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Comparative study of synthesis of methylamines from carbon oxides and ammonia over Cu/Al_2O_3

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Abstract

Methylamines have been synthesized from carbon dioxide, hydrogen and ammonia using Cu/Al_2O_3 catalysts with different copper loading. The reaction was performed in a fixed-bed micro reactor in the temperature range 473–573 K and at 0.6 MPa total pressure. The product amines were mono-, di- and trimethylamine (MMA, DMA, TMA). The distribution of the amines depended mainly on the reaction temperature and the NH_3/CO_2 ratio in the feed gas. At elevated temperatures and higher NH_3 concentrations methanol synthesis is suppressed and MMA is the main amine product, reaching a ratio of MMA:DMA:TMA of 1:0.23:0.07. Conversion and product distribution were compared to that of the corresponding reaction starting from CO or methanol instead of CO_2. With CO conversion was lower but the selectivity to MMA was higher. If CO_2 was replaced by methanol, conversion increased and TMA was the main product. In all experiments a change of space velocity had relatively little influence on both conversion and distribution of amines.

Keywords: Cu/Al_2O_3 catalysts; Methylamines synthesis

1. Introduction

The large scale availability of CO_2, produced in any combustion process, renders it a suitable starting material for the synthesis of valuable chemicals and fuels. Although much of the work in carbon oxides hydrogenation has concentrated on CO [1], the synthesis of methanol from carbon dioxide and hydrogen is well known [1–3]. In contrast, the formation of organo–nitrogen compounds such as amines has only been described starting from CO, H_2 and NH_3 [4–6]. In a preliminary report [7], we have demonstrated that methylamines can be readily produced from CO_2, H_2 and NH_3.

In this study, the effects of copper loading, space velocity, temperature, NH_3/CO_2 ratio and hydrogen on the overall catalytic performance were examined and the formation of methylamines from CO_2, H_2 and NH_3 was compared to that of the corresponding reactions starting from CO or methanol.

2. Experimental

The investigations were performed using two copper/alumina catalysts with loadings of (A)

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33.9 wt.-% and (B) 58.5 wt.-% CuO, respectively, prepared from $Cu(NO_3)_2 \cdot 3H_2O$ solution, aluminium hydroxide and KOH. Catalyst preparation was the same as described in detail elsewhere [8]. In brief, a slurry of aluminium hydroxide gel in an aqueous copper nitrate solution was mixed with a solution of potassium hydroxide (2.8 mol KOH per mol Cu^{2+}) at 353 K. The resulting precipitate was aged for 30 min at 353 K. After cooling and allowing to settle, the residue was filtered and washed until the filtrate was neutral. The wet precipitate was dried at 423 K for 6 h, crushed and sieved. Before use the catalysts were reduced at 453 K in a hydrogen/nitrogen mixture by increasing the mole fraction of hydrogen stepwise (30 min per step) in the sequence 10/20/50 to 100%. After increasing the temperature to 473 K for 10 min, hydrogen was replaced by the reaction gas mixture and the temperature was brought to 513 K. The BET surface areas measured by nitrogen adsorption at 77 K after reactions carried out with CO_2 amounted to 251 and 146 m^2 g^{-1} for sample (A) and (B), respectively. The copper metal surface areas of 7.4 m^2 g^{-1} and 11.6 m^2 g^{-1} for sample (A) and (B), respectively, were measured by N_2O titration using a pulse technique and assuming 1.46×10^{19} copper atoms per m^2 and an adsorption stoichiometry of $Cu_{(s)}/O_{(ads)} = 2$ [3]. XRD analysis showed only reflections due to metallic copper after reaction.

Catalytic tests were carried out in a continuous tubular fixed-bed micro reactor operated at a pressure of 0.6 MPa. The reactant gas, containing 60 mol-% H_2, 20 mol-% CO_2, 0–20 mol-% NH_3 and N_2 as a balance, was mixed from pure components using mass flow controllers. The total flow rate was varied in the range of 100–200 cm^3 (STP) min^{-1}. For comparative catalytic tests CO_2 was replaced by CO or methanol. Feed and product gas analysis were performed with a Hewlett–Packard 5890A gas chromatograph equipped with a thermal conductivity detector. Product separation was achieved with a SPB-1 fused silica capillary column (60 m, 0.53 mm ID, 5 μm film) and a Porapak QS column (5 m, 1/8 in. OD, 80–100 mesh), arranged in parallel.

Standard experiments with CO and CO_2 were carried out using 3 g (GHSV = 2250 h^{-1}), experiments with methanol using 0.5 g (GHSV = 13500 h^{-1}) of copper/alumina catalyst (120–300 μm) under a reactant flow-rate of 150 cm^3 (STP) min^{-1} in the temperature range 473–573 K. Carbon monoxide, carbon dioxide, MMA, DMA, TMA, methanol and water were the only products detected.

3. Results and discussion

3.1. Influence of reaction conditions

Both copper/alumina catalysts showed similar catalytic behaviour in the reaction starting from $CO_2/H_2/NH_3$, indicating that the copper loading had only a weak influence on the catalytic performance. The results reported were obtained using catalyst (B) with 58.5 wt.-% CuO. Variation of the space velocity in the range 1500–3000 h^{-1} also had little influence on both NH_3 conversion and distribution of amines. In contrast, the reaction temperature and the NH_3/CO_2 ratio greatly influenced both NH_3 conversion and methylamine distribution.

The temperature dependence, illustrated in

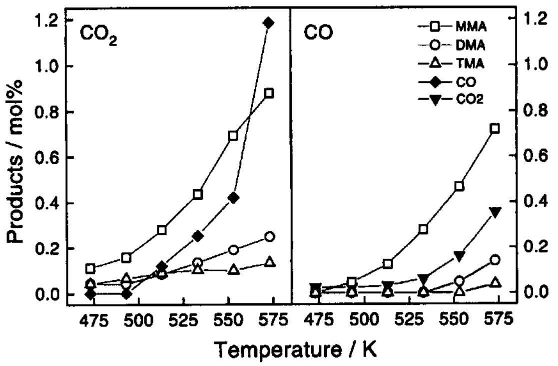

Fig. 1. Temperature dependence of formation of methylamines, CO and CO_2 from CO_2, H_2, NH_3 and CO, H_2, NH_3 mixtures, respectively. Conditions: 3 g Cu/Al_2O_3 (B), 0.6 MPa, 150 cm^3 min^{-1} $CO_x:NH_3:H_2 = 1:1:3$.

Fig. 1, shows that starting from CO_2 all three methylamines are produced over the whole temperature range investigated with MMA being favoured at higher temperatures. Carbon monoxide, produced via the reverse water gas shift (RWGS) reaction ($CO_2 + H_2 \rightleftarrows CO + H_2O$), appears at 513 K and develops to the predominant product at higher temperature. Reactions carried out without hydrogen in the feed resulted in lower activity and a strong deactivation of the catalyst. A similar deactivation of copper based catalysts in the absence of hydrogen was observed in the amination of aliphatic alcohols and was attributed to the formation of surface copper nitride [9,10]. Hydrogen was found to prevent catalyst deactivation by suppressing copper nitride formation on the catalyst, thus, explaining the role of hydrogen to maintain catalyst activity [9,10].

The reaction of CO, H_2 and NH_3 led to the same products as found for CO_2 but at lower overall conversions and with DMA and TMA being only produced at higher temperatures. Carbon dioxide is produced from product water and CO via the WGS-reaction.

Fig. 2 depicts the influence of NH_3 concentration on the product distribution at 513 K. Starting from CO_2, methanol and CO were the only carbon containing products observed in the absence of ammonia with CO reaching a concentration of 1.78 mol-% (not shown). At low NH_3 concentration TMA was the main amine product, while at higher NH_3 concentrations MMA was the dominant product. With increasing NH_3 concentrations, methanol synthesis was suppressed and CO production dropped to a value of 0.12 mol-% for 20 mol-% NH_3 (not shown). For NH_3 concentrations exceeding 10 mol-% methylamine formation started to decline slightly.

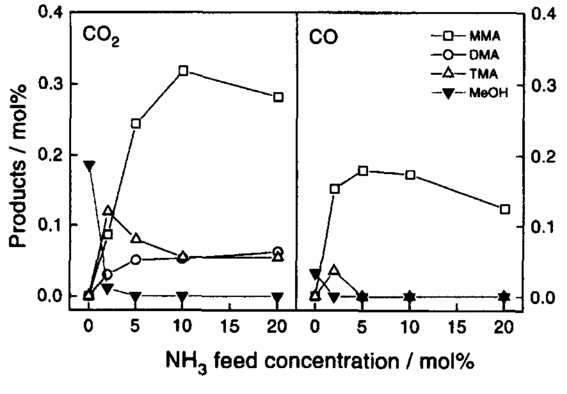

Fig. 2. Influence of NH_3 feed concentration on formation of products from CO_2, H_2, NH_3 and CO, H_2, NH_3 mixtures, respectively. Conditions: 3 g Cu/Al_2O_3 (B), 0.6 MPa, 513 K, 150 cm^3 min^{-1} CO_x:H_2 = 1:3.

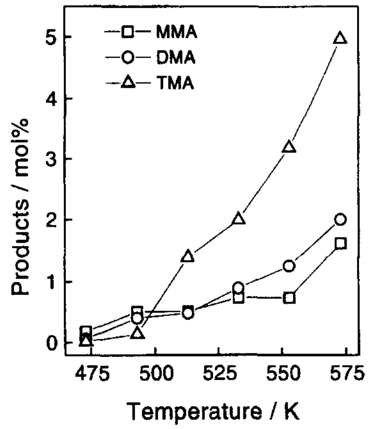

Fig. 3. Temperature dependence of formation of methylamines from methanol, H_2 and NH_3. Conditions: 0.5 g Cu/Al_2O_3 (B), 0.6 MPa, 150 cm^3 min^{-1} CH_3OH:NH_3:H_2 = 1:1:3.

Similar behaviour as with CO_2 was observed with CO as a carbon source but conversions remained significantly lower (Fig. 2). Methanol was the only product formed without NH_3 in the feed. Addition of NH_3 to the reactant gas suppressed methanol formation and MMA was the main product over the concentration range investigated. A minor amount of TMA was only observed at low NH_3 concentration, whereas DMA was not formed at all. Carbon dioxide formation showed the same tendencies as the formation of MMA and was not suppressed by the presence of NH_3 in the feed (not shown). It is interesting to note that for both reactants, CO_2 and CO, methylamines were produced on a higher rate compared to the formation of methanol.

Methylamines are produced commercially by the reaction of ammonia with methanol [11]. The selectivity of this reaction is determined by thermodynamics over conventional catalysts, TMA being the main product [11]. However, the products in greatest demand are MMA and DMA. This renders the product distributions shown in Figs. 1 and 2 particularly interesting. Results for the reaction of methanol with NH_3 are presented in Fig. 3 for comparison using 0.5 g of Cu/Al_2O_3 catalyst (B) instead of 3 g in the other experiments, resulting in a space velocity of 13500 h^{-1}. For temperatures < 500 K, affording low conversions, MMA and DMA are the main amine products, whereas at higher temperatures TMA is prevalent. Conversions were consistently higher compared to the reactions starting from carbon oxides.

3.2. Reaction pathway

Regarding the formation of methylamines from CO_2, H_2 and NH_3 two pathways seem most probable: (i) formation of methanol (intermediate) followed by its amination to the corresponding amines, (ii) reaction of ammonia and hydrogen with a surface intermediate from which methanol is obtained in the absence of NH_3. The observations that methanol is only detected in significant concentration when no NH_3 is fed to the reactor and that methylamines are produced on a higher rate compared to the formation of methanol indicate that the amine formation occurs mainly by the reaction of ammonia with a methanol precursor and not via methanol. This finding is in agreement with the mechanism suggested for the amination of alcohols [9,10], where an aldehyde type species, formed by the dehydrogenation of the alcohol, was found to be the crucial intermediate reacting with NH_3. Vedage et al. [12] also suggested that an aldehyde type intermediate and not the product methanol is involved in the reaction of CO/H_2 with diethylamine to the corresponding methyldiethylamine.

Acknowledgements

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