ERRATUM

Catalysis Letters 18 (1993) 59. On page 62 a wrong text has been printed. The complete paper should read as follows.

Selective N-monomethylation of aniline with dimethyl carbonate over Y-zeolites

Zi-hua Fu and Yoshio Ono

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Received 14 October 1992; accepted 12 December 1992

The methylation of aniline with dimethyl carbonate was studied and a very high selectivity for N-monomethylation was attained over alkali cation exchanged zeolites. Thus, a 93.5% selectivity for N-methylaniline was obtained at aniline conversion at 99.6% over KY at 453 K.

Keywords: Aniline; methylation; dimethyl carbonate; zeolite

1. Introduction

N-methylaniline is a useful substance as an intermediate for the production of synthetic dyes. The vapor phase methylation of aniline by methanol has been extensively studied [1–6]. However, the reaction usually accompanies the ring methylation, leading to the formation of toluidines [2,4,5], while studies on the selective N-methylation are rather scarce [1,3,5]. Furthermore, in most of the cases, the N-methylation gives mainly N,N-dimethylaniline [1] and report on the selective N-monomethylation of aniline has been very limited. Takamiya et al. [3] reported that N-methylaniline was obtained in a 30% yield over MgO at 753 K, while a German patent [5] claimed that a 27.9% yield of the compound was obtained with a 85% selectivity over a high silica-zeolite at 573 K.

Trotta et al. [6] reported that the reaction of aniline with dimethyl carbonate (DMC) gave a 60.5% of N-methylaniline at 91.4% aniline conversion (DMC/aniline=10), using α-alumina coated with potassium carbonate and polyethylene glycol as the catalyst,

$$C_6H_5NH_2 + CH_3O\underset{\underset{\displaystyle O}{\|}}{C}OCH_3 \rightarrow C_6H_5NHCH_3 + CH_3OH + CO_2\,.$$

In this letter, we report that selective N-methylation of aniline with a high conversion can be attained over Y-type zeolites using dimethyl carbonate as a methylation reagent.

2. Experimental

The X- and Y-type zeolites used had SiO_2/Al_2O_3 ratios of 2 and 5.6, respectively. The Na-mordenite and ZSM-5 zeolites had SiO_2/Al_2O_3 ratios of 10.2 and 43.5, respectively. Alkali-exchanged zeolites were prepared by a conventional ion-exchange procedure using an 1 M aqueous solution of a corresponding chloride or nitrate. The catalysts were pressed, crushed, and sorted into grains of 16–32 mesh.

The reactions were carried out with a continuous-flow reactor at atmospheric pressure. The catalyst was packed in a reactor of silica tubing (10 mm i.d.) placed in a vertical furnace and heated under an air stream at 773 K for 1 h. The mixture of aniline and DMC was fed into the reactor by means of a motor-driven syringe. The products were trapped and analyzed by a gas chromatograph.

The values of the conversion are calculated based on aniline. Contact time is defined as W/F, where W (in g) is the weight of the catalyst used, F being the total flow rate (aniline + DMC + N_2) in mol h^{-1}.

3. Results and discussion

Table 1 shows the activities and selectivities of various types of catalysts in methylation of aniline with DMC. In contrast with methylation with methanol, every catalyst gave only N-methylation products. The ring methylation did not

Table 1
The activities and selectivities of aniline methylation with dimethyl carbonate over various catalysts[a]

Catalyst	Temperature (K)	W/F (g h mol^{-1})	Aniline conversion (%)	Selectivity (%)
NaY	453	2.08	82.0	87.9
MgY	453	2.08	93.8	85.6
HY	453	2.08	4.1	97.6
NaX	453	2.08	94.1	91.7
KL	473	6.10	15.2	79.6
Na-mordenite	473	6.10	1.7	100
H-ZSM-5	473	6.10	2.1	95.2
Na-ZSM-5	453	2.08	10.4	99.0
	473	6.10	28.0	96.8
	513	6.10	32.1	97.5
Al_2O_3	523	12.1	22.0	92.7
MgO	523	12.1	1.0	100

[a] DMC/aniline = 1.24, N_2/(DMC + aniline) = 1.0.

Table 2
The activities and selectivities of aniline methylation with dimethyl carbonate over alkali-exchanged X-, and Y- zeolites[a]

Catalyst	Temperature (K)	W/F ($g\,h\,mol^{-1}$)	Aniline conversion (%)	Selectivity (%)
NaY	453	2.08	82.0	87.9
KY(98)[b]	453	2.08	99.6	93.5
RbY	453	2.08	89.0	94.0
CsY(59)[b]	453	2.08	92.2	91.7
NaX	453	2.08	94.1	80.1
KX	453	2.08	65.4	86.7
RbX	453	2.08	76.1	94.3
CsX(50)[b]	453	2.08	30.4	97.0
	473	6.10	95.8	83.1

[a] DMC/aniline = 1.25, N_2/(DMC + aniline) = 1.0.
[b] Numbers in parentheses show the degrees of ion exchange.

occur at all under the reaction conditions studied. Thus, the selectivity was defined as the ratio N-methylaniline/(N-methylaniline + N,N-dimethylaniline) in the product.

Among the catalysts studied, NaY, MgY, and NaX gave very high conversions of aniline at 453 K. The reaction proceeds at much lower temperature compared with methylation with methanol. Na-ZSM-5 gave a very high selectivity for N-methylaniline. However, the activity of Na-ZSM-5 was much lower than those of the faujasites, probably because of space constraint. Acidic zeolites, HY and H-ZSM-5 showed very low activities, indicating that the basic property of zeolites plays an important role in the catalysis; KL and alumina showed low activities, while Na-mordenite and MgO showed only negligible activity.

Table 2 shows the activities and selectivities in the methylation of aniline over alkali-exchanged faujasites. The reactant ratio, DMC/aniline was 1.25. Every catalyst showed a high activity for the methylation. The order of the activity does not agree with the order of the basicity of the catalysts. For example, CsX is less active than NaX, or CsY. It is generally accepted that the basicity is higher with the Cs-form than with the Na-form, and that X-zeolites are more basic than Y-zeolites [7,8]. This indicates that weakly acidic sites may be required in addition to basic sites for the reaction. A similar tendency was observed in the reaction of phenyl acetonitrile with DMC [9]. The most active catalyst was KY.

Table 3 shows the effect of DMC/aniline ratio on the conversion of aniline and the selectivity for N-methylaniline over KY at 453 K. When the ratio was less than 1, the yield of N-methylaniline was about 90% on DMC basis. The selectivity for N-methylaniline was very high ($\approx$ 99%). When the ratio was over 1, the conversion of aniline was more than 99%, the selectivity being $\approx$ 93%. When the DMC/

Table 3
The effect of DMC/aniline ratio on the activities and selectivities in aniline methylation over KY[a]

molar ratio DMC/aniline	0.80	1.0	1.25	2.0
conversion of aniline (%)	71.6	88.7	99.6	99.5
selectivity for N-methylaniline (%)	98.9	98.8	93.5	92.3
conversion of DMC (%)	93.0	100	85.6	56.9

[a] 453 K, $W/F = 2.08$ g h mol^{-1}.

aniline ratio was unity, the aniline conversion was 93.5%, the selectivity being 99.6%. Here, the conversion of DMC was 85.6% and thus, the selectivity for N-methylation based on DMC was 93.1%. It is clear that both the conversion and the selectivity are very high with respect to DMC as well as aniline.

Fig. 1 shows the change in the conversion and the yields of N-methylaniline and N,N-dimethylaniline with contact time at 453 K. The aniline conversion increases from 61.7% to 98.7% by increasing contact time from 0.33 to 2.08 g h mol^{-1}. The yields of both products increase with contact time, the selectivity for N-methylaniline decreases from 98.7% to 93.5% by increasing contact time from 0.33 to 2.08 g h mol^{-1}.

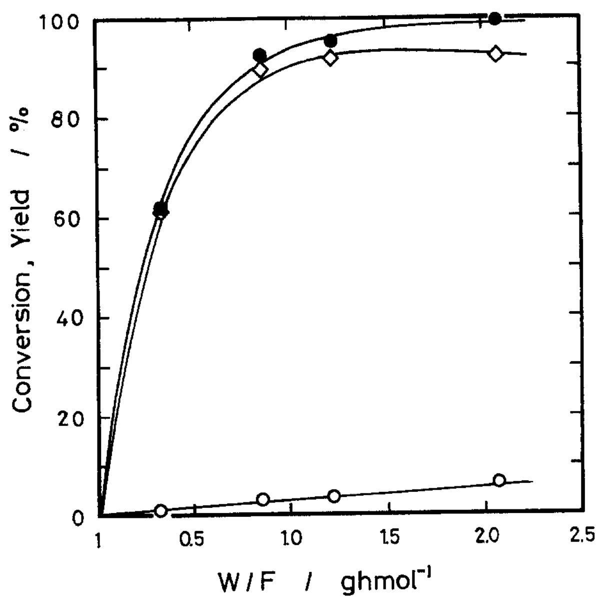

Fig. 1. Change in the conversion of aniline and the selectivity for N-methylaniline with contact time in the methylation of aniline with dimethyl carbonate. (●) Aniline conversion, (◇) yield of N-methyl-aniline, (○) yield of N,N-dimethylaniline.

References

[1] Y.H. Evance and A.N. Bourns, Can. J. Chem. 29 (1951) 1.
[2] A.G. Hill, J.H. Shipp and A.J. Hill, Ind. Eng. Chem. 43 (1951) 1579.
[3] N. Takamiya, Y. Koinuma, K. Ando and S. Murai, Nihon Kagaku Kaishi (1979) 1453.
[4] D.Y. Chen, M.C. Chen, H.Y. Chu, N.S. Chang and T.K. Chuang, *Proc. 7th Int. Zeolite Conf.*, eds. A. Iijima, J. Ward and Y. Murakami (Kodansha/Elsevier, Tokyo/Amsterdam, 1986) p. 739.
[5] G. Henkel, L. Feiler, W. Haenzel and D. Kottmann, DE (1990) 40 13613 A1.
[6] F. Trotta, P. Tundo and G. Moraglio, J. Org. Chem. 52 (1987) 1300.
[7] Y. Ono, Stud. Surf. Sci. Catal. 5 (1980) 19.
[8] D. Barthomeuf, J. Phys. Chem. 88 (1984) 42.
[9] Z. Fu and Y. Ono, to be published.