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Liquid and gas-phase Meerwein–Ponndorf–Verley reduction of crotonaldehyde on ZrO_2 catalysts modified with Al_2O_3, Ga_2O_3 and In_2O_3

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ABSTRACT

A series of catalysts consisting of ZrO_2 modified with Al, Ga and In by coprecipitation with their precursor salts or impregnation of previously synthesized ZrO_2 with the nitrates of the metals was prepared. The solids thus obtained were characterized using a wide range or techniques including TG/DTG; XRD, SEM-EDAX, ICP-MS, FTIR and FT-Raman spectroscopies; and nitrogen adsorption–desorption at 77 K. The catalysts prepared by impregnation were found to contain Al, Ga and In nitrates while those obtained by coprecipitation contained Al_2O_3, Ga_2O_3 and In_2O_3. The catalysts were analyzed for surface acidity and basicity by thermal programmed desorption of pyridine and CO_2, respectively. The impregnated solids calcined at 300 °C exhibited low basicity and moderate acidity due to Brønsted and Lewis sites. The coprecipitated solids were slightly more acid and basic than their impregnated counterparts, their acidity being mainly due to the presence of Brønsted sites. Both types of solids were used as catalysts in the Meerwein–Ponndorf–Verley reduction of crotonaldehyde with 2-propanol as hydrogen donor. The impregnated solids calcined at 300 °C (particularly the Ga/ZrO_2 catalyst) were the most active and selective ones in the liquid phase reaction. The selectivity towards 2-butenol in the reaction in the gas phase was high at temperatures up to 250 °C, above which it dropped in a rapid manner. Again, the impregnated solids calcined at 300 °C were the most active and selective systems in the process (particularly Ga/ZrO_2).

1. Introduction

The reduction of carbonyl compounds by hydrogen transfer from an alcohol is known as the “Meerwein–Ponndorf–Verley reaction” or “MPV reaction” in Organic Chemistry. The presence of a C=C double bond conjugated with the C=O group in an α,β-unsaturated carbonyl compound introduces an additional dimension in the process: the chemoselective reduction of the C=O group in the presence of the C=C bond, which leads to the formation of an α,β-unsaturated alcohol (Scheme 1). This selective synthesis for primary and secondary alcohols is an important process for the pharmaceutical, fragrance and food flavouring industries. Their preparation by catalytic hydrogenation with a metal-supported catalyst is rather difficult owing to the high reactivity of the C=C bond relative to the carbonyl group [1]. However, the MPV reaction has been successfully used for the selective reduction of the C=O bond in α,β-unsaturated carbonyl compounds to the corresponding unsaturated alcohols [2,3].

Traditionally, the MPV reaction has been conducted using a metal (Al, Zr) alkoxide as catalyst in a homogeneous process. The reaction mechanism involves the formation of a six-membered cyclic intermediate where both reactants coordinate to the same metal site in the alkoxide [4–6]. The past two decades, however, have seen a rise in research aimed at facilitating conduct of the process in a heterogeneous phase on account of the major advantages of operating in this way in large-scale processes [5]. The reduction of α,β-unsaturated carbonyl compounds by hydrogen transfer under heterogeneous catalysis has so far been studied in the presence of a variety of catalysts including magnesium hydroxides [7], magnesium oxides [8–10], calcined hydrotalcites [11], hydrous and calcined zirconia [8,12,13], and a wide range of active components supported on zeolitic [4,14], mesoporous [15,16] and various other materials [17].

Although the mechanism behind these heterogeneous hydrogen transfer processes is seemingly quite clear, there remains some uncertainty as to the respective roles of surface acid (Lewis or Brønsted) and/or basic sites in the catalysts. Rather than a unified mechanism, researchers have proposed a number of them dependent on the particular catalyst used in the heterogeneous MPV reaction. Thus, the reduction of carbonyl compounds by hydrogen transfer has been hypothesized to occur at Lewis acid sites [4],

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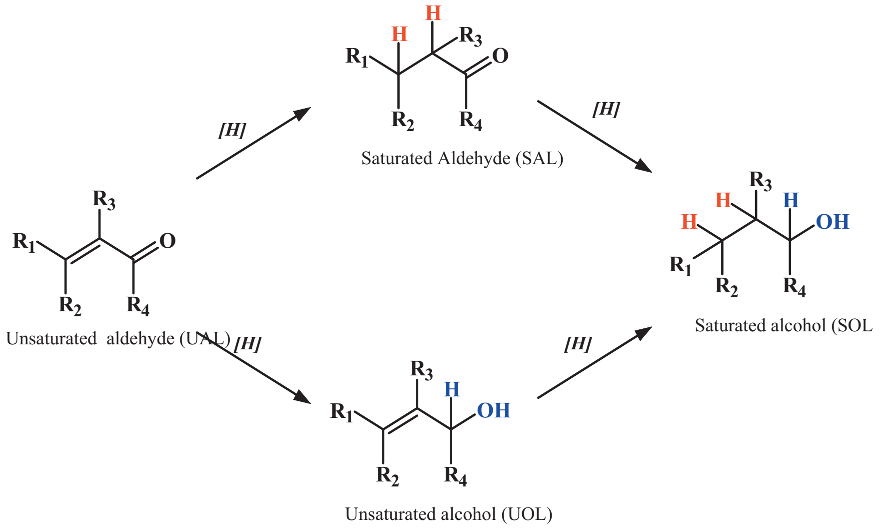

Scheme 1. Reaction network for the reduction of α,β-unsaturated carbonyl compounds.

Brønsted acid sites [12,13], basic sites [18,19] and acid–base pairs [10,20].

Zirconia has proved a highly effective choice among heterogeneous catalysts used in the MPV reaction [13]. Zirconium oxide is a solid with a high thermal stability and corrosion resistance in addition to a strong amphoteric character [21]. Textural and acid–base properties of ZrO_2 depend largely on its synthetic procedure and calcination temperature. Adjusting its acid–base properties is possible by modifying its surface with sulphate ions [22–24], phosphate ions [25] and mixtures of other oxides [3,26,27]; this has proved a highly effective method for tailoring the activity of zirconia towards many organic processes.

Some studies revealed catalytic activity in the MPV reaction to decrease with increasing calcination temperature (*i.e.* with increasing loss of surface hydroxyl groups) in hydrous zirconia; this underlines the significance of proton (Brønsted) sites to the process [12,13]. Moreover, it has been recently reported that the incorporation of boron into ZrO_2 leads to an increased catalytic activity in the liquid-phase MPV reduction of cinnamaldehyde consistent with an increased amount of highly strong proton (Brønsted) acid sites [3].

Modifying the surface chemical properties of ZrO_2 through the incorporation of Al_2O_3, Ga_2O_3 or In_2O_3 could allow to study the role of surface acid (Brønsted or Lewis) or basic sites on the activity and selectivity of the MPV reduction of crotonaldehyde with 2-propanol.

2. Experimental

2.1. Synthesis of catalysts

The studied catalysts were prepared by modifying zirconium oxide with 10% Al_2O_3, Ga_2O_3 or In_2O_3, either by coprecipitation with their precursor salts or by impregnation of previously synthesized pure ZrO_2, which was used as reference.

The reference zirconium oxide was obtained from zirconium oxychloride octahydrate (from Sigma–Aldrich). To this end, an appropriate amount of reagent was dissolved in 500 mL of water and precipitated by dropwise addition of 5 N NH_4OH to pH 9.5. The precipitate was allowed to stand overnight, filtered and washed with Milli-Q water as many times as required to give a negative chloride test with silver nitrate. The resulting solid was dried at 110 °C for 6 h, ground and sieved prior to calcination at 300 °C for 6 h, using a heating rate of 2 °C/min.

A similar procedure was used to obtain ZrO_2 catalysts modified with a 10 mol.% concentration of Al_2O_3, Ga_2O_3 or In_2O_3 by coprecipitation. The starting solution contained the corresponding precursors (*viz.* zirconium oxychloride and Al, Ga or In nitrate), appropriate amounts of which were dissolved in 500 mL of Milli-Q water and treated similarly as before. The resulting solids were also calcined at 175 or 300 °C for 6 h.

The reference zirconium oxide above described was split into four portions three of which were modified by impregnation with an aqueous solution of aluminium, gallium or indium nitrate (from Sigma–Aldrich). To this end, 6 g of ZrO_2 was suspended in 10 mL of Milli-Q water and supplied with the amount of nitrate needed to obtain a 10 mol.% concentration of the corresponding oxide in the final solid. The mixture was placed in a rotavapor for 2 h to obtain a homogeneous paste. Residual solvent was then evaporated by evacuation in a water bath at 60–80 °C. Once dry, the solid was calcined at 175 and 300 °C for 6 h, ground and sieved.

The catalysts were designated with the symbol for the zirconium-modifying element (Al, Ga or In), followed by that for the synthetic method used ("co" for coprecipitation and "im" for impregnation) and the calcination temperature used (175 or 300 °C). For example, the ZrO_2 catalyst containing 10 mol.% Al_2O_3, obtained by coprecipitation and calcined at 300 °C was designated Alco300.

2.2. Textural and structural characterization

Gels were subjected to thermogravimetric and differential thermal analysis on a Setaram Setsys 12 system, using Air at 40 mL/min as carrier gas, α-Al_2O_3 as reference material and a Pt/Pt–Rh (10%) thermocouple. The heating rate was 10 °C/min and the temperature range 30–1000 °C. The amount of gel used in each test was *ca.* 20 mg.

The textural properties of the solids were determined from nitrogen adsorption–desorption isotherms obtained at liquid nitrogen temperature on a Micromeritics ASAP-2010 instrument. All samples were degassed to 0.1 Pa at 110 °C prior to measurement. Surface areas were calculated using the Brunauer–Emmett–Teller (BET) method [28].

X-ray diffraction patterns were obtained on a Siemens D5000 diffractometer equipped with a graphite monochromator and using Co Kα radiation. The 2θ angle was scanned from 5 to 75° with a step size of 0.05°.