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NOTES

Rearrangement of *N*-Methylaniline over H–ZSM-5, H–Theta-1, and H–Y Zeolites

It was reported recently that aniline in the presence of ammonia was converted to picolines over zeolite catalysts (*1*). The picolines are important intermediates in the dye and resins industries. However, no report has appeared on the reactions of arylamines over zeolites despite the fact that nitrogen heterocycles make up part of the structure of oil shale kerogens (*2*). The thermal rearrangement of *N*-alkylaniline hydrochlorides in a sealed tube to give ring-alkylated anilines has long been known as the Hofmann–Martius rearrangement (*3*). In this note, we describe the rearrangement of *N*-methylaniline involving a methyl–N bond cleavage to ring-alkylated anilines and N-methylation to *N*,*N*-dimethylaniline over H–ZSM-5, H–Theta-1 and H–Y zeolites.

The zeolites H–ZSM-5 (Si/Al ratio of 18.6), NH_4–Theta-1 (Si/Al ratio of 35), and H–Y (Si/Al ratio of 5.8) used in these rearrangement reactions were obtained from BP Research Centre, Sunbury-on-Thames, U.K. The hydrogen form of H–Theta-1 was obtained by calcining the ammonium form at 500°C (3 h) in a muffle furnace.

The reactions were performed in a continuous flow fixed-bed quartz reactor containing about 1.0 g of previously calcined zeolite catalyst and activated under a stream of nitrogen for 1 h in the reactor. *N*-methylaniline (Fisons) purified by distillation at 196°C was metered into the reactor at a predetermined flow rate. The vapour was cooled successively in water-cooled and air-cooled condensers; the liquid samples were collected periodically, weighed, and analysed by gas chromatography (Carlo–Erba 2151), on a 12-m FSOT Carbowax 20M capillary column. The reaction products were identified by comparison of their retention times with those of authentic compounds in a calibration mixture of known composition.

The conversion of *N*-methylaniline on H–ZSM-5, H–Y, and H–Theta-1 decreased with time on stream due to the deactivation of the zeolites (Fig. 1). At the same contact time, a higher conversion was obtained on the large-pore HY zeolite than on the medium-pore H–ZSM-5 and H–Theta-1 zeolites. The higher conversion obtained on the H–Y zeolite compared to H–ZSM-5 and H–Theta-1 we have attributed to the number and nature of acid sites. Amines are known to poison the acid sites on zeolites; in addition, because of the high Si/Al ratio on the medium-pore zeolites, the available Brønsted acid sites are quickly poisoned, whereas on the large-pore zeolite with low Si/Al ratio the number of available Brønsted acid sites is higher and as such are not poisoned to the same degree. The medium-pore zeolites, being strongly acidic, adsorb aniline and its derivatives very strongly and thus deactivate rather quickly. Similar conclusions were reached by Chen *et al.* (*4*) and Woo *et al.* (*5*) in the methylation of aniline with methanol over ZSM-5 zeolites. They found that with a reduction in the Si/Al ratio of the ZSM-5 zeolites the conversion of aniline increased. Thus one can say that the poisoning of the Brønsted acid sites of the zeolites due to the very strong adsorption of the amines is responsible for the lower conversions on the medium-pore zeolites.

The major products of the reaction of *N*-methylaniline were aniline, *N*,*N*-dimethylaniline, *o*-, *m*-, and *p*-toluidines, and minor

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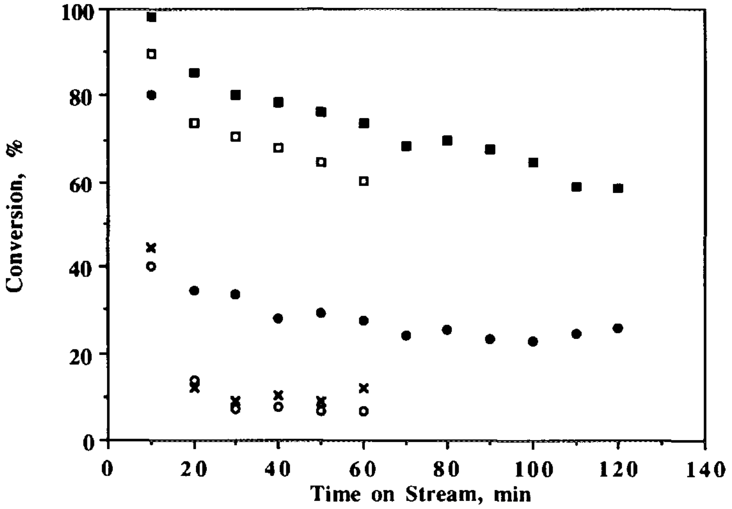

FIG. 1. Conversion of *N*-methylaniline on H-ZSM-5, H-Theta-1, and H–Y with time on stream. Contact time, W/F = 9 g h mol^{-1}. Filled symbols: W/F = 18.1 g h mol^{-1} (H-ZSM-5); W/F = 16.9 g h mol^{-1} (H–Y). (○) and (●) H-ZSM-5, (×) H-Theta-1, (□) and (■), H–Y.

amounts of benzene and xylidines on all the zeolites. Table 1 shows the effect of contact time (defined as weight of zeolite catalyst divided by the number of moles of reactant flowing through the zeolite catalyst per hour) on conversion, product selectivities, and selectivity in the toluidine isomers during 60 min on stream. In the reaction over

TABLE 1

Product Selectivity in the Conversion of *N*-Methylaniline over Zeolites at 364°C during 60 min on Stream

	Zeolite					
	H-ZSM-5		H-Theta-1		H–Y	
W/F (g h mol^{-1})	9.2	18.1	9.0	9.1	9.1	16.9
Conversion[a] (%)	6.8	27.6	12.1	3.6	60.5	73.6
Product selectivity (%)						
Aniline	34.1	39.8	37.1	36.5	31.9	31.3
N,*N*-Dimethylaniline	46.3	49.0	47.5	49.0	10.4	9.5
Toluidine	9.9	7.8	11.8	10.8	45.3	46.3
Others	9.6	3.4	3.6	3.7	12.4	13.0
Selectivity in toluidine isomers (%)						
ortho-	75.2	80.5	88.1	86.7	40.1	34.5
para-	15.8	4.1	11.6	12.8	56.9	62.6
meta-	9.0	15.3	0.3	0.5	3.0	2.8
o:*p* ratio	4.8	19.6	7.6	6.8	0.7	0.6
Deposits						
Coke[b] (%)	5.8	4.5	4.5	3.4	5.5	5.5
N on zeolite[b] (%)	0.8	0.7	0.8	0.6	0.6	0.6

[a] Conversion recorded during the period 50 to 60 min from the start of reaction.

[b] Recorded as percent of zeolite weight.

H–ZSM-5 at longer contact time the selectivity to aniline and *N,N*-dimethylaniline increased, whereas the selectivity decreased in toluidines and more so in *para*-toluidine. The toluidines are probably primary products. A similar effect of contact time on toluidine selectivity was reported by Ione and Kikhtyanin (*6*) during the methylation of aniline with methanol on H–ZSM-5. Over H–Y zeolite no significant change in selectivity was observed at both contact times. In contrast to the reaction over H–ZSM-5, where lower selectivity was observed in *para*-toluidine at longer contact time, the selectivity to *para*-toluidine over H–Y zeolite increased with a slightly lower selectivity to *ortho*- and *meta*-toluidines.

These selectivity changes are indications to the possible mechanistic pathways involved in the zeolite reactions. The difference between the medium-pore zeolite (H–ZSM-5) and the large-pore zeolite (H–Y) is probably that of pore structure. The medium-pore zeolites with 10-membered ring apertures seem to favour a bimolecular process which will give aniline and *N,N*-dimethylaniline because of the close fit of the reactant molecules in the channels. By contrast, the large-pore zeolite with a 12-membered ring aperture seems to favour a monomolecular process, and hence a higher proportion of the toluidines.

As mentioned earlier, the amines will be strongly adsorbed on the medium-pore zeolites because of their strong acid sites, thus high selectivity to *ortho*-toluidine (a primary product since it increases at longer contact time over H–ZSM-5) observed over H–ZSM-5 and H–theta-1 is an indication of the strong adsorption of the reactant on the zeolite, such that the only reaction possible is the methyl group migration from N- to aryl carbon at the *ortho* position because of its proximity to the adsorption site. That this is an intramolecular process is noted in the high $o:p$ ratios (Table 1). It has been shown recently (*7*) that the toluidines do not interconvert readily on H–ZSM-5 zeolite, based on the mechanistic argument that the toluidines would be protonated at nitrogen, rather than at the alkyl bearing carbon of the aromatic ring, and so we must expect very little contribution from the isomerization reactions. Over H–Y zeolite, where the acid sites are not as strong as on H–ZSM-5, *para* selectivity is observed. The $o:p$ ratios over H–Y are less than 1. For the Hofmann–Martius and Reilly–Hickinbottom rearrangement reactions, Shine (*3*) suggests that the rearrangement of *N*-methylaniline hydrochlorides takes place by an intermolecular process. Ogata *et al.* (*8*) also favoured the intermolecular process in the hydrogen halide catalysed rearrangement of *N*-methylaniline because of the high $p:o$ ratio observed. This being the case, then an intermolecular process can account for the high *para* selectivity on H–Y zeolite. Intermolecular processes are possible in Y zeolites because of the large electrostatic field gradient in its α-cage (*9*), which results in a high concentration of the reactant molecules in this cage.

It was observed that at about 55% conversion of *N*-methylaniline the selectivity to *ortho* and *para* toluidine on H–Y zeolite is reversed. We think that this happens because of zeolite deactivation resulting from fewer acid sites which strongly adsorb the amine, and thus N- to C-methyl group migration is favoured. It could be that at still lower conversions the selectivity to *ortho* isomer over the *para* isomer would become very apparent.

In separate experiments performed over H–Theta-1, in which the flow rate of nitrogen carrier gas was increased from 26.8 mmol h^{-1} to 80.4 mmol h^{-1}, thus diluting the concentration of *N*-methylaniline, it was observed that the conversion dropped from 12.6 to 3.6% during the period 50 to 60 min from the start of reaction (Table 1). Slight changes were observed in the selectivity to products. These observations indicate the bimolecularity of the rearrangement over the zeolites.

In these reactions neither pyridine nor picolines and their derivatives were detected, probably because of the low contact time employed in these reactions and also the absence of ammonia compared to the reactions observed by Chang and Perkins (*1*).

The reaction of *N*-methylaniline over these zeolite catalysts gave rearranged products, the toluidines, aniline and *N,N*-dimethylaniline. Over the large-pore H–Y zeolite higher conversions were obtained than over the medium-pore H–ZSM-5 and H–Theta-1 zeolites. These observations have been explained on the basis of the acidity of the zeolites and on their affinity for the aniline reactants. On the large-pore H–Y zeolite toluidines were favoured, whereas on the medium-pore H–ZSM-5 and H–Theta-1 zeolites, aniline and *N,N*-dimethylaniline were favoured.

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