

Amination of Carbon Monoxide over Zeolite Catalysts

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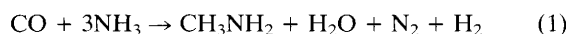
By treating carbon monoxide with ammonia over modified ZSM-5, mordenite, Y-zeolite and SAPO-5 catalysts, methyl- and dimethyl-amines are obtained; HZSM-5 is the most active catalyst and methylamine the major product.

Amines have been synthesized by treating alcohols, ethers, aldehydes, ketones, halogen derivatives and unsaturated hydrocarbons with ammonia over acidic or metal supported catalysts.¹⁻⁴ The catalysts used in the amination were binary transition metal oxides, supported alumina and silica-alumina. More recently, the dehydrative amination of alcohols was carried out over zeolites such as Rho, ZSM-5.⁵ We report the first zeolite-catalysed amination of carbon monoxide.

The reaction was carried out using a down-flow, fixed-bed Pyrex reactor of 12 mm diameter. The flow rates of carbon monoxide and ammonia were 100 cm³ min⁻¹. The reaction was carried out in the temperature range 320 to 400 °C and the amount of catalyst used was 1 to 4 g. The products were analysed by gas chromatography using 5% SE-30 and Chromosorb 101 columns and confirmed by mass spectrometry.

The catalysts used in the amination of carbon monoxide were sodium and H forms of ZSM-5, mordenite, Y-zeolite and SAPO-5. The major products obtained under these experimental conditions were methylamine and dimethylamine. The highest activity was observed with HZSM-5. In the case of HY, a small amount of coke formation was observed. The amount of products collected over HZSM-5 were 0.49 to 1.4 g h⁻¹. With the increase of the flow of ammonia from 100 to 200 cm³ min⁻¹ the amount of product increased. It is evident from the results that the yield of amines should increase at higher pressure.

The results are given in Table 1 which shows that the catalyst which is more active in the reaction at lower temperatures (*e.g.* HZSM-5) showed less selectivity to methylamine at higher temperature, see eqn. (1).



The activity of the zeolite catalyst in this reaction is due to the exchangeable cations. The acidic protons, Brønsted acidic centres, showed higher activity. The temperature-programmed desorption of ammonia over HZSM-5 showed the desorption peak corresponding to ammonia adsorbed on protons at 350–400 °C.⁶ So the activation of ammonia and desorption of amines can take place in the temperature range 350 to 400 °C. The formation of water in the product was observed. The ratio of methylamine to dimethylamine is given

Table 1 Selectivity of methylamine in the amination of carbon monoxide over zeolites

Catalyst	Temperature/°C	Methylamine % selectivity (MA/DMA ^a)	
HZSM-5 (Si/Al = 30)	400	56	2.0
HZSM-5 (Si/Al = 129)	325	100	—
HZSM-5 (Si/Al = 280)	350	72	Trace DMA
ZnO-ZSM-5	400	100	—
NaM ^b	325	71	Trace DMA
NaM	360	90	9.0
HM	400	100	—
PtNaM	360	Trace	—
NaY	400	70	2.3
HY	400	55	1.4
SAPO-5	400	80	Trace DMA

^a (Methylamine/dimethylamine) % selectivity ratio. ^b M = mordenite.

in Table 1. Methylamine can be obtained by the reaction of methanol with ammonia over a catalyst, in which dimethyl ether is a byproduct. In our present system there are no byproducts under certain experimental conditions and the reactants can be recycled. In conclusion we have demonstrated for the first time, the amination of carbon monoxide selectively to methylamines.

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References

- 1 V. A. Nekrasova and N. I. Shuikin, *Russ. Chem. Rev.*, 1965, **34**, 843.
 - 2 A. Baiker and J. Kijenski, *Catal. Rev. Sci. Eng.*, 1985, **27**, 653.
 - 3 M. V. Klyuev and M. L. Khidekel, *Usp. Khim.*, 1980, **49**, 28.
 - 4 M. Deeba, M. E. Ford and T. A. Johnson, *J. Chem. Soc., Chem. Commun.*, 1987, 562.
 - 5 L. Abrams, D. R. Corbin and M. Keane Jr., *J. Catal.*, 1990, **126**, 610.
 - 6 S. J. Kulkarni, H. Hattori and K. Tanabe, *Appl. Catal.*, 1989, **49**, 27.
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