Silver supported on hierarchically porous SiO_2 and Co_3O_4 monoliths: Efficient heterogeneous catalyst for oxidation of cyclohexene

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ABSTRACT

This study describes silver (Ag) nanoparticles supported on hierarchically porous SiO_2 and Co_3O_4 monoliths and the use of these materials as heterogeneous catalysts for the oxidation of cyclohexene. Structural characterization of these materials was carried out by various techniques including scanning electron microscopy (SEM), N_2 adsorption, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Characterization results revealed that Ag nanoparticles were incorporated into hierarchically porous SiO_2 and Co_3O_4 without significantly affecting the structures of the supports. The oxidation of cyclohexene was investigated for hierarchically porous Ag/SiO_2 and Ag/Co_3O_4 monoliths and powdered forms of the catalysts using H_2O_2 as oxidant. Detailed parameters including the effect of temperature, oxidant, catalyst loading, and substrate to oxidant ratio were thoroughly studied. The catalyst was found to be stable and could be reused several times without affecting its catalytic activity under the optimized reaction conditions.

1. Introduction

There has been great interest during the past decade in improving heterogeneous catalysts by controlling the surface chemistry, crystal structure and shape, size, and by selection of suitable supports. In many cases enhanced catalytic activity can be obtained from nanomaterials due to their large surface area to volume ratio [1]. The catalytic activity of nanoparticles can be optimized with the use of supports that also make separation of the catalyst from the products much simpler as well as allowing for continuous production [2,3]. Metal containing metal oxide supports are used as catalysts in all fields of heterogeneous catalysis, including oil refining, fine chemical synthesis, pharmaceutical industry, and in production of pesticides, plant protection agents, epoxy paints, and rubber promoters [4]. Finding new catalysts remains highly desirable, particularly to address the increasing demand for sustainable and environmentally benign chemical feedstocks and processes [5–9]. Oxidation is one such important process that leads to a number of critical intermediates. Although homogeneous catalysts have higher activity in oxidation reactions, homogeneous catalytic systems have significant drawbacks in catalyst recovery and product separation. Therefore, heterogeneous catalyst systems with high activity, stability and reusability are of interest. In particular, the development of more active and selective heterogeneous catalysts for the epoxidation of olefins is an attractive topic.

In general, epoxides can be prepared by the oxidation of the corresponding alkenes using an oxidant in the presence of metal and metal oxide catalysts. The use of heterogeneous catalysts is complemented by the use of continuous processes, particularly in the use of microreactors [10–15], which allow effective reaction optimization and production of small quantities of product. In such systems high accessible surface area is desirable in giving higher throughput. A particularly effective approach is hierarchically porous materials in which networks of mesopores (diameter 2–50 nm) are connected by macropores (micrometer diameters) [16–22]. Such materials have recently been explored for use as monolithic microreactors in which a monolithic piece of the hierarchically porous material serves as the reactor [23–27]. For use in a continuous process the catalyst needs reasonable activity to enable a sufficient level of conversion to occur in a time scale compatible with a continuous process. To the best of our knowledge there has been no report of a monolithic microreactor for carrying out an epoxidation as a continuous process.

This paper reports the first steps in developing such a catalyst. The aims of the present study are to (1) synthesize Ag supported on hierarchically porous monoliths of SiO_2 and Co_3O_4, and to optimize the Ag material for cyclohexene oxidation, (2) investigate the catalytic performance of the prepared catalysts in the selective

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epoxidation of cyclohexene, in solution phase, and (3) determine the impact of using a whole monolith as catalyst compared to using the powdered form of the catalysts.

2. Experimental

2.1. Materials

All chemicals used were commercially available and used as received. Tetraethylorthosilicate (TEOS, 96%), polyethylene glycol 35000 (PEG 35000 g/mol), cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$], potassium hydroxide (KOH), 30% nitric acid (HNO_3), ammonium hydroxide (NH_4OH), methanol, silver nitrate ($AgNO_3$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), hydrogen peroxide (H_2O_2, 30% v/v), *tert*-butyl hydroperoxide (TBHP, 98%), acetonitrile and dichloromethane (DCM, 98%) were obtained from Sigma-Aldrich, St Louis, MO, USA. Octadecyltrimethylammonium bromide ($C_{18}TAB$) was obtained from Genscript, USA. The assay of all the chemicals was >99% unless stated otherwise.

2.2. Synthesis of SiO_2 monoliths

The SiO_2 monoliths were synthesized according to the procedure described by Sayler et al. [28]. In a typical synthesis, Tetraethylorthosilicate, 30% HNO_3, deionized (DI) water, polyethylene glycol, and octadecyltrimethylammonium bromide were mixed in a 250 mL beaker at a molar ratio of 1:0.26: 14.5:5.5 × 10^{-4}:0.14, respectively. The resulting sol was transferred to molds and allowed to gel at 40 °C for 24 h, followed by treatment of the gel with 1 M NH_4OH at 90 °C for 12 h to increase the stability of the monoliths. The resulting monoliths were rinsed with DI water, three times with acetone and dried for 3 days at 40 °C. Finally, the monoliths were calcined in air at 550 °C for 5 h with a heating rate of 1 °C/min.

2.3. Synthesis of Co_3O_4 monolith replica

The fully reproducible nanocrystalline Co_3O_4 replicas exhibiting hierarchically mesoporous structures were synthesized by a nanocasting method using the SiO_2 monoliths as templates as reported earlier [28]. The SiO_2 monoliths were impregnated with 4.5 M solution of $Co(NO_3)_2 \cdot 6H_2O$ by incipient wetness. The infiltrated SiO_2 templates were heated at 150 °C for 8 h under nitrogen (N_2) flow. This was followed by heating the monoliths at 250 °C for 4 h to convert the infiltrated $Co(NO_3)_2 \cdot 6H_2O$ to Co_3O_4. The infiltration, heating, and decomposition processes were repeated three times to ensure the optimum filling of mesopores of the SiO_2 templates. The SiO_2 was subsequently etched using 4 M KOH solution, followed by rinsing with methanol and DI water to ensure complete removal of residual hydroxide.

2.4. Synthesis of Ag supported on the SiO_2 and Co_3O_4 catalysts

Synthesis of Ag nanoparticles supported on the SiO_2 and Co_3O_4 monoliths was performed by infiltrating 0.1 M $AgNO_3$ into SiO_2 and Co_3O_4 monoliths, separately under vacuum at room temperature (RT). The impregnated monoliths were dried at 40 °C for 8 h. Finally, the reduction of the $AgNO_3$ salt to metallic Ag was performed overnight under $N_2H_4 \cdot H_2O$ vapors at 35 °C in a closed container containing the monoliths and a beaker of $N_2H_4 \cdot H_2O$. The resultant catalysts are named as Ag/SiO_2 and Ag/Co_3O_4. The properties of these new catalysts were compared with the Ag supported on monolithic SiO_2 and Co_3O_4 catalysts reported in our previous work in which the reduction of the $AgNO_3$ salt to metallic Ag was performed under ethylene glycol vapors at 160 °C [26]. These catalysts will be denoted as Ag/SiO_2-EG and Ag/Co_3O_4-EG. Powdered forms

of the catalysts were prepared by grinding the monolithic form into powder. For the hydrazine reduced catalysts the suffixes '-M' and '-P' are used to denote the monolithic and powdered forms of the catalysts respectively. The monolithic forms of the hydrazine reduced Ag catalysts were used for gas sorption analysis and XRD, and the powdered forms for XPS and SEM analysis.

2.5. Catalyst characterization

Scanning electron microscope (SEM) images of all the samples were taken on a JOEL 7000 FE-SEM (Tokyo, Japan) with diode based back-scatter electron detector equipped with an Oxford Energy Dispersive Spectroscopy (EDS) detector for elemental analysis. The amount of Ag loading on the respective supports was determined using the EDS accessory on the SEM JEOL 7000. ImageJ (version: 1.48 v; National Institutes of Health: Bethesda, MD, USA, 1997) was used to carry out the determination of the particle sizes from the SEM images. The Nitrogen (N_2) physisorption measurements were carried out on a Quantachrome Nova 2200e (Boynton Beach, FL) pore size analyzer at −197 °C with He mode to determine the surface area and void volume of the monoliths, respectively. Isotherms were analyzed with Quantachrome NovaWin software version 11.1. Powder X-ray diffraction (XRD) patterns of the monoliths were obtained on a Bruker D8 Discover (Madison, WI) with GADDS (General Area Detector Diffraction System) (wavelength Co Kα, 1.79 Å) and a Hi-Star area detector. The X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos Axis Ultra spectrometer employing unmonochromated Al Kα radiation (1486.6 eV) operated at 15 kV, 20 mA under a pressure below 10^{-9} Pa to evaluate the compositions of each component in Ag/SiO_2 and Ag/Co_3O_4 with analyzer pass energy of 20 eV for elemental scans. Spectra were analyzed by first subtracting a Shirley background and then obtaining accurate peak positions by fitting the peaks using a mixed Gaussian/Lorentzian line shape.

The loading of Ag on the monolithic supports was determined by leaching the silver from the monoliths overnight with aqua regia (concentrated nitric and hydrochloric acids in a 1:3 ratio) and determining the concentration of the Ag ions in the resultant solutions by Atomic Adsorption Spectrometry (Perkin Elmer AAnalyst 400).

2.6. Catalytic tests

The liquid phase oxidation of cyclohexene was carried out in a 25 mL two-necked round bottom flask charged with 1 mmol of cyclohexene, 2 mmol of oxidant, 6 mL of acetonitrile, 0.02 g of catalyst and a magnetic stir bar. The flask was fitted with a reflux condenser and immersed in a thermostatic oil bath at 80 °C. The reaction assembly was placed on a magnetic stirrer and the reaction mixture was stirred vigorously for 24 h. The samples were filtered and analyzed on a Varian GC model CP-3800 equipped with flame ionization detector (FID) and EC-5 column (length 30 m × ID 0.25 mm × film thickness 0.25 μm). Product identification was carried out by injecting authentic samples into the GC and matching the retention times with those of the products formed in the reaction. The catalytic activity was compared to that of previously reported Ag/SiO_2-EG and Ag/Co_3O_4-EG catalysts. The activity of the catalysts was compared using the respective monolithic and powdered forms of the catalysts.

2.7. Catalyst recycle studies

The recycle studies were performed using Ag/SiO_2-P as catalyst and H_2O_2 as oxidant. The recycle reactions were performed using the conditions described in Section 2.5. After 24 h the reaction mixture was cooled and filtered. The residual catalyst was washed with acetonitrile followed by DCM and dried at 30 °C for 4 h. The flask