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Understanding the role of Co in Co–ZnO mixed oxide catalysts for the selective hydrogenolysis of glycerol

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ABSTRACT

A series of Co–ZnO catalysts with varying Co to Zn ratio were prepared by co-precipitation method and these were characterized by X-ray diffraction, temperature programmed reduction, H_2 chemisorption, X-ray photoelectron spectroscopy and transmission electron microscopy. The developed catalysts were evaluated for selective hydrogenolysis of glycerol to 1,2-propanediol. Glycerol conversion was found to be dependent on the ratio of Co to ZnO and a weight ratio Co/Zn of 50:50 was shown about 70% glycerol conversion with 80% selectivity to 1,2-propanediol. Glycerol hydrogenolysis activity was found to be related to Co metal area as well as amount of ZnO in the catalyst. The proposed catalysts were stable under the reaction conditions and reusable with consistent activity. Different reaction parameters were studied and optimum reaction conditions were established. A kinetic model for the hydrogenolysis reaction was also derived.

1. Introduction

Glycerol is a by-product in the preparation of biodiesel by transesterification of vegetable oils or animal fats is being produced in huge volumes and being accumulated worldwide with the expanding demand for biodiesel production [1]. The present demand for glycerol cannot compensate its production, and new efficient procedures for the transformation of glycerol to valuable chemicals are highly desired [2]. In future, glycerol will be a cost-effective raw material for the preparation of a wide range of valuable chemicals and fuel additives. Several routes are proposed for the conversion of glycerol to various value-added chemicals [3]. One of the methods for glycerol transformation is hydrogenolysis to 1,2-propanediol [4–6]. It is an attractive pathway as 1,2-propanediol is a major commodity chemical with a 4% annual market growth. 1,2-Propanediol is widely used in the preparation of several industrially important chemicals including unsaturated polyesters resins, functional fluids (antifreeze, de-icing, and heat transfer devices), pharmaceuticals, food, cosmetics, liquid detergents, tobacco humectants, flavors, fragrances, personal care, paints and animal feed [7–9]. Further there is increasing demand for 1,2-propanediol in antifreeze and deicing market due to the concern over toxicity of ethylene glycol based products to humans and animals.

Acid or base catalysts are effective for the dehydration of alcohols, whereas metals are effective for hydrogenation. For hydrogenolysis of glycerol, metal–acid/base bifunctional catalysts have been studied [8]. A variety of heterogeneous catalysts have been tested for this reaction which can be classified mainly into two groups. The first type of catalysts are based on noble metals such as Rh, Ru, Pd, Ir, Re and Pt [10–15] and other type of catalysts are non-noble metals such as Cu, Co and Ni [16–20]. The Cu based catalysts are highly selective toward 1,2-propanediol as compared to noble metal catalysts due to its lower activity for C—C bond cleavage. However, sintering of metal particles during the course of reaction often resulted in catalyst deactivation. Also it is reported that the conversion and selectivity of glycerol is effected by the acidic [6,21,22] and basic promoters [23,24]. Comparison of different catalysts under neutral [4], acidic [6] and basic conditions [7] have been reported in the literature. Guo et al. studied glycerol hydrogenolysis using Co supported on MgO catalysts resulting 44.8% glycerol conversion and 42.2% selectivity toward 1,2-propanediol [25]. Recently, Balaraju et al. reported Cu/MgO catalysts for hydrogenolysis of glycerol with improved selectivity toward 1,2-propanediol [26]. However, with these catalysts the glycerol conversion was found to be low and the problems such as conversion of support MgO to $Mg(OH)_2$ and aggregation of cobalt particles occurred during the reaction. Therefore, in order to

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overcome the above drawbacks, improved catalysts consisting of Co supported on ZnO are proposed for the selective hydrogenolysis of glycerol to 1,2-propanediol.

In the present work, a series of Co–ZnO catalysts were prepared with varying Co/Zn weight ratios and studied for selective hydrogenolysis of glycerol. These catalysts were characterized by employing different spectroscopic methods. The derived physicochemical properties were correlated with the observed glycerol hydrogenolysis activity. Further, the process conditions were optimized to improve the conversion and selectivity. Finally a kinetic model was proposed for the glycerol hydrogenolysis.

2. Experimental

2.1. Catalyst preparation

Co–ZnO catalysts with varying Co/ZnO weight ratio were prepared using co-precipitation method. Calculated amounts of aqueous solutions of $Co(NO_3)_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were taken and 0.5 M solution of potassium carbonate was added drop wise with constant stirring until the pH of the solution becomes 10. The formed precipitate was kept on stirring for a period of 12 h. The formed solid was collected by filtration and washed thoroughly with water to remove any traces of potassium. The sample was then dried in oven for overnight at 100 °C. The dried samples were calcinated in air at 400 °C for 3 h to obtain final catalyst. Different catalyst compositions were prepared by varying the amount of Co in Co–ZnO from 20 to 70 wt%.

2.2. Catalyst characterization

The surface area of the samples was measured by N_2-physisorption at −196 °C using Micromeritics ASAP 2000. Approximately 0.2 g of sample was used for each analysis. The moisture and other adsorbed gases present in the sample were removed before analysis by degassing the sample at 200 °C.

X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan speed of 2° min^{-1} and a scan range of 10–80° at 30 kV and 15 mA.

Hydrogen chemisorption was carried out on a pulse adsorption apparatus. Prior to adsorption measurements each catalyst sample (100 mg) was reduced in a flow of hydrogen (50 ml/min) at 450 °C for 2 h and flushed subsequently in pure Ar flow and cooled to 150 °C in the same gas flow. H_2 uptake was measured by injecting number of H_2 pulses through a calibrated on-line sampling valve. H_2 pulses were injected until there was no more adsorption by catalyst. The metal surface area and particle size of the catalysts were calculated assuming the stoichiometric factor for hydrogen atom to Co as 1.

Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 5% H_2/Ar mixture gas at a flow rate of 60 ml/min with a temperature ramp of 10 °C/min. Before TPR run the catalysts were pretreated in Ar at 300 °C for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector.

X-ray photo electronic spectroscopy (XPS) measurements were conducted on a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using Al K_α anode. The non-monochromatized Al-K_α X–ray source ($h\nu$ = 1486.6 eV) was operated at 12.5 kV and 16 mA. Before acquisition of data the sample was out-gassed for about 3 h at 100 °C under vacuum of 1.0×10^{-7} Torr to minimize surface contamination. The XPS instrument was calibrated using Au as standard. For energy calibration, the carbon 1*s* photoelectron line was used and the carbon 1*s* binding energy was taken as 285 eV. Charge neutralization of 2 eV was used to balance the charge up of the sample. The spectra were deconvoluted using Sun Solaris based Vision-2 curve resolver. The location and the full width at half maximum (FWHM) value for the species were first determined using the spectrum of pure sample. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within ±0.1 eV.

The morphology features of the catalysts were obtained by transmission electron microscopy (TEM). TEM investigations were carried out using Philips CM20 (100 kV) transmission electron microscope equipped with a NARON energy-dispersive spectrometer with a germanium detector. The specimens were prepared by dispersing the samples in methanol using an ultrasonic bath and evaporating a drop of resultant suspension onto the lacey carbon support grid. The sizes of the catalyst particles were measured by digital micrograph software (version 3.6.5, Gatan Inc.).

Semi-quantitative chemical analyses on grains were carried out using Hitachi S-3400N Scanning Electron Microscope coupled with Energy Dispersive Spectrometer (SEM-EDS). Horiba EDS detector was used for the analysis with operating conditions: accelerating voltage of 15 kV beam current of 2.9 nA and measurement time 60 s. Atomic ratios were calculated with the ZAF-4® program, which performs the necessary corrections for the overlapping peaks of different elements.

2.3. Glycerol hydrogenolysis activity measurements

Hydrogenolysis of glycerol was carried out in 100-mL Hastealloy PARR 4843 autoclave. Prior to the experiment, the Co–ZnO catalyst was reduced at 450 °C for 2 h with a hydrogen flow of 60 ml/min. In a typical run, 20 g of the aqueous glycerol solution (20 wt% glycerol) and 0.6 g of catalyst were loaded into the reactor. The autoclave was purged with H_2 flow to drive off the air present in it. The glycerol hydrogenolysis reaction was conducted at a temperature of 180 °C with a H_2 pressure of 40 bar at a rotation speed of 300 rpm. During the reaction, hydrogen pressure was noticed to be decreased and it was maintained by introducing additional H_2.

2.4. Analysis of glycerol hydrogenolysis products

After completion of the reaction, gaseous products were collected in a gasbag and the liquid phase products were separated from the catalyst by filtration. The liquid products were analyzed using a gas chromatograph (Shimadzu 2010) equipped with a flame ionization detector by separating them on Inno wax capillary column (diameter 0.25 mm, length 30 m). The products were identified by using GC–MS (Shimadzu, GCMS-QP2010S) analysis. The gas phase products were analyzed by a gas chromatograph equipped with Porapak Q column and thermal conductivity detector. The products identified during glycerol hydrogenolysis were 1,2-propanediol and ethylene glycol (EG) as main products and 1-propanol, 2-propanol, ethanol, methanol, ethane and methane as degradation products. Following are the equations used for evaluating the conversion and selectivity of glycerol to 1,2-propanediol.

$$\text{Conversion}\quad(\%) = \frac{\text{moles of glycerol consumed}}{\text{moles of glycerol intitially charged}} \times 100.$$

$$\text{Selectivity}\quad(\%) = \frac{\text{moles of carbon in specific product}}{\text{moles of carbon in all detected product}} \times 100.$$