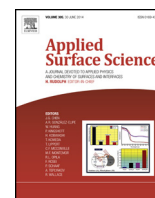




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Vapour phase dehydration of glycerol to acrolein over tungstated zirconia catalysts

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ABSTRACT

Tetragonal (TZ) and monoclinic (MZ) polymorphs of zirconia supports were synthesised by sol-gel method followed by variation of the calcination temperature. Tungstated (10 wt% WO₃) supported on the zirconia polymorphs were prepared by impregnation method by using ammonium metatungstate precursor. The physico-chemical properties of the calcined catalysts were characterised by X-ray diffraction, UV-vis diffused reflectance spectroscopy, X-ray photoelectron spectroscopy (XPS), surface area and pore size distribution measurements to gain insight into the effect of morphology of the catalyst textural properties, and structure. The surface acidic properties have been determined by NH₃ TPD method and also with FT-IR spectra of pyridine adsorption. Vapour phase dehydration of glycerol to acrolein was employed to investigate the catalytic functionalities. Glycerol conversion and acrolein selectivity was mainly dependent on the fraction of moderate acid sites with majority of them are due to Brønsted acidic sites. Monoclinic zirconia based catalysts have shown the highest activity and acrolein selectivity compared to the corresponding tetragonal zirconia catalysts.

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1. Introduction

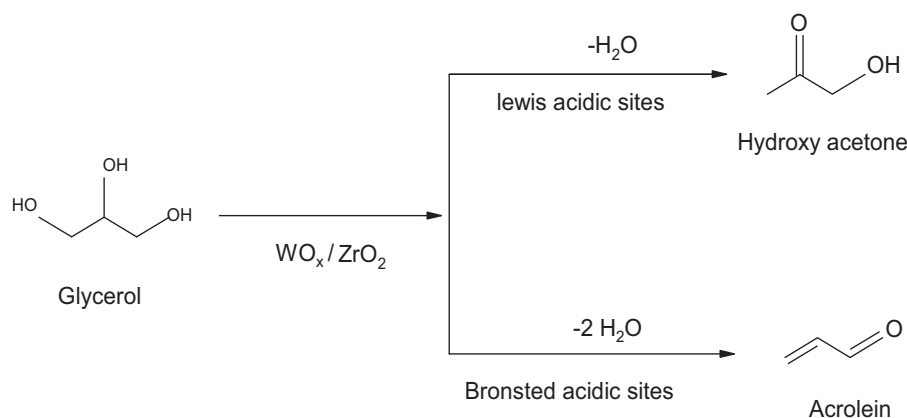
The valorization of glycerol obtained from biodiesel production is a big challenging task in recent years. An effective usage or conversion of crude glycerol to specific products will further reduce the cost of biodiesel production. Therefore, new uses of glycerol need to be explored for its effective valorization. Although glycerol can be burned as a fuel, it can also be converted into more valuable commodity chemicals. Glycerol can be converted to acrolein, which is an important chemical intermediate for the production of acrylic acid, acrylic acid esters, super absorbers, polymers and detergents [1,2]. Currently, acrolein is commercially manufactured by the catalytic partial oxidation of propylene over mixed metal oxides containing mainly Bi–Mo (W)–O, Mo–Te–O, Sn–Sb–O, U–Sb–O, Fe–Sb–Ti–O, and cuprous oxide as catalysts phase [3]. Compared with petroleum-based processes, the dehydration of glycerol to acrolein has attracted a great deal of attention as a significant route by virtue of its being an environmentally benign process.

The dehydration of glycerol in gas phase on acidic catalysts is a typical example of double dehydration reaction and proceeds via

the formation of 3-hydroxypropionaldehyde, 1-hydroxyacetone [4] as shown in Scheme 1. The highest selectivity to acrolein reported until now is 65–80% by the dehydration of glycerol in either gaseous or in liquid-phase. It was found that a solid acid catalyst with Hammett acidity (H_0) between –10 and –16 are the most suitable catalyst for the dehydration of glycerol to acrolein than catalysts of lower acidity with H_0 between –2 and –6 [5]. However, such strong acidity of the catalyst causes rapid deactivation due to deposition of carbonaceous species which blocks the activity on the catalyst surface, particularly in the presence of large number of micro pores.

In the recent past zirconium oxide has received considerable attention as a support for variety of catalytic reactions. The advantages of using ZrO₂ as support include, (i) interacts strongly with the active phase (ii) possesses high thermal stability and more chemically inert than the classical supported oxides, (iii) is the only metal oxide which may possess four chemical properties, namely acidity, basicity as well as the reducing and oxidizing ability, (iv) exhibit super-acidic properties when modified with tungstated active phase [6]. Apart from the extensive use in the preparation of super-acidic catalysts, zirconia has been employed as a catalyst support in many industrially important reactions such as hydro processing [7], selective oxidation of methanol [8], conversion of low grade renewable feed stocks to biodiesel [9,10] and steam

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Scheme 1. Schematic representation of the dehydration of glycerol to acrolein and hydroxy-acetone.

reforming of naphthalene [11]. The extreme hardness and high specific mass of zirconia can also be an advantage for its potential use as a catalyst support.

It is well known that coordination environments of zirconium and oxygen in zirconia polymorphs are apparently different. In the tetragonal lattice the Zr⁴⁺ cation is octacoordinated and the O²⁻ anion is tetracoordinated. Whereas in the monoclinic lattice the Zr⁴⁺ cation is heptacoordinated and the O²⁻ anion is either tri- or tetracoordinated [12]. These significant structural differences make the use of both the tetragonal zirconia (TZ) and monoclinic zirconia (MZ) as potential catalyst supports for metals and metal oxides. The activity of methanol synthesis from CO hydrogenation on Cu/ZrO₂ was strongly influenced by the zirconia polymorphs. The methanol synthesis activity was higher for Cu/t-ZrO₂ than Cu/m-ZrO₂ catalysts [13]. Yori and Parera reported that the larger the fraction of the tetragonal phase of zirconia in Pt/WO₃-ZrO₂, the higher the activity of *n*-butane isomerization and the lower the metallic activity of Pt [14]. Stichert et al. [15] observed the activity of monoclinic sulphated zirconia is lower by a factor of 2–5 compared to tetragonal sulphated zirconia for *n*-butane isomerization reaction. Zhao et al. [16] studied the surface acidic properties of both monoclinic and tetragonal zirconia phases and reported that the monoclinic zirconia contains both Brønsted acid sites and Lewis acid sites, while tetragonal zirconia possesses only Lewis acidic sites.

WO₃/ZrO₂ catalysts exhibit unique catalytic properties in the dehydration of glycerol to acrolein [17–19]. Ulgen et al. [17] evaluated the catalytic performance of WO₃/ZrO₂ catalysts with various WO₃ loadings and reported 73% acrolein selectivity on 19 wt% WO₃/ZrO₂ at an optimal temperature of 280 °C. Similar acrolein selectivity was reported at 300 °C with total conversion using a commercial WO₃/ZrO₂ catalyst [18]. On the other hand, improvement of tungstated zirconia catalyst with SiO₂ doping, results in better selectivity (80%) of acrolein with long catalyst life and thermal stability [19]. However, not much research activity has been devoted towards understanding the effect of morphology and the nature of active sites and the role played by the catalyst in the vapour phase dehydration reactions. The actual state of the active component on the surface depends mainly on the method of preparation, the acidity/basicity of the support and the amount of the active component. The active component may remain in a highly dispersed or as crystallite form on the support surface.

In view of the potential use of zirconia as a catalyst support, in the present work we report a systematic investigation to investigate the structural and catalytic properties of zirconia polymorphs and tungstated zirconia polymorphs. The catalysts were characterised by an array of complimentary spectroscopic and adsorption techniques. The catalytic properties were evaluated for the dehydration of glycerol and correlated with the surface acidic properties

on different ZrO₂ phases and also using other characterization techniques.

2. Experimental

2.1. Catalyst preparation

The tetragonal and monoclinic zirconia supports were prepared by the following procedure. Zirconium *n*-propoxide (Sigma–Aldrich, 70 wt% in 1-propanol) was used as a zirconia precursor (0.025 M) [20]. In a typical experiment, 17.7 g of Zirconium *n*-propoxide diluted with *n*-propanol (41.3 g) was hydrolyzed by dropwise addition of aqueous ammonia with continuous stirring until the pH of 10–10.5. After the completion of hydrolysis, the sol was continuously stirred for an hour at ambient temperature to polymerize the gel. Tetragonal and monoclinic phases of zirconia supports are prepared by varying the calcination temperature of as-synthesised Zr(OH)₂ by sol–gel preparation method. The samples were subsequently dried at 110 °C for 12 h and calcined in a muffle furnace at 400 and 700 °C respectively for 4 h to yield tetragonal zirconia (TZ) and monoclinic (MZ). Tungstated zirconia polymorphs are prepared by impregnation method by adding aqueous solution of ammonium metatungstate to the calcined zirconia supports. The samples were subsequently dried at 110 °C for 12 h and calcined in a muffle furnace at 400 °C for 5 h. The samples synthesised were named as WTZ, WMZ, respectively.

2.2. Catalyst characterization

X-ray powder diffraction patterns of the samples obtained by a model: D8 diffractometer (Advance, Bruker, Germany), using Cu K α radiation (1.5406 Å) at 40 kV and 30 mA. The measurements were recorded in steps of 0.045° with a count time of 0.5 s in the range of 2–40°. Pore size distribution measurements were performed on Autosorb-1 instrument (Quntachrome, USA) using by nitrogen physisorption. The UV–vis diffused reflectance spectra were recorded on a GBC UV–vis Cintra 10_e spectrometer with an integrating sphere reflectance accessory. The spectra were recorded in air at room temperature and the data was transformed according the Kubelka–Munk equation $f(R) = (1 - R\alpha) / 2R\alpha$. The X-ray photoelectron spectroscopy (XPS) spectra of the catalysts were measured on a XPS spectrometer (Kratos-Axis 165) with Mg K α radiation (1253.6 eV) at 75 W. The C 1s line at 284.6 eV was used as an internal standard for the correction of binding energies. The background pressure during the data acquisition was kept below 10⁻¹⁰ bar. NH₃-TPD experiments were conducted on AutoChem 2910 instrument. Prior to TPD analysis the sample was pretreated by passing high purity (99.999%) helium (50 ml/min) at 300 °C for 1 h. After

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