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Synthesis of isobutyraldehyde from methanol and ethanol over mixed oxide supported vanadium oxide catalysts

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Abstract

A one step synthesis of isobutyraldehyde from methanol and ethanol over mixed oxide (TiO_2-Al_2O_3, TiO_2-SiO_2, TiO_2-ZrO_2 and TiO_2-SiO_2-ZrO_2) supported vanadium oxide catalysts was investigated at atmospheric pressure and 350°C. The V_2O_5/TiO_2-SiO_2 catalyst showed a better performance in terms of total conversion and product selectivity than the other catalyst systems.

Keywords: ethanol; isobutyraldehyde; methanol; mixed oxides; titania-alumia; titania-silica; titania-silica-zirconia; titania-zirconia; vanadium oxide

Isobutyraldehyde and its derivatives (e.g., isobutanol, isobutyric acid and neopentyl glycol) are very useful as solvents and plasticizers in the plastics industry [1]. Isobutyraldehyde is one of the side products recovered and separated in the OXO process [1–3]. In a recent communication Wang and Lee [4] reported that isobutyraldehyde can be synthesised in one step from methanol and ethanol over a V_2O_5/TiO_2 catalyst. However, the conversions and product selectivities are limited on that catalyst. In the present communication we report a better mixed oxide supported vanadium oxide catalyst for the reaction. Mixed oxide supports have recently attracted attention because of their better performance than their constituent single oxide supports in various reactions [5–10]. In this study various mixed oxide supports viz., TiO_2–Al_2O_3, TiO_2–SiO_2, TiO_2–ZrO_2 and TiO_2–SiO_2–ZrO_2 obtained via a homogeneous precipitation method and impregnated with a single monolayer equivalent of V_2O_5 loading were tested for the synthesis of isobutyraldehyde in one step

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from methanol and ethanol mixtures. The V_2O_5/TiO_2–SiO_2 catalyst system appears to be a promising system for this reaction.

The various mixed oxide supports used were prepared by a homogeneous precipitation method using urea as a hydrolysing agent [11]. All the reagents used were procured either from Fluka or from Loba Chemie and were AnalaR grade. In a typical experiment, in order to yield the desired composition of the mixed oxide support, the requisite quantities of titanium tetrachloride and sodium aluminate (or sodium silicate and/or zirconium oxychloride) were dissolved separately in deionized water and mixed together. To this was added an excess amount of urea solid before mixing thoroughly. Cold titanium tetrachloride was first digested in cold concentrated HCl and subsequently diluted with deionized water. The homogeneous and clear mixture solutions of mixed oxide precursors and urea thus obtained were heated slowly on a hot plate with vigorous stirring. Precipitation was complete after 4–5 h at which time the pH of the solution was approximately 7. The precipitates thus obtained were filtered, washed several times with deionized water until free from chloride ions, and dried at 110°C for 16 h. In order to remove sodium ions, the oven dried precipitates were again washed with ammonium nitrate solution several times and dried once again at 110°C for 16 h and were finally calcined at 500°C for 6 h in an air circulation furnace. To impregnate V_2O_5, the desired amount of ammonium metavanadate was dissolved in 1 *M* oxalic acid solution and the support material was added to this solution. Excess water was evaporated in a water bath with continuous stirring. The resultant solid was then dried at 110°C for 12 h and calcined at 480°C for 5 h in flowing oxygen. X-ray powder diffraction patterns of all the samples were recorded on a Philips PW 1051 diffractometer by using Ni-filtered Cu Kα radiation.

Catalytic tests were carried out in a previously described fixed-bed microreactor system at atmospheric pressure [12]. Mixtures of methanol and ethanol (2:1 mole ratio) were fed by a metering pump at a rate of 2–4 ml h^{-1}. Nitrogen was used as a carrier at a fixed flow-rate of 45 ml min^{-1}. For each run about 1 g of catalyst sample was used and the reaction products were analyzed by gas chromatography with a 10% Carbowax 20 M column (2 m long). The main reaction products observed were isobutyraldehyde, formaldehyde, acetaldehyde with some traces of C_2–C_3 hydrocarbons, acrolein, CO and CO_2, respectively. Conversion and product selectivities were calculated as follows

$$\text{Conversion}\ (\%) = \frac{\text{No. of moles of ethanol reacted}}{\text{No. of moles of ethanol introduced}} \cdot 100$$

$$\text{Selectivity}\ (\%) = \frac{\text{No. of moles of product formed}}{\text{No. of moles of ethanol reacted}} \cdot 100$$

Catalyst composition and N_2 BET surface areas are presented in Table 1. All the mixed oxide supports obtained were X-ray amorphous and exhibited

TABLE 1

Composition and BET surface areas of various mixed oxide supported V_2O_5 catalysts

Catalyst	Support composition (mole ratio)	V_2O_5 content (wt.-%)	N_2 BET surface area of support
V_2O_5/TiO_2-Al_2O_3	1:1	12	159
V_2O_5/TiO_2-SiO_2	1:1	15	238
V_2O_5/TiO_2-ZrO_2	1:1	12	160
V_2O_5/TiO_2-SiO_2-ZrO_2	1:1:1	15	330

reasonably high N_2 BET surface areas. The binary oxides prepared via the homogeneous precipitation method using urea as hydrolysing agent were also reported to be uniform throughout the bulk [6,9,13]. The V_2O_5 contents (wt.-%) were selected in order to obtain a single monolayer of V_2O_5 on the surface of the binary oxide supports. The amount of V_2O_5 required to achieve a monolayer on the surface of the support was estimated from the area occupied per $VO_{2.5}$ unit of bulk V_2O_5, which was 0.105 nm^2. This corresponds to about 0.145 wt.-% of V_2O_5 per m^2 of support surface [14]. However, Bond et al. [15] and Baiker et al. [16] have reported a value of approximately 0.07–0.1 wt.-% V_2O_5 per m^2 of titania anatase surface deduced from a study of the application of surface specific preparative methods such as the reaction of vanadyl triisobutoxide with surface hydroxyl groups of the titania support. Therefore, an empirical definition of a monolayer has been proposed [15], which is equivalent to 70% of the theoretical monolayer capacity. However, in the present study the V_2O_5 contents selected were based on experimental observations [17,18]. The X-ray diffraction patterns of the finished catalysts and oxygen uptake measurements revealed that vanadium oxide was in a highly dispersed state. No X-ray diffraction lines due to crystalline V_2O_5 phase or compounds between vanadia and mixed oxide supports were observed either [18].

The activities and selectivities of various mixed oxide supported vanadia catalysts were studied between 250 and 400°C. The activity and selectivity trends on the various catalysts followed the same pattern with temperature. In general, an increase in conversion with an increase in temperature was observed. The formation of some additional side products with traces of CO and CO_2 were also occasionally noted at higher temperatures. The change in conversion and selectivity as a function of contact time at a fixed temperature of 350°C was also studied on various catalyst systems. In order to achieve a better comparison, the activity and selectivity results obtained at 350°C and at a fixed optimum contact time are presented in Fig. 1. A very high conversion (98%) with reasonably better selectivity (85%) to isobutyraldehyde is achieved on the V_2O_5/TiO_2–SiO_2 catalyst which is followed by V_2O_5/TiO_2–Al_2O_3. Even

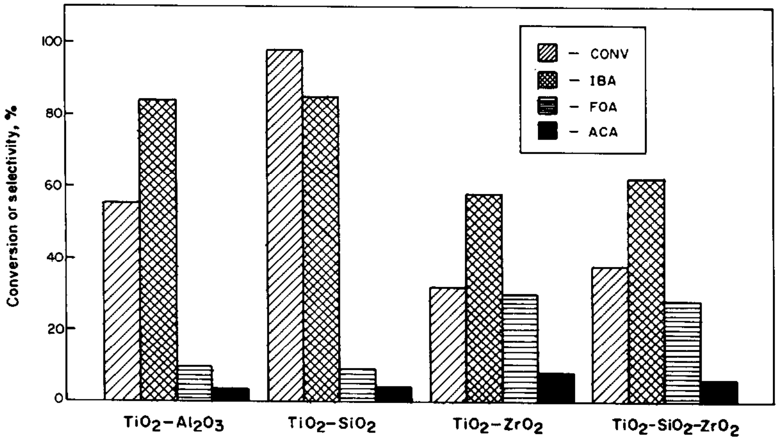

Fig. 1. Conversion and product selectivities on various mixed oxide supported V_2O_5 catalysts at 350°. CONV, total conversion of ethanol; IBA, isobutyraldehyde; FOA, formaldehyde; ACA, acetaldehyde.

at the same conversion level the selectivity towards isobutyraldehyde was greater on V_2O_5/TiO_2-SiO_2. On TiO_2-ZrO_2 and $TiO_2-SiO_2-ZrO_2$ supported systems relatively fewer conversions and product selectivities are noted. A considerable amount of formaldehyde formation was observed on these samples. The pure supports also exhibited some conversion with very poor product selectivity. In all the V_2O_5/TiO_2-SiO_2 catalyst shows better performance in terms of total conversion and isobutyraldehyde selectivity. Wang and Lee [4] reported about 85% conversion with 59% selectivity (or 50% yield) to isobutyraldehyde on a V_2O_5/TiO_2 (2.5 wt.-% V_2O_5, TiO_2 surface area is not given) catalyst at 350°C. The better results on the TiO_2-SiO_2 mixed oxide supported V_2O_5 catalyst may presumbly be due to the higher content of V_2O_5 and the very high surface area of the mixed oxide support, apart from other acid and base properties.

The mechanism of isobutyraldehyde formation, although not yet established, consists of a series of dehydrogenation, condensation, dehydration and hydrogenation steps. Acetaldehyde (dehydrogenation product of ethanol) appears to be the intermediate which upon the addition of two molecules of methanol or formaldehyde followed by several rearrangements yields isobutyraldehyde as the main reaction product [4]. Accordingly, better results were observed when an ethanol and methanol mole ratio of 1:2 or a slight excess of methanol were used. Further work is needed in order to fully understand the mechanism of this reaction. However, the present study once again demonstrates that isobutyraldehyde can be produced more selectively from methanol and ethanol in one step over V_2O_5/TiO_2-SiO_2 catalysts.

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