



Highly dispersed Cr₂O₃–ZrO₂ binary oxide nanomaterials as novel catalysts for ethanol conversion



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ABSTRACT

Novel Cr₂O₃–ZrO₂ binary oxide catalysts (CZ) were successfully prepared by simple co-precipitation method. The as-prepared nanomaterials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), energy dispersive spectroscopic (EDS) and N₂ adsorption. The XRD analysis indicated the formation of amorphous materials of binary oxides, at higher ZrO₂ content, which exhibited significantly modified textural characteristics, as indicated by N₂ adsorption studies. The characteristics of the binary oxides were dependent on the Cr/Zr ratio. The composite with molar Zr/(Zr + Cr) ratio equals 75% (CZ75), in particular, exhibited significantly higher specific surface areas and porosity than other composites and pure oxides. The TEM images clearly illustrate how ZrO₂ could control the particle size of Cr₂O₃ catalyst. The catalytic conversion of ethanol was studied at 200–400 °C. The catalytic activities exhibited by the binary oxides were significantly higher than those of the pure oxides. The total ethanol conversion (TC%) and dehydration/dehydrogenation selectivity were dependent on the Cr/Zr ratio. A CZ75 nanomaterial, treated suitably, can be used as a reusable active catalyst in the ethanol conversion.

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1. Introduction

Conversion of ethanol to hydrocarbons has received wide attention due to the heavy demand for hydrocarbons; such as ethylene, diethyl ether (DEE) and butadiene [1–3]. Catalytic transformation of alcohol into hydrocarbons is useful for petrochemical raw materials or as a motor fuel [1]. The decomposition of alcohols over metal oxide catalysts has been the subject of numerous studies due to its applicability to a variety of chemical synthesis processes [4–7]. In recent years, this subject has gained particular interest due to growing environmental, economic, and political concerns [5].

It is well known that ZrO₂ possesses high thermal stability and durability at high temperatures. It was reported that zirconia suppressed the sintering of the active components when they were dispersed mutually [8,9]. Besides, chromium oxide (Cr₂O₃) is one of the most important transition metal oxides that are widely used in many industries. They include, but are not limited to: green pigments [10], hydrogen storage [11], gas sensors [12], coating, wear and corrosion resistance materials [13,14] and catalysts [15].

Moreover, chromia possesses interesting electrical, magnetic as well as surface properties that affect its usage as an industrial catalyst in many reactions. Such reactions include ethylene polymerization [16], propane oxidative dehydrogenation [17] and CO oxidation [18].

ZrO₂-based solids and binary oxides catalysts are attracting a great deal of attention in recent years. Several ZrO₂-based catalysts have been reported such as Co₃O₄/ZrO₂ [19], Co–ZrO₂/SiO₂ [20], WO_x/ZrO₂ [21], CuO–ZrO₂ [22], TiO₂–ZrO₂ [23], CeO₂–ZrO₂–CuO [24], NiO–MgO–ZrO₂ [25] and Rh/ZrO₂ [26]. Furthermore, these catalysts are active and selective in many important reactions such as CO preferential oxidation [19], Fischer–Tropsch synthesis [20], oxidative desulfurization [21], combustion of methane [22] and photocatalysis [23].

There are several reports concerning preparing ZrO₂-based solids and binary oxides catalysts [19–26]. However, the preparation of Cr₂O₃–ZrO₂ binary oxide catalysts was not studied. The purpose of this work is to prepare Cr₂O₃–ZrO₂ nanomaterials. Furthermore, the as-synthesized nanomaterials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), energy dispersive spectroscopic (EDS) and N₂ adsorption–desorption isotherms. The ethanol conversion and catalyst reusability were investigated.

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2. Experimental

2.1. Materials

Chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Oxford), zirconium (IV) oxychloride hydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Oxford), ammonia solution (NH_4OH , Alfa) and ethanol (absolute) (for HPLC, $\geq 99\%$) were used as received. Bi-distilled water was used for the preparation of all the catalysts.

2.2. Catalyst preparation

Cr_2O_3 – ZrO_2 binary oxide catalysts were prepared by a coprecipitation method. In a typical experiment, the required quantities of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved separately in bi-distilled water and mixed together at 60°C . The aqueous solution of metal salts with a total cation concentration of 1.0 M was contacted with a basic solution of aqueous ammonium of 2.0 M dropwise with constant stirring until pH 9. The precipitate formed was aged in the mother liquid overnight, then filtered, washed with bi-distilled water several times until free from anion impurities. The obtained hydroxide precipitate was oven dried at 110°C for 8 h and finally calcined at 500°C for 3 h. The molar ratios of Zr in the composition were set for 0%, 25%, 50%, 75% and 100%. The formula CZ– x will be used throughout the paper to represent the different composites where x refers to the molar % Zr content, $\text{Zr}/(\text{Zr} + \text{Cr}) \times 100$.

2.3. Catalyst characterization

X-ray diffraction powder patterns were recorded at room temperature on a Philips Xpert powder diffractometer, using the Bragg–Brentano configuration and the $\text{CuK}\alpha$, radiation $\lambda = 1.5406 \text{ \AA}$. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Jasco IR 4100 spectrometer (Japan) using KBr pellets. The morphology of the catalysts was observed by transmission electron microscope (TEM) equipped with energy dispersive spectroscopic (EDS) microanalysis system (JEM-2100CX (JEOL)). The surface characteristics of the prepared catalysts were obtained using nitrogen gas adsorption at 77 K on a Quantochrome AS1Win™-automated gas-sorption apparatus (USA). Before each N_2 sorption measurement, samples were degassed at 200°C for 2 h.

2.4. Catalytic activity test

Catalytic activity tests of the prepared catalysts were determined by using ethanol conversion reaction at different temperatures varying between 200 and 400°C , the catalytic reaction was conducted in a flow reactor under atmospheric pressure. Thus, a 100 mg catalyst sample was held between two glass wool plugs in a Pyrex glass reactor tube 20 cm long and 1 cm internal diameter packed with quartz fragments 2–3 mm length. The temperature of the catalyst bed was regulated and controlled within $\pm 1^\circ\text{C}$. Argon gas was used as the diluent and the ethanol vapor was introduced into the reactor through an evaporator/saturator at the ethanol pressure equal 100 Torr. The flow rate of the argon was maintained at 30 ml/min. Before carrying out such catalytic activity measurements each catalyst sample was activated by heating at 300°C in a current of argon for 1 h then cooled to the catalytic reaction temperature. The injection time of the sample products and the unreacted ethanol was fixed after 15 min, and many injections were carried out to give constant conversion. The reaction products in the gaseous phase were analyzed chromatographically using Perkin–Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. The column used was stainless steel chromatographic columns, 4 m length, packed with 10% squalane

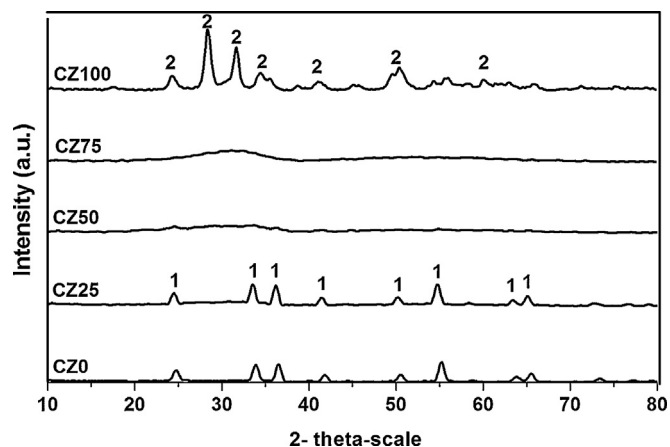


Fig. 1. XRD patterns of Cr_2O_3 – ZrO_2 binary oxide catalysts calcined at 500°C . Peaks (1) refer to Cr_2O_3 phase and (2) refer to ZrO_2 phase.

supported on chromosorb. The reaction products were analyzed at a column temperature of 60°C in all conversion runs. Detector temperature was kept at 250°C .

2.5. Catalyst reusability

To study the reusability of catalyst, after each ethanol conversion experiment, the used catalyst was regenerated at 300°C in a current of argon for 1 h.

3. Results and discussion

3.1. XRD analysis

XRD is used for identification of the crystal phase and crystallite size of each phase present. XRD patterns of Cr_2O_3 – ZrO_2 binary oxide catalysts calcined at 500°C are shown in Fig. 1. For CZ0 and CZ25 nanomaterials, only had the characteristic peaks of the crystallized α - Cr_2O_3 phase (Eskolaite) (JCPDS No. 38-1479). At lower ZrO_2 content, i.e. CZ25 nanomaterial, there are no diffraction peaks of the crystalline ZrO_2 phase in the XRD pattern, implying that ZrO_2 in this sample exists in a highly dispersed state on Cr_2O_3 surface. At higher ZrO_2 content, i.e. CZ50 and CZ75 patterns, no characteristic peaks were visible, indicating that they were amorphous materials. Several studies have reported that zirconia-based binary metal oxides at higher ZrO_2 content calcined at 500°C were an amorphous material [27,28]. It has been reported that ZrO_2 may inhibit the formation of well crystalline particles, i.e., binary oxides mostly exist in the form of microcrystals [29,30]. The peaks in the pattern of CZ100 nanomaterial could be assigned only to the presence of both monoclinic and tetragonal ZrO_2 phases (JCPDS No. 37-0031) [31]. It is well known that pure ZrO_2 has two coexisting structurally stable phases, namely m- ZrO_2 and t- ZrO_2 . The 2θ of 24.1° , 28.2° , 31.4° , and 34.1° are assigned to the m- ZrO_2 , and the peaks centered at about 35.2° , 50.2° , and 60.3° are assigned to the t- ZrO_2 [32,33].

For CZ0, CZ25 and CZ100 nanomaterials, the crystallite sizes were estimated using the Scherrer equation [34] and the results are listed in Table 1. As shown in Table 1, increasing the ZrO_2 content from 0 to 100 mol% led to a significantly decreased the crystallite size.

3.2. FT-IR analysis

Fig. 2 shows the FT-IR spectra of CZ0, CZ75 and CZ100 binary oxide catalysts. The broad absorption peak at 3600 – 3200 cm^{-1} can be attributed to the hydroxyl groups of hydrated oxide surface

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