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Gold nanoparticles on mesoporous Cerium-Tin mixed oxide for aerobic oxidation of benzyl alcohol

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ABSTRACT

In the era of sustainable chemistry the development of nanocatalysis has drawn special attention. Here we report the preparation of nanocrystalline, mesoporous cerium-tin oxide solid solutions and tested for selective oxidation of benzyl alcohol, cinnamyl alcohol, 4-methylbenzyl alcohol, 2-octanol, and geraniol using molecular oxygen as an oxidant. Among different mesoporous supports with Ce/Sn compositions (98/2, 95/5, 90/10 and 80/20, the highest activity was found for the Ce-Sn mixed oxide (Ce/Sn = 95/5) supported gold nanoparticles. The microkinetic study shows that there was no mass transfer limitation in three phase catalytic system. The supports and the corresponding gold catalysts were extensively characterized by N_2 physisorption, XRD, H_2-TPR, NH_3-TPD, TEM, XPS, RAMAN and XAFS techniques. The nanocrystalline solid solution of $Ce_xSn_{1-x}O_2$ was detected by XRD analysis. The presence of oxide vacancy was confirmed by XPS and RAMAN studies. The reducibility of Ce-Sn mixed oxide support increased upon gold deposition which was confirmed by H_2-TPR techniques. The TPD study indicates the alteration of acid-basic sites of the CeO_2 oxide upon incorporation of tin and gold nanoparticles. The cooperative role between the gold species and the ceria-tin support has been observed while correlating the catalytic activity results with the characterization studies.

1. Introduction

Selective oxidation of organic compounds plays a prominent place in both the science of catalysis and catalysis-based modern chemical industry. This reaction provides the easiest route for functionalization of the starting compound e.g. biomass to fine chemicals. Among different reaction selective oxidation of benzyl alcohol has got a special attention as benzaldehyde is a valuable compound for different use e.g. perfumery, cosmetics, food, agrochemicals and pharmaceutical industries [1,2]. It is commercially produced as a by-product of the oxidation of toluene to benzoic acid or by the hydrolysis of benzal chloride. However, the benzaldehyde selectivity was less in first process and the second process provides benzaldehyde with trace contamination from chlorine which is not acceptable in perfumes and pharmaceuticals. Thus, selective oxidation of benzyl alcohol to benzaldehyde is more challenging [3].

Ceria and metal doped ceria are well-known materials with important applications in catalysis, solar cell, fuel cells etc. Its usefulness derives from the high oxygen storage capacity (OSC), which is related to the facile Ce^{3+}/Ce^{4+} redox cycle [4]. The oxygen vacancies which are generated by using dopants [5] of lower valent cations to the ceria lattice are known to improve its catalytic activity in oxidation reactions [6].

Gold support interaction through surface oxygen vacancies improves the benzyl alcohol oxidation [7]. Density functional theory calculations (DFT) showed there was a strong integration between gold and oxygen vacancy on CeO_2 surfaces [8]. These works revealed that well dispersed Au clusters nucleate mainly on the oxygen vacancies in reduced CeO_x surface, which facilitate the reactivity of the catalyst.

The development of mesoporous non-silicious oxides needs to be cultivated extensively as easy diffusion of reactants and products lead to high catalytic activity for several reactions [9,10]. Despite of several reports emphasizing the role of Lewis acidic sites and

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population of Ce^{3+} for benzyl alcohol oxidation reaction, there is still a lack of consciousness on those aspects in the case of doped oxides. The unsolved issue is the (1) oxidation state of Ce^{3+} (2) role of oxygen vacancies (3) iconicity/covalency for metal oxygen bond (4) surface redox and acid-base properties of the doped ceria surface. In some of our recent studies on doped mesoporous ceria material synthesized by using triethanolamine/water mixture could effectively correlate the physicochemical property with the catalytic activity for benzyl alcohol oxidation reaction using molecular oxygen [6]. It was observed that apart from redox property the acid-base property of the doped ceria oxide play an important role towards the catalytic activity [11]. Among several dopant cations e.g. Ba^{2+}, Ca^{2+}, Mg^{2+}, Sm^{3+} are of bigger size compared to Ce^{4+} ion. Therefore an investigation incorporating smaller size metal cation in the IV oxidation state to the CeO_2 will be an interesting study from the fundamental approach.

Tin, though not a transition metal, it has similar redox chemistry as ceria. Tin oxide is useful in sensor, energy storage, catalyst support, photocatalysis etc [12,13]. Most of these applications are based on the acid-base and/or redox properties of stania [11]. Therefore we aim to investigate the role of equivalent and smaller size of Sn^{4+} cation incorporated to the CeO_2 lattice which might change the physicochemical properties of nanocrystalline mixed oxide solid solution [14]. We have prepared $Ce_xSn_{1-x}O_2$ with different Ce/Sn compositions 98/2, 95/5, 90/10 and 80/20 mixed oxide catalysts on which gold was deposited by deposition-precipitation method. For simplicity, in case of support materials are denoted by C/S; where C: cerium and S: tin respectively; and gold supported catalysts as Au-C/S throughout the text. The catalytic activity was evaluated for benzyl alcohol oxidation reaction using molecular oxygen as an oxidant. After screening the catalytic activity the selected catalysts were characterized by SEM-EDS, BET surface area and porosity measurement, XRD, HRTEM, STEM-EDS, RAMAN, XPS, XAFS, TPR and TPD techniques. The results are quite promising as it demonstrates the dual role of tin and gold nanoparticles towards the catalytic activity of aerobic benzyl alcohol oxidation reaction.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of tin-Ceria mixed oxide support

Mixed tin-ceria oxides were prepared by the non-hydrothermal sol-gel method [6]. In brief, a solution of $Ce(NO_3)_3{\cdot}6H_2O$ [>99%; Aldrich) was added to triethanolamine (TEA) [>99%; Acros] under stirring at room temperature. $SnCl_2{\cdot}2H_2O$ [>99%; Merck] was added to the solution under stirring. The resulting mixture was stirred for 10 min and tetraethylammonium hydroxide [TEAOH; 20% aqueous solution; Merck] was added dropwise. In case of C/S = 95/5 mixed oxide, the final gel had a composition of TEA:Ce:H_2O:Sn:TEAOH = 0.2:0.095:1.1:0.005:0.1. The gel was aged for 24 h under stirring and then dried at 110 °C for 24 h. The final material was obtained by calcination at 700 °C for 10 h under static air atmospheric conditions (ramp rate 1 °C/min). The EDX spectra with peaks of Ce, Sn and O elements of the catalysts are shown in **Fig. S1** and Table **S2** (Supporting Information).

Deposition of gold on Tin-Ceria mixed oxide support: Gold nanoparticles were deposited on the support by the previously reported procedure [6]. Typical 150 mL deionized water was taken in a beaker and required amount of $HAuCl_4.3H_2O$ (0.053 g for 3.5 wt% of nominal catalyst gold loading) was added to it. Then the solution was heated to 70 °C from the ambient temperature. The pH was raised to 7.0 by adding aqueous 0.1 M NaOH (or 0.1 M Na_2CO_3) solution drop-wise at 70 °C. Afterwards, the support material (0.75 g) was added and the whole content was stirred for 1 h. Finally, the material was filtered off, washed with water (20 mL) and dried in vacuum for 12 h at ambient temperature and calcined at 300 °C for 4 h with temperature ramp 1 °C/min in muffle furnace at static air atmosphere.

Urea hydrolysis method: The catalyst was prepared by deposition-precipitation with urea (DP-urea). Typically, a solution of $HAuCl_4$ (0.053 g for 3.5 wt% of nominal catalyst gold loading) was dissolved in 150 mL deionised water followed by the addition of urea (1.08 g). The support material (0.75 g) was then added and the suspension was stirred and heated to 80 °C for 16 h in dark in a closed container. After filtration, obtained solid was washed with distilled water (near about 30 mL) and dried under vacuum at 5 °C for 12 h. The final catalyst was obtained after calcinations under air at 300 °C (1 °C/min ramp) in a muffle furnace at static air for 4 h.

2.2. Catalyst characterization

2.2.1. Inductively coupled plasma-Optical emission spectroscopy (ICP-OES)

An inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XDL, Thermo Jarrel Ash) was used to determine the concentration of gold ions in the aqueous solutions of various gold supported catalysts.

2.2.2. X-ray diffraction (XRD)

XRD patterns were recorded on a D8 ADVANCE (BRUKER AXS, Germany) diffractometer using CuKα radiation with parallel beam (Gobel Mirror). Peaks are identified by the search match technique using DIFFRAC^{plus} software (BRUKER AXS, Germany) with reference to the JCPDS database. The software TOPAS 3.0 from Bruker AXS (2005) was used for refinement of the diffraction peak (111) located at $2\theta = 28.68°$ to determine the average crystallite size, by employing the integral breadth, $_{\beta i}$ (= $\lambda/L_{Vol}Cos\theta$) proposed by Balzar et al. [15].

2.2.3. Temperature programmed reduction (TPR) and temperature programmed desorption (TPD)

TPR and TPD profiles of the catalysts were obtained with Chemisorb 2720 (Micrometrics, USA) equipped with a TCD detector. The H_2-TPR profiles were obtained by reducing the catalysts by a gas mixture of 10% H_2 in Ar with a flow rate of 20 mL/min, while the temperature was increased from ambient to 700 °C at a rate of 10 °C/min. Hydrogen consumption in the TPR peak area was evaluated by the peak area of the CuO TPR calibration. NH_3-TPD was carried out by heating the catalyst under He flow starting from room temperature to 350 °C for 30 min. The dried catalyst was cooled to ambient temperature. The NH_3 uptake on the catalyst surface took place when the gas flow was changed to 4% NH_3 in He. The NH_3-TPD profile was obtained by a temperature-programmed desorption under He with a flow rate of 20 mL/min from ambient temperature to 1000 °C at a rate of 10 °C/min. The amounts of NH_3 desorbed in the TPD peak area were evaluated by comparing with a calibration graph which was obtained by measured pulses of NH_3 in a flow of He.

2.2.4. BET surface area and porosity measurement

The nitrogen adsorption-desorption isotherm of the sample were measured at liquid nitrogen temperature on an Autosorb-1C-TPD (Quantachrome) at −196 °C. Pre-treatment of the samples was done at 200 °C for 3 h at reduced pressure. The surface area was determined from the isotherm by use of the Brunauer-Emmett-Teller (BET) equation. Pore size distributions were calculated using the NLDFT method using the cylindrical pore approximation.