Synthesis of Methylamines from Carbon Dioxide and Ammonia

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Methylamines were synthesized from carbon dioxide, hydrogen and ammonia over Cu–Al_2O_3 catalysts, affording a distribution of monomethylamine : dimethylamine : trimethylamine of 1 : 0.23 : 0.07.

The abundance of CO_2 renders it a suitable starting material for the synthesis of valuable chemicals such as alcohols.[1] Although the reaction of CO–H_2 synthesis gas and ammonia to methylamines has already been described in the literature,[2,3] to our knowledge, the direct production of methylamines from CO_2, H_2 and NH_3 has not been reported so far. This prompted us to study the feasibility of a corresponding heterogeneous catalytic process.

The reaction was carried out using a fixed-bed microreactor at a pressure of 0.6 MPa, in the temperature range of 473–553 K. The feed gas mixture contained 20% CO_2, 60% H_2, 0–20% NH_3 and N_2 as a balance. The total flow rate was varied in the range of 100–200 ml min^{-1}. For all experiments 3 g of copper–alumina catalyst were used with CuO loadings of 33.9 and 58.5 mass%, respectively. Preparation and pretreatment (calcination and reduction by hydrogen) were the same as reported elsewhere.[4] The products were analysed by GC using an SPB-1 fused silica capillary column and a Poropak QS column.

The only carbon-containing products detected were mono-, di- and tri-methylamine (MMA, DMA, TMA, respectively), methanol and carbon monoxide. Both catalysts showed similar catalytic behaviour, indicating no significant influence of the copper loading. The ammonia conversion and the product distribution were influenced by the reaction temperature and the NH_3 concentration in the feed gas. The temperature dependence, illustrated in Fig. 1, indicates that MMA and CO formation are favoured at higher temperatures. CO is produced *via* the reverse water gas shift reaction ($CO_2 + H_2 \longleftarrow\!\!\longrightarrow CO + H_2O$). The influence of NH_3 concentration on the product distribution is illustrated in Fig. 2. At low NH_3 concentration TMA is the main amine product, whereas at higher NH_3 concentrations MMA was prevalent.

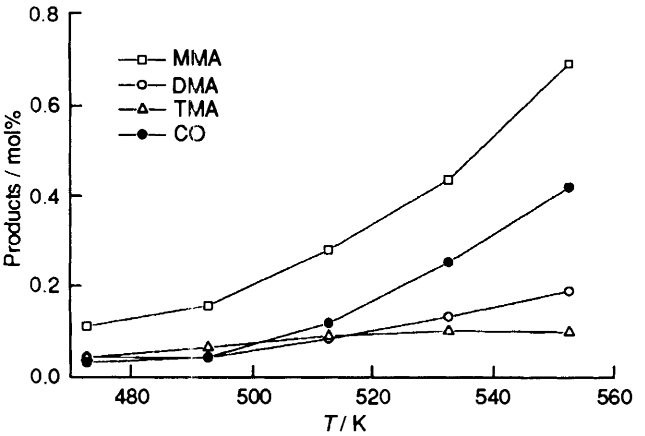

Fig. 1 Temperature dependence of formation of methylamines and CO over Cu–Al_2O_3. *Conditions*: 3 g catalyst (58.5 mass% CuO), 0.6 MPa, 150 cm^3 min^{-1}, CO_2 : NH_3 : H_2, 1 : 1 : 3.

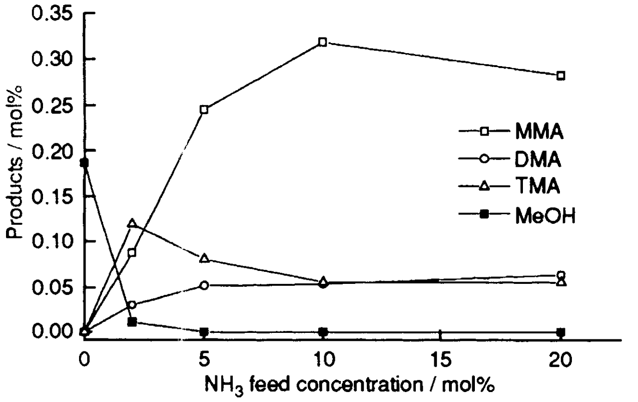

Fig. 2 Dependence of concentrations of methylamines and methanol on ammonia feed concentration. *Conditions*: 3 g catalyst (58.5 mass% CuO), 0.6 MPa, 513 K, 150 cm^3 min^{-1}, CO_2 : H_2, 1 : 3.

Methylamines are prepared commercially by the reaction of ammonia with methanol.[5] The thermodynamic equilibrium composition of this reaction favours the formation of TMA,[5] whereas the products in greatest demand are MMA and DMA. So from this point of view the product distributions shown in Figs. 1 and 2 are very interesting.

Copper–alumina catalysts have been reported to be active for the synthesis of methanol from carbon dioxide and hydrogen.[6,7] Methanol formation which could therefore be expected over Cu–Al_2O_3 catalysts under the conditions used (*cf.* experiment without NH_3 in feed), seems to be suppressed by the presence of ammonia in the feed gas and MMA is selectively produced, as shown in Fig. 2. Methanol was only observed in significant concentration when no NH_3 was fed to the reactor, reaching values comparable to results reported earlier for Cu–Al_2O_3.[6] Note that methylamines are produced at a higher rate compared to the formation of methanol under the conditions employed (Fig. 2). This finding is in agreement with the mechanism suggested for the amination of alcohols[8] where an aldehyde-type species (formyl) was found to be the crucial intermediate reacting with NH_3. The reaction of the aldehyde-type species with ammonia (condensation) may occur unassisted by a catalyst. This indicates that methanol is not a necessary intermediate for the amine formation when starting from CO_2–H_2–NH_3.

The space velocity was varied in the range of 1500–3000 h^{-1} but relatively little influence on both NH_3 conversion and distribution of amines was observed. Reactions carried out without hydrogen in the feed resulted in lower activity and a strong deactivation of the catalyst, indicating that hydrogen is probably necessary to maintain catalyst activity. Deactivation in the absence of hydrogen was also observed in the amination of aliphatic alcohols over Cu–Al_2O_3.[8] The reason for the deactivation was the formation of surface copper nitride ($3Cu + NH_3 \longleftarrow\!\!\longrightarrow Cu_3N + 3/2\ H_2$) which is unstable in the presence of hydrogen, explaining the role of hydrogen to suppress catalyst deactivation.[9]

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