Nanosized samarium modified Au-Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalysts for oxidation of benzyl alcohol

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ABSTRACT

In this study, Au-Ce$_{0.5}$Zr$_{0.5}$O$_2$ (Au-CeZr) and Sm modified AuCeZr catalysts were synthesized by organic deposition-precipitation method using gold acetate and samarium acetate as Au and Sm precursors and tetrapropyl ammonium hydroxide as precipitating agent. The synthesized nanocrystalline Au-CeZr and Sm modified Au-CeZr materials found be effective catalysts for benzyl alcohol oxidation at low reaction temperatures. The catalysts were characterized by XRD, SEM, TEM, DRIFT spectra after pyridine adsorption, N$_2$-physisorption, XPS and H$_2$-TPR techniques. The Au nanoparticles are highly dispersed on CeZr support and XRD reflections due to presence of Au metal were not observed for the samples which contained less than 1.0 wt% Au. The XPS and H$_2$-TPR results revealed that at lower Au loadings, strong Au-CeZr interaction resulted an easy exclusion of surface oxygen ions in Au-CeZr and Sm-Au-CeZr catalysts. Pyridine adsorption results indicated an increase of Lewis acid sites of the CeZr support after Au deposition and Sm modification. The 2.0Sm-0.5Au-CeZr catalyst is most active and selective catalysts for benzyl alcohol oxidation among the synthesized catalysts due to optimum loading of Au and Sm. An optimal surface acidity and redox properties is accountable for the improved catalytic activity of 2.0Sm-0.5Au-CeZr catalyst in the benzyl alcohol oxidation.

1. Introduction

In recent years, selective oxidation of benzyl alcohol to benzaldehyde is of considerable importance in the industry, because benzaldehyde is considered a versatile chemical and widely used as a starting material in perfumery, cosmetic, pharmaceutical, dyestuff, flavoring and agro chemical industries [1,2]. Traditionally, benzyl alcohol oxidation was performed using various hazardous and expensive inorganic oxidants, such as hypochlorite, manganese (IV) oxide, permanganate, chromium (IV) oxide and dichromate [3–6]. With growing environmental concern, clean oxidants like molecular oxygen and aqueous hydrogen peroxide are preferred as water is the only main side product of these reactions [5].

Choudary and co-workers first tested benzyl alcohol oxidation in liquid phase by using a range of transition metals catalysts supported on hydrotalcite-like supports without the use of any solvent [6]. Among the numerous non-noble metals tested for the reaction, Cu and Mn catalysts were proved to be the most active but with low selectivity towards benzaldehyde and with the need of high reaction temperature 210 °C. Typical noble metals such as Pt, Pd, and Au were used to

catalyze this reaction. More enhancements in this reaction were reported by Hutchings et al [4], indeed they showed that supported gold catalysts were very active for the liquid phase selective oxidation of benzyl alcohol. They investigated a range of supports and preparation methods and discovered that Fe$_2$O$_3$ supported gold catalysts prepared by co-precipitation method displayed the highest conversion. A screening of supports for gold catalysts was also performed by Choudhary et al [7]; the authors claimed that ZrO$_2$, MnO$_2$, Sm$_2$O$_3$, and Al$_2$O$_3$ were found to have the highest turnover frequencies.

The synergistic influence of combining the Au with Pd was established, for selective oxidation benzyl alcohol [4]. The authors found the bimetallic catalysts to be more active than Au only catalysts but less active than Pd only catalysts. However bimetallic catalysts displayed, over the duration of the reaction, both higher conversions and selectivity towards benzaldehyde, 74%, and 91% respectively. In another report, Dimitratos et al [8] prepared Au catalyst with very small particle size and it showed higher activity than the catalysts prepared via impregnation. They also investigated the role of different calcination atmospheres and found out that air calcined samples are superior to the catalysts calcined under hydrogen or nitrogen. It is widely reported that

CeZr mixed oxides possessed exceptional redox characteristics and huge lattice oxygen mobility [9]. These possessions powerfully be contingent on Ce/Zr molar ratio. Chloroauric acid (HAuCl$_4$) has been widely used as a source to synthesize Au containing catalysts. However, chloride anion contained in the precursor often causes problems, such as coagulation of Au particles, poisoning of catalytic activity and corrosion of matrix materials [10]. To deposit fine Au nanoparticles on supports, co-precipitation or deposition-precipitation methods were employed [11], although incomplete washing by water will cause residual Cl$^-$ ions.

Total organic synthesis routes have been widely utilized to synthesize novel materials; these methods have advantages that includes relatively simple procedures that allows for flexibility in introduction of foreign elements, composition control, scalability, and high purity [12]. In this work, we used novel organic deposition-precipitation method by utilizing gold acetate [Au(CH$_3$COO)$_3$] as a Cl-free gold precursor and tetrapropyl ammonium hydroxide as hydrolyzing agent. The aim of this work is to synthesize nanosized Au supported CeZr and Sm modified Au-CeZr catalysts and use the synthesized materials for selective oxidation of benzyl alcohol. This strategy was allowed us to obtain fine nanoparticles of Au, and the mild preparation conditions also lend themselves well to Sm modification. In addition, structural properties of the catalysts were determined using various analytical techniques to correlate the oxidation catalytic activity of the catalysts.

2. Experimental

2.1. Materials

All the reagents were procured from commercial suppliers and used as received. Ce$_{0.5}$Zr$_{0.5}$O$_2$ (Alfa-Asser, UK), gold acetate and samarium acetate and tetrapropyl ammonium hydroxide were purchased from Aldrich, UK. Ethyl alcohol, benzyl alcohol, 99%, benzaldehyde, 99%, benzoic acid, 99% Sigma-Aldrich, decane, HPLC grade, Fisher Scientific, toluene, AR grade, Sigma-Aldrich, UK. Double distilled water was used in the preparation.

2.2. Synthesis of catalysts

The Au deposited CeZr catalysts with different Au loadings (0.1, 0.2, 0.5 and 1.0 wt%) were prepared by novel organic deposition-precipitation route. Calculated amount of commercial Au(OCH$_3$COO)$_3$ powder was dropped into ethanol and sonicated for two hours to form a brown colored solution. Calculated amount of CeZr powder was mixed with ethanoic gold precursor solution under constant stirring and the pH of the contents was adjusted to 10–11 by adding tetrapropyl ammonium hydroxide solution. The stirring was continued for one hour and the excess of the solvent was removed by heating contents at 50 °C. The obtained powders were oven dried at 110 °C for 5 h and finally calcined at 500 °C for 5 h under the flow of air. The catalysts were symbolized as xAu-CeZr, where x = Au loading (0.1, 0.2, 0.5 and 1.0 wt %). The samarium (0.5, 1.0, 2.0 and 4.0 wt%) modified 0.5Au-CeZr catalysts were prepared by incipient-wetness impregnation of calcined 0.5Au-CeZr powder with solution of samarium acetate (99.9%, Acros) in ethanol: water mixed solvent (70%:30%). A sample containing only 2 wt.% of Sm over the CeZr support was also prepared for the sake of comparison. After the impregnation process, the Sm containing catalysts were treated as gold deposited samples. The samples were symbolized as xSm-0.5Au-CeZr, where x = Sm loading (0.5, 1.0, 2.0 and 4.0 wt%).

2.3. Characterization of catalyst samples

The X-ray diffraction patterns of samples were obtained using Philips PW1700 diffractometer. A Cu Kα radiation and graphite monochromator with automatic divergent slit were utilized to conduct the XRD analysis. The obtained XRD patterns were compared with standard JCPDS files. The crystallite size of CeZr and Au crystallites were calculated from major reflections of CeZr and Au phases using the Scherrer equation. Scanning electron microscopy (SEM) images of the samples obtained using JEOL JSM840 A instrument (JEOL, Japan). TEM analysis of the samples was performed using Philips CM200FEG microscope equipped with a field emission gun operated at 200 kV. High-resolution images with a pixel size of 0.044 nm were taken with a CCD camera.

DRIFT spectra of calcined samples and pyridine adsorbed samples were collected using Perkin-Elmer Spectrum 100 FTIR spectrometer. The DRUV-*vis* reflectance spectra of the samples were collected using Thermo-Scientific evolution spectrophotometer conjugated with an integrating sphere in the wavelength range of 200–800 nm. N$_2$-physisorption measurements for synthesized samples were carried at −196 °C using ASAP 2010 Micromeritics Instrument. Specific surface area (S$_{BET}$) of the samples were determined by applying the BET equation. The average pore diameter was calculated by applying the BJH method. The X-ray photoelectron spectra of the samples were obtained using Thermo Scientific Escalab 250 Xi XPS instrument using Al Kα X-rays. The C1s peak binding energy was used for the correction of peak shift due to charge compensation. The reducibility of the catalysts was determined by an H$_2$-temperature-programmed reduction using CHEMBET-3000 instrument (Quantachrome, USA). Typically, a sample of 50 mg was first pretreated with helium gas at 120 °C for 2 h, and then the temperature of the sample brought to 30 °C and subsequently the gas flow was switched from helium to H$_2$ gas and the temperature of the sample raised from 30 °C to 700 °C with heating rate of 10 °C min^{-1}. The response from the thermal conductivity detector were recorded to obtain H$_2$-TPR patterns of the samples.

2.4. Oxidation of benzyl alcohol

The benzyl alcohol oxidation experiments were conducted in a three-necked round-bottomed flask equipped with a reflux condenser. The reactions were performed at different reaction temperatures (precisely controlled oil bath) under atmospheric pressure. For typical oxidation reaction, benzyl alcohol (50 mmol) and 0.05 ml decane (use as external standard) was added with 0.1 g of catalyst. The resulting mixture was stirred at selected reaction temperature with a stirring speed of 500 rpm under 1 atm of O$_2$. Liquid samples were taken from the round-bottomed flask for every 30 min and analyzed by gas chromatography GC (HP-6890) equipped with FID and HP-5 capillary column. The benzyl alcohol conversion was calculated based on the benzyl alcohol remained in the product solution after particular reaction time. The selectivity to the benzaldehyde was calculated as the amount of benzaldehyde divided by a number of total products and multiplied by 100.

3. Results and discussion

3.1. Powder X-ray diffraction

Powder XRD patterns of bare CeZr support and gold supported CeZr samples are shown in Fig.1. The XRD pattern of the pure CeZr support is in accordance with the pattern presented for Ce$_x$Zr$_{1-x}$O$_2$ solid solution [13].

Characteristic XRD peaks attributed to (111), (200), (220), (311), (222), (400), (331) and (420) planes of fluorite-type cubic structured Ce$_x$Zr$_{1-x}$O$_2$ were observed in CeZr and gold supported CeZr samples [14]. The XRD peak positions and intensities of Au deposited CeZr samples are almost same as bare CeZr sample [Fig. 1 (A)], which is an indication that CeZr crystalline structure is intact without changing its size after Au deposition. Absence of Au diffraction peaks were observed for the 0.1Au-CeZr and 0.2Au-CeZr samples indicating that the size of gold particles might be under the X-ray detection range (< 5 nm) [15]. In contrast, presence of small diffraction peak at 2θ = 38.2° [JCPDS