Selectivity to N-mono or dialkylation in the reaction of aniline with dimethyl carbonate on faujasite, EMT and beta alkaline zeolites

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Zeolite K-EMT is as active and selective to N-mono methylation as K-Y in the alkylation of aniline with dimethyl carbonate at 408 or 453 K. No C-alkylation occurs in the temperature range studied. At 503 K, K-X and Cs-X are about 75% selective for dialkylation to N,N-dimethylaniline with about 97% conversion.

Keywords: aniline; dimethyl carbonate; alkylation; zeolite; EMT; beta; faujasite

1. Introduction

The N-alkylated products of aniline (N-methylaniline (NMA) and N,N-dimethylaniline (NNDMA)) are useful raw materials for organic synthesis as well as important intermediates in dye stuffs, pharmaceuticals and agrochemical industries. N,N-dimethylaniline is also used as solvent and additive in the production of synthetic rubber.

Several reports have appeared on the alkylation of aniline using methanol as methylating agent [1]. Recently, it was shown that on faujasite catalysts, dimethyl carbonate (another methylating agent) is very selective for the alkylation of aniline to N-methylaniline [2], the *o*-methylation of phenol to anisole [3] or the α-monomethylation of phenylacetonitrile to α-methylphenylacetonitrile [4]. In the case of the alkylation of aniline, faujasites X or Y are shown to be better catalysts than Na-ZSM-5, K-L or Na-mordenite with regards to activity or selectivity [2]. In particular, in the experimental conditions used (453 K, K-Y is a very good catalyst giving up to 99.6% conversion with 93.5% N-methylaniline selectivity, the other product being N,N-dimethylaniline [2].

We present experimental results obtained with other zeolitic systems in the alkylation of aniline and compare the influence on selectivity of the alkylating agent (methanol or dimethyl carbonate (DMC)) and that of the zeolite structure.

2. Experimental

Zeolites Y and X (Union Carbide), EMT (Elf Company) and beta (PQ Corporation) were exchanged with alkaline cations using 0.5 M solutions of the corresponding chloride [1]. After washing, the catalysts were centrifuged, dried and calcined at 723 K. Their chemical compositions are given in table 1.

Catalytic tests were performed in a micro reactor at various temperatures after activation of the sample at 723 K in an oxygen flow of 120 ml/min for 12 h. Experiments were typically carried out with 30 mg of catalyst and $W/F = 0.206$ g h mol^{-1} (where W is weight (in gram) of catalyst and F is the total flow rate (aniline + alkylating agent + carrier gas) using nitrogen as carrier gas). In order to compare methanol and DMC as alkylating agents, the flow of nitrogen and the ratios DMC/aniline = 3 and N_2/(aniline + DMC) = 46 were chosen to be the same as those previously used for reactions involving methanol [1]. The selectivities are calculated in wt% of products.

3. Results and discussion

In the case of alkylation of aniline with methanol on beta and EMT, it has been previously reported that deactivation occurs when the zeolites are exchanged with alkaline cations while the protonic forms are rather stable with time on stream [1]. Fig. 1 compares the % conversions obtained on protonic (H-β) or alkaline (Na-β, Cs-β and Na-EMT) zeolites during a run at the same reaction temperature (573 K) using methanol (fig. 1A, from ref. [1]) or DMC (fig. 1B) as alkylating agents. The

Table 1
Chemical analysis of zeolites

Zeolite	Si/Al	Alkaline cation [a] (except Na)	Na [a]	Alkaline cation/Al [b]
H-beta	12.3	0	0.4	0.08
Na-beta	14.5	0	3.0	0.73
K-beta	13.7	3.4	290 [c]	0.77
Cs-beta	13.7	3.3	100 [c]	0.75
Na-EMT	3.8	0	18.0	0.90
K-EMT	3.9	18.7	0.7	0.96
Cs-EMT	4.0	14.8	6.0	1.04
K-Y	2.4	54.0	2.0	1.00
Cs-Y	2.6	45.0	9.0	1.00
K-X	1.2	84.0	2.0	1.00
Cs-X	1.2	57.0	29.0	1.00

[a] Atom/U.C.

[b] Difference from 1 arises from unexchanged protons.

[c] ppm.

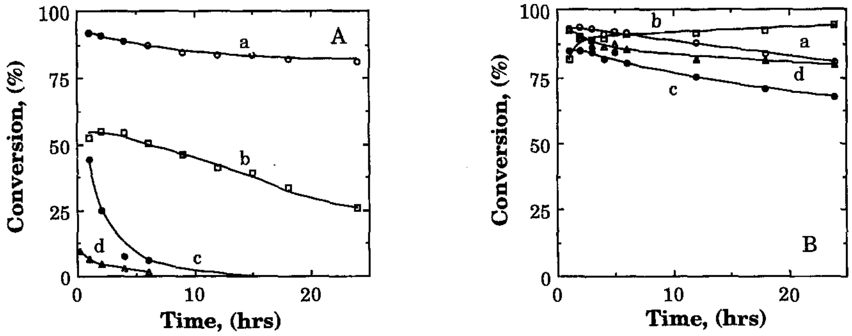

Fig. 1. Alkylation of aniline at 573 K with methanol (A) from ref. [1] and dimethyl carbonate (B). (a) H-beta; (b) Na-beta; (c) Cs-beta and (d) Na-EMT.

figure indicates that for H-β (curve a), the alkylating agents do not bring any significant changes either in conversion or in deactivation. However, for all alkaline samples (curves b, c, d) the percent conversion of aniline is high and the deactivation is less when the alkylating agent is DMC. With DMC, Na-beta shows no deactivation, and Cs-beta and Na-EMT which were rapidly deactivated during alkylation with methanol are the least stable. This deactivation was thought to arise from anionic polymerisation of aniline involving methanol or formaldehyde formed from it [1]. Such a problem does not seem to be important when the alkylating agent is DMC.

Table 2 compares the product selectivities at similar conversion levels (80–92%) and at a constant reaction temperature 573 K. In the case of H-β, the selectivities appear to be comparable whether the alkylation is conducted with methanol or DMC, the N-and C-alkylations being in the ranges 60–70% and 10–12% respectively. This may suggest that similar adsorbed active alkylating species are formed from methanol and DMC. On alkaline zeolites the activities using methanol and DMC are very different (fig. 1) and hence, comparison of the effect of alkylating agent on the product distribution is not possible. Table 2, however, clearly indicates that by contrast with the case of the protonic H-β, alkylation with DMC on alkaline zeolites (Na-beta, Cs-beta or Na-EMT) always gives 100% alkylation on N. While the alkaline beta catalysts preferentially form N,N-dimethylaniline (about 65%), the Na-EMT favours the formation of monomethylated product, N-methylaniline (about 58%). The differences for N-selectivity on protonic and alkaline zeolites strongly suggest that the C-alkylation with DMC may be favoured on protonic sites while methylation on N would rather occur on other active centers such as basic and/or Lewis acid sites present in the alkaline samples.

The high alkylating activity of DMC allows to decrease the reaction temperature. The high activity and selectivity to NMA of K-Y at 453 K [2] suggests to compare the EMT and beta catalysts to K-Y at lower reaction temperatures. Table 3 presents the catalytic activity results obtained at 408 K after 6 h on stream. Under

Table 2
Comparison of product selectivity for alkylation of aniline on H-, Na-, Cs-beta and Na-EMT zeolites after 6 h on stream at 573 K

Zeolite	Alkylating agent	% aniline conversion	NMA[a]	NNDMA[a]	NNDMPT[a]
H-beta	methanol	87.4	20.5	40.9	28.5
	DMC	91.2	22.5	48.1	17.2
Na-beta	DMC	91.0	36.6	61.7	1.3
Cs-beta	DMC	80.2	31.3	68.7	0
Na-EMT	DMC	85.4	58.5	41.5	0
		o-tol.[a]	*p*-tol.[a]	N-alkylation[b]	C-alkylation[c]
H-beta	methanol	8.8	1.3	61.4	10.1
	DMC	10.7	1.4	70.7	12.1
Na-beta	DMC	0.4	0	98.3	1.3
Cs-beta	DMC	0	0	100	0
Na-EMT	DMC	0	0	100	0

[a] NMA: N-methylaniline (N-alkylation); NNDMA: N,N-dimethylaniline (N-alkylation); NNDMPT: N,N-dimethyl-*p*-toluidine (N + C-alkylation); *o*-tol and *p*-tol: *o*- and *p*-toluidines (C-alkylation).

[b] NMA + NNDMA.

[c] *o*-tol. + *p*-tol.

the conditions used, all the catalysts are 100% selective to alkylation on N and the deactivation with time on stream is small. The % conversion and selectivity to monomethylation are close for K-Y, K-EMT and Cs-EMT, the catalyst K-EMT being even slightly better on both values than K-Y. The least active catalyst, K-beta is nevertheless as selective as Cs-EMT or K-EMT for NMA.

The best sample K-EMT (high conversion and NMA selectivity, table 3) is compared to K-Y at 453 K (same temperature as in ref. [2]) in table 4. In the present

Table 3
Alkylation of aniline with dimethyl carbonate at 408 K after 6 h on stream ($W/F = 0.206$ g h mol^{-1})

Zeolite	% conversion	NMA[a] (%)	NNDMA[a] (%)	Deactivation[b] (%)
K-Y	78.3	91.6	8.4	1.8
K-X	86.0	81.8	18.2	5.5
Na-EMT	84.6	82.7	17.3	0
K-EMT	81.3	92.5	7.5	4.3
Cs-EMT	75.0	92.8	7.2	8.5
K-beta	63.4	93.0	7.0	14.3

[a] NMA: N-methylaniline; NNDMA: N,N-dimethylaniline.

[b] $100(C_1 - C_6)/C_6$, where C_1 and C_6 are conversions at times 1 and 6 h.

Table 4
Influence of reaction temperature on the alkylation of aniline with dimethyl carbonate after 6 h on stream. ($W/F = 0.206$ g h mol^{-1})

Zeolite	Reaction temperature (K)	% conversion	NMA[a] (%)	NNDMA[a] (%)	Deactivation[b] (%)
K-Y	408	78.3	91.6	8.4	1.8
	423	90.1	87.1	12.9	0
	453	90.9	64.5	35.5	1.8
K-EMT	408	81.3	92.5	7.5	4.3
	453	90.6	73.6	26.4	0.8

[a] NNDMA: N,N-dimethylaniline; NMA: N-methylaniline.

[b] $100(C_1 - C_6)/C_6$, where C_1 and C_6 are conversions at times 1 and 6 h.

experimental conditions, i.e. different DMC/aniline and N_2/reactant ratios, the performance of K-Y is slightly lower than in ref. [2] with smaller % conversion and selectivity of NMA. Nevertheless, K-EMT is as good as K-Y with regard to % conversion and even better for monomethylation to NMA. The deactivation is still less. It is observed that increasing the temperature from 408 to 453 K decreases the NMA selectivity. This suggests to check whether a further rise in reaction temperature could reverse the selectivity, then favouring NNDMA. Table 5 shows that at 503 K and a space velocity of 0.411 g h mol^{-1}, four catalysts K-Y, K-X, Cs-X and K-beta become selective up to about 60–76% for NNDMA with small C-alkylation for K-X and Cs-X and with less deactivation. The two X zeolites are the most active and selective to NNDMA. A better selectivity to this product was already observed in the alkylation with methanol on X compared to Y catalysts in the exchanged forms K, Rb or Cs [5]. The results indicate that high temperatures favour N,N-alkylation rather than N-monomethylation as already observed for alkylation with methanol on faujasites [5].

Table 5
Alkylation of aniline with dimethyl carbonate at 503 K after 6 h on stream ($W/F = 0.411$ g h mol^{-1})

Zeolite	% conversion	NMA[a] (%)	NNDMA[a] (%)	Deactivation[b] (%)
K-Y	95.7	29.2	70.8	0
Cs-Y	92.5	54.0	46.0	2.5
K-X[c]	97.1	22.3	76.4	0.5
Cs-X[c]	96.5	26.2	72.8	0
K-EMT	92.3	55.7	44.3	0
K-beta	84.2	39.8	60.2	5.1

[a] NMA: N-methylaniline; NNDMA: N,N-dimethylaniline.

[b] $100(C_1 - C_6)/C_6$, where C_1 and C_6 are conversions at times 1 and 6 h.

[c] NNDMPT 1.3% for K-X and 1% for Cs-X.

With regard to active sites, all the catalysts tested have framework basic oxygens and cations as Lewis acid sites, acting as conjugated Lewis acid–base pairs [6]. Both of them might have been involved to get 100% alkylation on N obtained. It is likely that aniline is adsorbed in the 12R windows of Y, X, EMT or beta structures as benzene in the same basic zeolites [6], the CH interacting with basic oxygen. Such a location was proposed for aniline in YbNa-Y from neutron diffraction studies conducted from 0 to 158°C, the molecule being slightly tilted from the oxygen planes of the 12R window [7]. The NH_2 may protrude in the supercage where it is accessible for alkylation and interact strongly with the large electric field associated with the cation/framework oxygens. The Lewis acid sites may activate DMC. Further work is needed to better understand the nature of active sites and reaction mechanism.

As a conclusion K-EMT is as selective as K-Y for the formation of NMA from aniline and DMC. One may expect that EMT zeolite exchanged with K or other cations will be a good catalyst for alkylation of other compounds. Alkaline X zeolites are the best catalysts for the production of NNDMA. The experimental conditions could very likely be optimized (space velocity, reactant ratios) to improve the performances in the formation of NMA and NNDMA respectively.

References

[1] P.R. Hari Prasad Rao, P. Massiani and D. Barthomeuf, Stud. Surf. Sci. Catal. 84 (1994) 1449, and references therein.
[2] Z.H. Fu and Y. Ono, Catal. Lett. 18 (1993) 59; 22 (1993) 277.
[3] Z.H. Fu and Y. Ono, Catal. Lett. 21 (1993) 43.
[4] Z.H. Fu and Y. Ono, J. Catal. 145 (1994) 166.
[5] B.L. Su and D. Barthomeuf, to be published;
B.L. Su, Thesis, Paris, France (1992).
[6] D. Barthomeuf, J. Phys. Chem. 88 (1994) 42;
S. Dzwigaj, A. de Mallmann and D. Barthomeuf, J. Chem. Soc. Faraday Trans. 86 (1990) 431;
B.L. Su, J.M. Manoli, C. Potvin and D. Barthomeuf, J. Chem. Soc. Faraday Trans. 89 (1993) 857.
[7] M. Czijzek, T. Vogt and H. Fuess, Zeolites 11 (1991) 832.