM-5 were studied at 250-300°C, finding a strong selectivity for 1,2,4-trimethylbenzene in the disproportionation, which was accompanied by isomerization [5]. Dealkylation was also found at 370-400°C [6].

We undertook a study of toluene and xylene disproportionation on HZSM-5 crystals of different size, looking for shape-selectivity effects and aiming at discriminating between channel diffusion resistance and transition state steric inhibition as their cause [7]. In order to

get further information on catalyst behaviour, a few runs were also carried out on 1,2,4-trimethylbenzene.

The catalyst employed was the same zeolite, of high and stable activity, previously used for kinetic measurements on toluene disproportionation [8]. However, for the present work, besides using "mixed crystals" (M), three samples with average crystal size 7.5 μm (A), 4 μm (B) and 2.5 μm (C) were separated and tested.

The following reactions were carried out on each catalyst sample in the order given: a) toluene disproportionation (carrier H_2) in standard kinetic conditions; b) toluene disproportionation (carrier H_2) at higher conversion; c) reactions of xylenes, fed as an equilibrium mixture of isomers (carrier H_2); d) (only on catalysts B and M) reactions of 1,2,4-trimethylbenzene (carrier H_2); e) toluene disproportionation (prolonged runs with carrier N_2).

For some reactions over catalyst M, poisoning experiments were also effected, by using 4-methylquinoline, which should inhibit only the acid sites on the outer surface of HZSM-5 [9,10], because of its molecular size.

EXPERIMENTAL

Materials. All reactants and standards were commercial "pure reagents", which gave single peaks by GC analysis, apart from 1,2,4-trimethylbenzene, that contained ca.1% of 1,3,5-isomer.

Catalyst. HZSM-5 was prepared by a standard procedure [11]; it was the same binderless catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3$ wt.ratio 15.0) described elsewhere [8] as HZSM-5(HA). Samples A, B and C were separated from it by elutriation in deionized water, leaving behind a small amount of smaller particles. Crystal sizes were evaluated on SEM micrographs. All samples were pressed, crushed and sieved to 40-80 mesh before use. Elemental analysis by A.A. revealed differences between the samples, the content of aluminium (as Al_2O_3) being 4.63% for A and for B, 5.91% for C and 5.06% for the mixed crystals. However, surface acidity, as measured by titration with n-butylamine in anhydrous solvent [12] ($\text{pK}_a \leq 1.5$), was found scarcely dependent on Al content: A, 1.0; B, 1.1; C, 1.0 meq/g. When using the bulky tributylamine, the corresponding acidity of the mixed crystals was titrated as 0.075 meq/g.

Apparatus and procedure. A tubular flow reactor with a fixed bed of catalyst (0.5 g), immersed in a thermostatted bath, was employed [8]. Reactants were fed by a glass syringe with PTFE piston and with a carrier to hydrocarbon ratio of 5, at atmospheric pressure (partial pres-

sure of the hydrocarbon in the feed = 17 kPa). The reactor effluent was passed through a condensing trap, kept at ca. -17°C , and liquid products analyzed by GC, using a standard 1:1 Didecylphthalate-Bentone 34 column 4.5 m long.

Selective poisoning experiments were performed following a reported procedure [9], applied to a series of runs on the same catalyst sample. Before each reaction a single dose of 4-methylquinoline was injected (first run, 15 μl ; successive runs, 5 μl , to compensate for a possible partial desorption of the poison). Reactions were carried out in the order a, c, d, a.

RESULTS

Products were usually analyzed by gas-chromatography. A more detailed identification, based on GC-MS analyses, was carried out only for runs on the "mixed crystals" catalyst.

The products from a feed of toluene (T) were mainly benzene (B) and the three xylenes (DMB). Small amounts of C9 hydrocarbons were also found, i.e. ethyltoluenes (EMB), not resolved by the standard GC analysis, and trimethylbenzenes (TMB), which were resolved and found to be predominantly represented by the 1,2,4-isomer.

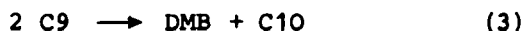
The reaction of xylenes, effected by feeding a mixture close to the isomeric equilibrium, gave toluene and trimethylbenzenes (mostly 1,2,4-TMB) as main products, but also benzene, ethyltoluenes and C10 hydrocarbons in minor amounts. A GC-MS analysis, with a column longer than the standard one, showed that the three isomers of EMB were all present, in the abundance order characteristic of equilibrium ($m > p > o$). As to the C10 hydrocarbons, they were mainly recognized by GC-MS in two peaks, with M.W. 134 and 132, respectively. The former peak corresponded neither to a tetramethylbenzene nor to a diethylbenzene nor to a propyltoluene; it could reasonably be an ethyldimethylbenzene. The latter peak had a retention time just in the region of the tetramethylbenzenes (TTMB), but it was ascertained that TTMB's were absent or negligible; the relevant compound could be a vinyl dimethylbenzene.

When feeding 1,2,4-TMB, the reaction products were mainly xylenes and toluene, with lesser amounts of benzene and C10 hydrocarbons, and a partial isomerization to 1,2,3-TMB. The latter was detected as a shoulder on the peak of the reactant, but sometimes it was not enough for a quantitative integration; in these cases it was only approximately estimated. As to the C10 hydrocarbons, the GC-MS analysis showed

that they were a mixture of isomeric tetramethylbenzenes.

On the basis of the products identified, the chemical behaviour of the system was summarized as follows:

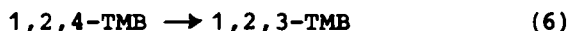
disproportionation



demethylation



isomerization



Demethylation reactions, when xylenes or 1,2,4-TMB were fed to the reactor, were evidenced by the sum of the side-chain carbons in the products falling short of the theoretical.

Fractional conversions for disproportionation (y_{dis}), demethylation (y_{dem}), and isomerization (y_{iso}) were therefore defined as follows, for different feed compositions (x_i = molar fraction of component i):

Feed: toluene

$$y_{dis} = x_B + \Sigma x_{DMB} + 2\Sigma x_{C9} \quad (7)$$

Feed: xylenes

$$y_{dis} = 2(\Sigma x_{C9} + 2\Sigma x_{C10}) \quad (8)$$

$$y_{dem} = 2 - x_T - 2\Sigma x_{DMB} - 3\Sigma x_{C9} - 4\Sigma x_{C10} \quad (9)$$

Feed: 1,2,4-TMB

$$y_{iso} = x_{123\text{-TMB}} \quad (10)$$

$$y_{dis} = 2\Sigma x_{C10} \quad (11)$$

$$y_{dem} = 3 - x_T - 2\Sigma x_{DMB} - 3\Sigma x_{C9} - 4\Sigma x_{C10} \quad (12)$$

Reaction selectivities were also evaluated. The isomer distribution within the xylene fraction of products was expressed as S_o , S_m and S_p , defined as $S_o = x_{o\text{-DMB}}/x_{DMB}$ and analogously for S_m and S_p . For the reaction of toluene, a further selectivity S_{DMB} was given by the ratio $\Sigma x_{DMB}/(\Sigma x_{DMB} + 2\Sigma x_{C9})$, which represents the fraction of DMB produced by reaction (1) and not entered into further disproportionation. Analogously, for a xylene feed, the ratio $S_{C9} [= \Sigma x_{C9}/(\Sigma x_{C9} + 2\Sigma x_{C10})]$ represents the fraction of C9 hydrocarbons produced by reaction (2) and not further reacted.

For the reaction of xylenes, the isomer distribution within the C9 fraction was firstly evaluated as the ratio $\Sigma x_{TMB}/\Sigma x_{C9}$ (the differ-

ence to 1 gives the relative weight of the EMB product), and then as the isomer fractions within the TMB product, essentially as S_{124} (the ratio $x_{124-TMB}/\sum x_{TMB}$).

For comparison, it can be mentioned that the equilibrium fractions of isomeric xylenes at 300-360°C are calculated as: ortho, 0.22; meta, 0.54; para, 0.24. The equilibrium fractions of TMB's at 350°C are similarly calculated as: 1,2,3-TMB, 0.07; 1,2,4-TMB, 0.66; 1,3,5-TMB, 0.27 [13].

Experimental results, worked out as described above, are presented in Tables 1-4 and in Figure 1.

Table 1

Disproportionation of toluene in standard runs (carrier H_2 ; $T=300^\circ C$; $W/F_T^O=164$ g h/mol). Average values of measurements. ^a

Catalyst (size)	Y_{dis}	S_{DMB}	S_o	S_m	S_p
A (7.5 μm)	0.056	0.95	0.22	0.54	0.24
B (4 μm)	0.064	0.96	0.21	0.53	0.26
C (2.5 μm)	0.050	0.96	0.20	0.55	0.25
M (mixed)	0.052	0.95	0.21	0.53	0.26
M^b	0.038	0.95	0.09	0.20	0.71

^a C9 hydrocarbons were exclusively EMB, within the detection limits; ^b sampling 6 h after poisoning by 4-Me-quinoline (15 μl).

Table 2

Disproportionation of toluene at higher conversion (carrier H_2 ; $T=360^\circ C$; $W/F_T^O=504$ g h/mol). Average values of measurements. ^a

Catalyst	Y_{dis}	S_{DMB}	S_o	S_m	S_p
A	0.219	0.98	0.22	0.51	0.27
B	0.258	0.97	0.22	0.53	0.25
C	0.213	0.98	0.22	0.54	0.24
M	0.205	0.98	0.22	0.53	0.25

^a C9 hydrocarbons were EMB and TMB in an approximate ratio of 2:3.

Table 3

Reaction of xylenes^a (carrier H₂; T=350°C; W/F_{DMB}^o=94 g h/mol). Measurements after ca.24 h on-stream.

Catalyst	Y _{dis}	Y _{dem}	S _{C9}	Ex _{TMB} /Ex _{C9}	S ₁₂₄
A	0.099	0.075	0.94	0.98	1.00
B	0.108	0.082	0.92	0.98	1.00
C	0.143	0.063	0.94	0.98	0.97 ^b
M	0.134	0.051	0.94	0.99	1.00
M ^c	0.023	0.049	0.92	0.89	1.00

^a isomers in the feed: o, 0.22; m, 0.54; p, 0.24; unreacted xylenes: o, 0.22-0.24; m, 0.52-0.54; p, 0.24; ^b 1,2,3- and 1,3,5-TMB were both present; ^c after poisoning by 4-Me-quinoline (15+5 μl injected 30 and 3 h, respectively, before sampling).

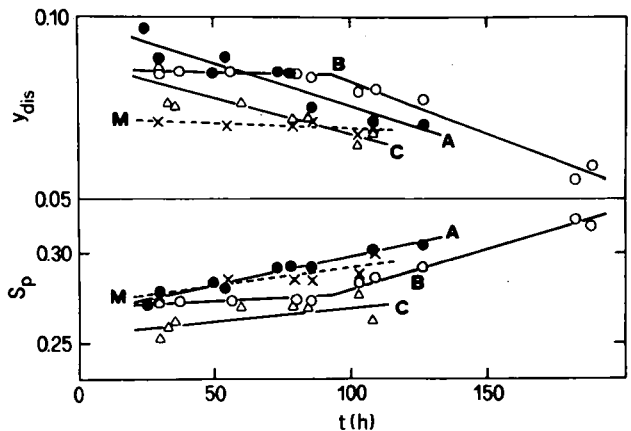
Table 4

Reaction of 1,2,4-trimethylbenzene (carrier H₂; T=350°C; W/F_{TMB}^o=105 g h/mol). Average values of measurements.

Catalyst	Y _{dis}	Y _{iso}	Y _{dem}	S _o	S _m	S _p
B	0.0030	0.0264	0.0753	0.20	0.52	0.28
M	0.0039	0.01-0.02	0.0721	0.21	0.51	0.28
M ^a	0.0018	nil	0.0253	0.16	0.45	0.39

^a after poisoning by 4-Me-quinoline (15+5 μl injected 34 and 7h, respectively, before sampling).

Figure 1. Disproportionation of toluene in prolonged runs with carrier N₂ (T = 300°C; W/F_T^o=164 g h/mol): y_{dis} (upper plot) and S_p (lower plot) vs. time-on-stream. Catalyst samples: ●, A; ○, B; △, C; ×, M. Average values of S_{DMB} were in the range 0.97-0.98.



DISCUSSION

According to the measured kinetics [8], for standard runs (a) on toluene a value 0.052 for y_{dis} and an equilibrium xylene isomer distribution were expected. Results in Table 1 show that this was actually found, within experimental error, not only for the mixed crystals of HZSM-5, but even for the largest particles (catalyst A). This evidences that channel diffusion resistance is negligible in this case and that the measured kinetics refers to the reaction under chemical control. Values of y_{dis} , S_o , S_m and S_p appear independent of catalyst crystal size also for runs (b) to higher conversion (Table 2).

Poisoning was effected on runs (a) by injecting a quantity of 4-methylquinoline exceeding by an order of magnitude the amount required to saturate an HZSM-5 catalyst [9], although corresponding to only 1/5 of the theoretical to neutralize all medium-to-high strength ($pK_a \leq 1.5$) acid sites, should the base penetrate the pores. The poison effects on the toluene standard run over M catalyst (Table 1) were a slight decrease of y_{dis} and a substantial change in the xylene selectivities, favouring p-xylene. The former effect proves that toluene disproportionation occurs mainly in the zeolite pores; the latter is very likely due to the fact that the usual isomerization of the preferred primary product on the acid sites at the pore mouth is prevented by the poison.

As to the C9 fraction, EMB was its only component for runs (a) and it was largely present also in runs (b). A side-chain attack is known to occur on X and Y zeolites exchanged with large or medium size alkali cations, from Cs^+ to Na^+ , for alkylations of toluene [14], xylene [15] and pyridine [16] by methanol. Perhaps a similar mechanism operates in the present case, due to residual Na^+ ions and favoured also by the smaller pore diameter of the zeolite. TMB, when present, was predominantly the 1,2,4-isomer. It can be noticed that S_{DMB} was close to unity, that is the further reaction of xylenes was a very restricted phenomenon.

Xylene reactions (runs c; Table 3) did not include isomerization, because isomeric equilibrium was present in the feed and was preserved in the unreacted xylene output. The various catalyst samples, while showing slight differences in overall activity ($y_{dis} + y_{dem} = 0.174$, 0.190, 0.206 and 0.186 for A, B, C and M, respectively), presented more marked differences in the relative weight of the two reactions. Demethylation gained more weight when the catalyst was in larger crystals

(A and B); on the contrary, Y_{dis} increased in the order $A < B < C$. The effect of 4-Me-quinoline was remarkable, the poison scarcely affecting demethylation but heavily depressing disproportionation. It can be suggested that demethylation occurs mainly within the catalyst pores and without intervention of significant diffusive resistance, while disproportionation, in the absence of poison, occurs partly on the outer surface and partly within the zeolite pores, in this case with significant channel diffusion resistance effects (see values of Y_{dis}).

Disproportionation gave almost always 1,2,4-TMB as the only trimethylbenzene, independently of the site of reaction; it seems therefore that the predominance of this isomer, which is favoured by electronic as well as by statistical factors, is not clear evidence of shape-selectivity. The fraction of EMB within C9's is a more interesting parameter, since the figures in Table 3 (1-2% EMB on unpoisoned catalysts, 11% after poisoning) show that the rate of formation of EMB was little affected by poisoning, which instead markedly reduced the rate of TMB formation, indicating that the former reaction does not require those acid centres that catalyze the latter one.

Surprisingly, TTMB was practically absent from the C10 fraction of runs (c). Apparently, reaction (3) occurs mainly to C9 molecules just formed within the pores, thus favouring side-chain attack, with the possible formation of ethyldimethylbenzene and vinyl dimethylbenzene. In the mentioned cases of side-chain methylation [14-16], formation of both ethyl and vinyl side groups was common.

The main reaction of 1,2,4-TMB (runs d; Table 4) was demethylation. The small amount of disproportionation gave TTMB, as expected, and no EMB was found among the products. Isomerization resulted rather slow, so justifying the very high values of S_{124} of runs (c) at the same temperature. Poisoning depressed demethylation and disproportionation, while preventing isomerization, to the point that the small impurity of 1,3,5-TMB, present in the feed, was found (only in this case) as unreacted. Poisoning slightly favoured p-xylene.

Results of selectively poisoned reactions have been reported up to an overall addition of 20 μ l of 4-Me-quinoline and for samples taken up to 34 h after the first poison injection. Results obtained from runs (d) and (a) after further poison additions showed an abrupt decrease of the catalytic activity, so compromising the reliability of GC analyses.

Prolonged reaction of toluene in N_2 (runs e) gave similar re-

sults for catalysts A, B and C (Figure 1). A "coking" effect was detected, giving decreasing values of y_{dis} and increasing values of S_p (up to 0.32) vs. time-on-stream. Interestingly, the activity of the mixed-crystal sample M was more constant than for samples A-C. This might be connected with slight structural alterations introduced by the elutriation procedure.

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