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ORIGINAL ARTICLE

Gold & silver nanoparticles supported on manganese oxide: Synthesis, characterization and catalytic studies for selective oxidation of benzyl alcohol

Saad Alabbad, S.F. Adil, M.E. Assal, Mujeeb Khan, Abdulrahman Alwarthan, M. Rafiq H. Siddiqui *

Department of Chemistry, College of Science, King Saud University, P.O. 2455, Riyadh 11451, Saudi Arabia

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Abstract Nano-gold and silver particles supported on manganese oxide were synthesized by the co-precipitation method. The catalytic properties of these materials were investigated for the oxidation of benzyl alcohol using molecular oxygen as a source of oxygen. The catalyst was calcined at 300, 400 and 500 °C. They were characterized by electron microscopy, powder X-ray diffraction (XRD) and surface area. It was observed that the calcination temperature affects the size of the nanoparticle, which plays a significant role in the catalytic process. The catalyst calcined at 400 °C, gave a 100% conversion and >99% selectivity, whereas catalysts calcined at 300 and 500 °C gave a conversion of 69.51% and 19.90% respectively, although the selectivity remains >99%.

1. Introduction

The selective oxidation of aromatic alcohols to aldehydes is extremely important owing to the significant role played by aromatic aldehydes such as building blocks for many organic compounds. This area of research, which has been of emphasis for many years now, is still being studied with same fervor, which can be implicit, by the recent reports in the literature. (Chiranjit et al., 2013; Pritchard et al., 2013; Yokoyama et al., 2012; Christopher et al., 2012).

Heterogeneous catalysts using noble metals such as Pt, Ru, Pd and their derivatives have been reported in the literature for the conversion of alcohols to aldehydes using molecular oxygen as an oxidant. (Caravati et al., 2004; Opre et al., 2005; Abad et al., 2005; Enache et al., 2006; Miyamura et al., 2007; Haider et al., 2008; Marx and Baiker, 2009; Dimitratos et al., 2009) Pt-based catalysts have been found to be easily poisoned which make them sensitive and hence can be used only under mild conditions.

* Corresponding author. Tel.: +966 507889048.
E-mail address: rafiqs@ksu.edu.sa (M. Rafiq H. Siddiqui).
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Gold catalysts have also been reported for various organic conversions and are well known for their excellent catalytic performance as a catalyst for a variety of reactions such as Au-supported Pt–Au and thin Pd layers on Au for oxidation of formic acid (Mallat and Baiker, 2004, Huang et al., 2012, Obradović and Gojković, 2013), conversion of CO_2 and CH_4 to acetic acid over the Au-exchanged ZSM-5 catalyst (Panjan et al., 2012), for aerobic selective oxidation of benzylic alcohols (Xie et al., 2012) and bimetallic gold/palladium alloy nanoclusters for Ullmann coupling (Dhital et al., 2012). They have also been extensively reported for oxidation of benzyl alcohol (Alhumaimess et al., 2012; Fang et al., 2011; Miedziak et al., 2011; Dimitratos et al., 2009; Haider et al., 2008; Yang et al., 2008; Pina et al., 2008; Choudhary et al., 2009) and have demonstrated high selectivity toward aldehydes in most of the studies. However, these procedures are not very economical. Nevertheless, the attention received by Ag-based catalyst (Liotta et al., 2001; Nagaraju et al., 2008; Mitsudome et al., 2008; Adam et al., 2008) for the selective oxidation of alcohols in liquid phase is very less. Recently, our group reported the use of nano Ag-doped manganese (Adil et al., 2013) for the oxidation of benzyl alcohol, which shows that silver, could be explored as a potential for catalytic oxidation reactions in the liquid phase.

However, the recent reports of employing bimetallic Au–Ag alloys supported on titania (Bokhimi et al., 2013) for CO oxidation and hydrogenation of esters carried out using Au–Ag/SBA-15 (Zheng et al., 2013) catalyst prompted us to study the synergistic effect between Au and Ag for an improved and more durable catalyst. Hence, in continuation of our previous efforts to explore new and efficient catalyst for the selective liquid phase oxidation of alcohols to aldehydes, we herein report the synthesis of nano-gold and silver particles supported on manganese oxide and their application as catalyst for the oxidation of benzyl alcohol as a model compound.

2. Experimental

2.1. Preparation of gold and silver nanoparticles supported on manganese oxide

To a 500 mL round bottomed flask 180 mL of 0.2 M solutions of manganese nitrate and 10 mL of 0.2 M silver nitrate and 10 mL of 0.2 M $HAuCl_4$ solutions were added. The resulting solution was refluxed to 80 °C, while stirring using a mechanical stirrer. 1 M solution of $NaHCO_3$ was added drop-wise until the solution attained a pH 9. The solution was continued to be stirred at the same temperature for ~3 h and then left for stirring over night at room temperature. The solution was filtered using a Buchner funnel under vacuum and dried at 70 °C overnight. The obtained product was characterized using SEM, TEM and EDAX. The resulting powder was then calcined in air at different temperatures and evaluated for its catalytic activity using benzyl alcohol as substrate and molecular oxygen as oxidant.

2.2. Catalyst characterization

Scanning electron microscopy (SEM) and elemental analysis (Energy Dispersive X-Ray Analysis: EDAX) were carried out using Jeol SEM model JSM 6360A (Japan). This was used to determine the morphology of nanoparticles and its elemental composition. Transmission electron microscopic studies (TEM) were carried out using Jeol TEM model JEM-1101 (Japan), which was used to determine the shape and size of nanoparticles. Powder X-ray diffraction studies were carried out using an Altima IV [Make Regaku] X-ray diffractometer. BET surface area was measured on a NOVA 4200e surface area using a pore size analyzer. Thermogravimetric analysis was carried out using a Perkin–Elmer Thermogravimetric Analyzer 7.

2.3. Performance of the catalyst

In a typical reaction run, 300 mg of catalyst was loaded in a glass flask pre-charged with 0.2 ml (2 mmol) benzyl alcohol with 10 mL toluene as solvent; the mixture was then refluxed at 100 °C with vigorous stirring. Oxygen was bubbled at a flow rate of 20 mL min^{-1} into the mixture, once the reaction temperature was attained. After reaction, the solid catalyst was separated by centrifugation and the liquid samples were analyzed by gas chromatography to evaluate the conversion of the desired product by (GC, 7890A) Agilent Technologies Inc, equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column.

3. Result and discussion

3.1. Catalyst characterization

The synthesized catalyst was characterized, using electron microscopic studies to evaluate the morphology. The scanning electron micrographs (Fig. 1) show that the particles obtained are well defined and are spherical in shape. The effect of calcinations temperature on the catalyst morphology can be studied from the micrographs. From these micrographs it can be seen that the morphology of the catalyst does not change with the calcination temperature and all catalysts appear to have a well-defined spherical shape and similar size. The EDAX analysis of the sample gives an approximate value of percentage composition of the elements present in the synthesized catalyst; the values obtained were close to the composition used in making the catalyst.

The TEM images showed that as the calcination temperature increases, there was an increase in the particles size of the metal nanoparticles (Figs. 2–4). The particle size distribution observed in the TEM images was calculated using the program Image J and plotted in graph (Figs. 2–4), it was confirmed from these graphs that the average size of the particles is ~3 nm, 3.6 nm and 4.4 nm in the catalyst calcined at 300, 400, and 500 °C, respectively. From the TEM images it can be concluded that the small particles observed in the image is from the gold and silver nanoparticles supported on manganese oxide, which appear as bigger square particles in the TEM image.

From the XRD pattern of the catalyst calcined at 300 °C, it was observed that the catalyst is composed of a mixture of trigonal/rhombohedral $MnCO_3$ (ICSD-80867) and orthorhombic silver manganate (ICDD: 01-076-1584). The XRD pattern of catalyst calcined at 400 and 500 °C suggests that the catalyst undergoes phase transition as the calcination temperature increases and the structure changes to higher symmetry, which can be confirmed by the disappearance of