

## A Single-step Synthesis of Isobutyraldehyde from Methanol and Ethanol over CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> Catalyst

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Selective synthesis of isobutyraldehyde from methanol and ethanol in a single step over CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst is reported.

Isobutyraldehyde and its derivatives (*e.g.* isobutanol, isobutyric acid, and neopentyl glycol) are very useful chemical feedstocks in the plastics industry.<sup>1</sup> Isobutyraldehyde is produced as a byproduct in the OXO process of hydroformylation of propylene with CO and H<sub>2</sub>.<sup>1–3</sup> This is, of course, an energy-consuming and uneconomical process. In a recent communication Wang and Lee<sup>4</sup> reported that isobutyraldehyde can be synthesised in one step over V<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub> catalysts. The conversions and product yields are, however, very limited since it is an acidic catalyst<sup>5,6</sup> which selectively produces undesired side products in large quantities. In this communication we report an efficient CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst for the selective production of isobutyraldehyde from methanol and ethanol in one step.

The CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst (1 : 2.3 : 2.7 mol ratio) was prepared by a deposition–precipitation method using urea as a hydrolysing agent.<sup>7,8</sup> The required quantities of copper nitrate (Fluka, AR grade) and zinc nitrate (Loba Chemie, GR grade) to yield the desired composition of the catalyst was dissolved in deionised water to which an excess of urea (Loba Chemie, AR grade) was also added. Alumina support (Harshaw Al-III-61,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, surface area 204 m<sup>2</sup> g<sup>-1</sup>, pore volume 0.65 cm<sup>3</sup> g<sup>-1</sup>, particle size <0.1 mm) in fine powder form was then added to this solution and heated to 95 °C with vigorous stirring. Precipitation to neutral pH was complete in 3–4 h. The precipitates thus obtained were filtered off, washed

several times with deionized water, dried at 110 °C for 16 h and calcined at 450 °C in air for 12 h. The finished catalyst had an N<sub>2</sub> BET surface area of 80 m<sup>2</sup> g<sup>-1</sup>. The X-ray powder diffraction pattern of this sample revealed that the material to be in an amorphous state.

Catalytic tests were carried out in a previously described fixed-bed microreactor system at atmospheric pressure.<sup>9</sup> Mixtures of methanol and ethanol (2 : 1 mol ratio) with or without water (50% v/v) were fed at a rate of 4–6 cm<sup>3</sup> h<sup>-1</sup>, with nitrogen or air as carrier at a flow rate of 45 ml min<sup>-1</sup>. For each run about 1 g of catalyst sample was used and the reaction products were analysed by gas chromatography with a 10% Carbowax 20 M column (2 m long). The main reaction products observed were isobutyraldehyde, acetaldehyde and formaldehyde with some traces of C<sub>2</sub>–C<sub>3</sub> hydrocarbons, acrolein, CO and CO<sub>2</sub>, respectively.

Activity and selectivity results obtained at various temperatures ranging from 260–410 °C are illustrated in Fig. 1. An increase in conversion approaching 100% with increase in temperature is noted irrespective of the gas atmosphere. However, product selectivities varied very interestingly depending on the gas-phase atmosphere as well as water vapour. The formation of side products, formaldehyde and acetaldehyde, is greater in the presence of air. Air appears to facilitate the direct selective oxidation of methanol and ethanol to their corresponding aldehydes. Replacement of air

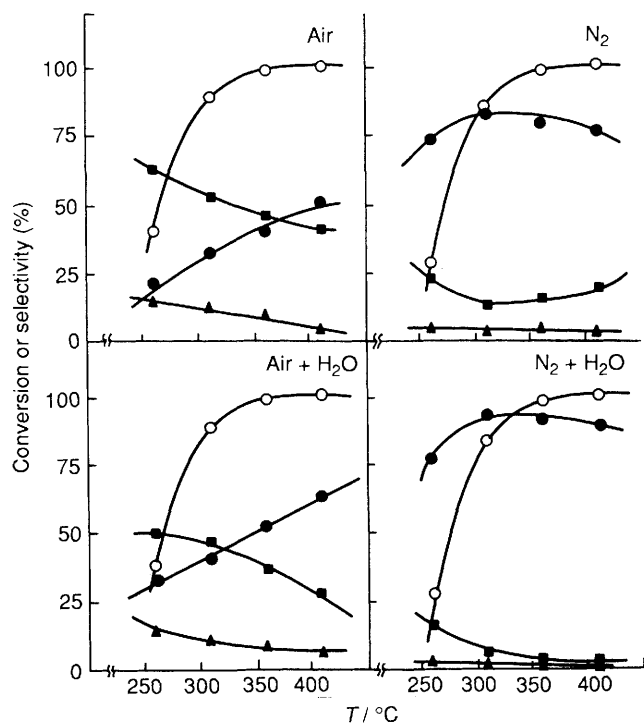


Fig. 1 Variation of conversion and selectivities as a function of temperature; ○ total conversion, ● isobutyraldehyde, ▲ acetaldehyde, ■ formaldehyde

with nitrogen resulted in the suppression of these side products and enhancement of isobutyraldehyde formation. Similarly, in the absence of water as diluent formation of more side product was noted. Dilution of methanol and ethanol mixture with water (50% v/v) and admission of nitrogen as carrier gas showed more than 90% selectivity towards the formation of isobutyraldehyde. A similar substantial enhancement in the selectivity for 2-methylpyrazine ammoxidation to

2-cyanopyrazine was observed by Forni<sup>10</sup> in the presence of water vapour on various catalysts. However, the role of water vapour in enhancing the product selectivities is not known.

An opposite trend in between the selectivities of acetaldehyde and isobutyraldehyde is observed at various temperatures. As reported by Wang and Lee,<sup>4</sup> acetaldehyde (dehydrogenation product of ethanol) appears to be the intermediate which undergoes methanol addition followed by dehydration and several rearrangements to yield isobutyraldehyde as the main product. The CuO-Al<sub>2</sub>O<sub>3</sub> is known to be a better catalyst system for the selective dehydrogenation of ethanol to acetaldehyde.<sup>7</sup> Similarly, zinc oxide being basic in nature is also known to be active for selective dehydrogenation functionalities of various catalysts.<sup>11</sup> Therefore, the combination of CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst system appears to be the promising one for the title reaction.

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