Catalytic Synthesis of Isobutyraldehyde from Methanol and Ethanol over Titanium Oxide-supported Vanadium Oxide Catalysts

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Isobutyraldehyde was synthesized from methanol and ethanol in one step over a V/TiO_2 catalyst.

The preparation of isobutyraldehyde and its derivatives (*e.g.* Bu^iOH, methacrylic acid and neopentyl glycol) has attracted attention because of their wide use as solvents or plasticizers in the plastics industry.[1] Currently, isobutyraldehyde is obtained from separation of the by-products in the OXO process.[2,3] However, this is an energy-consuming process. We have now developed a novel catalytic method for synthesizing isobutyraldehyde from methanol and ethanol in one step by using V/TiO_2 catalysts.

The reactions were carried out in a fixed-bed system at atmospheric pressure. Mixtures of methanol and ethanol were fed by a syringe pump and vapourized. The vapour was diluted with nitrogen and the total flow rate was controlled at 45 ml min^{-1}. The V/TiO_2 catalyst was prepared by impregnating titanium oxide with vanadium(III) chloride solution. All the catalysts were heated in air for 2 h at 500 °C before the reaction.

A decrease in the conversion rate of ethanol during the initial reaction period was observed for all the catalysts used but stable activities were obtained within a few hours. Almost all the excess of methanol was recovered, together with a small amount of methane, after the reaction. The activities of the

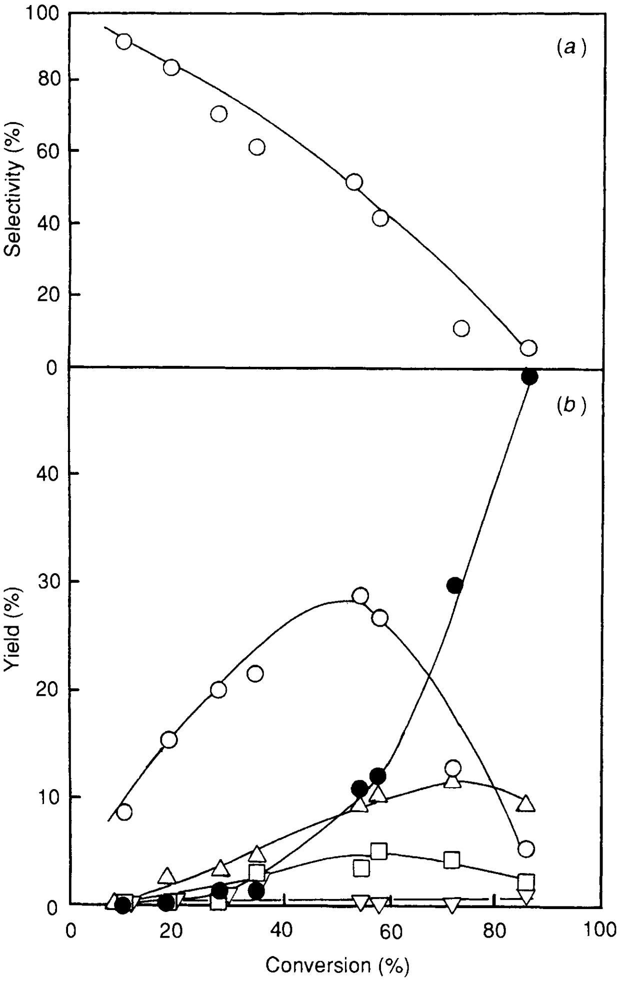

Fig. 1 (*a*) Variation of the selectivity to acetaldehyde, (*b*) Variation of the yields of the products with the conversion of ethanol. ○ acetaldehyde, ● isobutyraldehyde, △ C_2 hydrocarbons, ▽ C_3 hydrocarbons, □ acrolein. Catalyst: V(2.5 wt%)/TiO_2; packing density: 0.9 g ml^{-1}; weight: 1, 0.6 and 0.5 g at 86, 58 and 11% conversion, respectively; temperature: 350 °C, reactant mixture: methanol 31%, ethanol 3.1%, remainder nitrogen, flow rate: 45 ml min^{-1}.

catalysts strongly depend on the concentration of vanadium: a high concentration of vanadium gives better activities, but lower selectivities for the formation of isobutyraldehyde. The formation of acetaldehyde and C_2 hydrocarbons increases with increasing activities. The optimum results for conversion and selectivity were obtained for V(2.5 wt%)/TiO_2.

Fig. 1 illustrates the yields of products and the selectivity for acetaldehyde formation *vs.* conversion in the reaction of methanol and ethanol over the V(2.5 wt%)/TiO_2 catalyst. Extents of conversion were controlled by adjusting the contact time. The selectivity for acetaldehyde formation decreases continuously with the conversion of ethanol, but the maximum yield of acetaldehyde is obtained at a conversion of about 60% and the yield of isobutyraldehyde increased markedly from this point. This suggests that the isobutyraldehyde is formed by a subsequent reaction of acetaldehyde which is formed from ethanol by dehydrogenation. This conclusion is strongly supported by a separate experiment in which isobutyraldehyde was also selectively formed in high yield (50%) from methanol and acetaldehyde.[4]

In order to confirm the role of the methanol in this reaction, labelled methanol (CD_3OD) was used in the reaction with ethanol, yielding [$^2H_5$]isobutyraldehyde (88%) as the main product. This result implies that the attachment of two methyl group to the ethanol skeleton is not a direct process. When formaldehyde instead of methanol was used in reactions with ethanol or acetaldehyde, the main product was acrolein with a little isobutyraldehyde. This differs from results for the alkylation of toluene by methanol to give ethylbenzene and/or styrene[5] or the reaction of methanol and acetone to form methyl vinyl ketone and/or methyl ethyl ketone,[6,7] which takes place *via* a formaldehyde intermediate formed from the methanol. These results suggest that the mechanism for the formation of isobutyraldehyde, although not entirely clear yet, might consist of a series of dehydrogenation, condensation, dehydration and hydrogenation steps. It is interesting that such a multi-step reaction readily takes place on the surface of the catalyst.

We have also found that this catalyst may be applicable to other alcohols,[4] aldehydes[4] and ketones[4] for catalytic alkylation using methanol as a methyl group source.

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