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ORIGINAL ARTICLE

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

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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.

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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

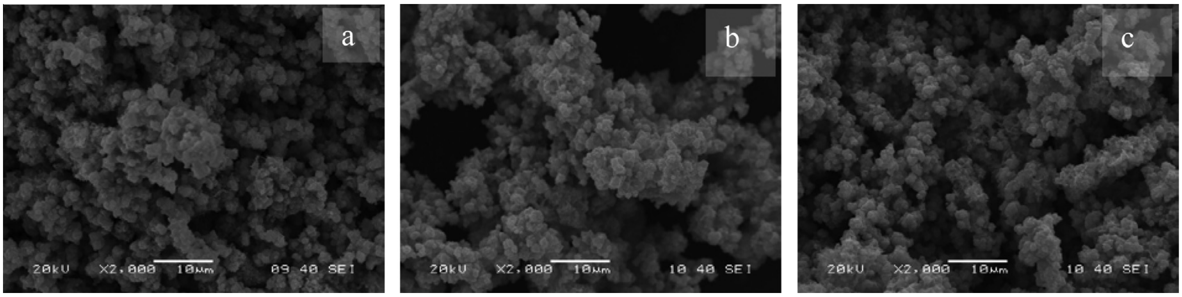

Figure 1 SEM image of the catalyst 5% Ag–MnO_2–5% Au calcined at (a) 300 °C, (b) 400 °C, (c) 500 °C.

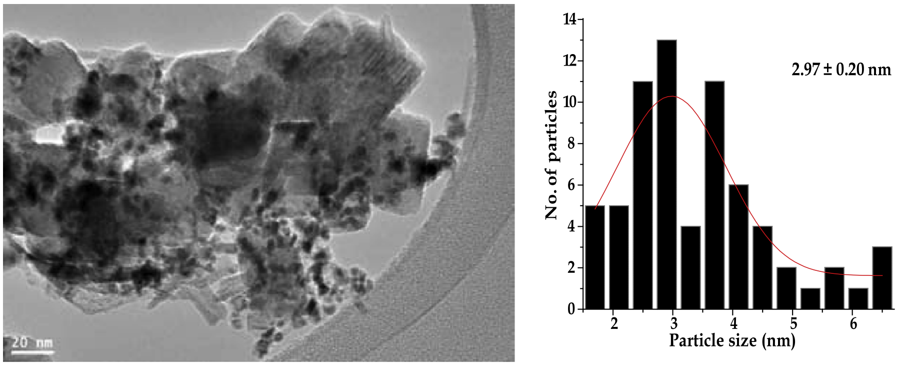

Figure 2 TEM image of 5% Ag–MnO_2–5% Au catalyst calcined at 300 °C.

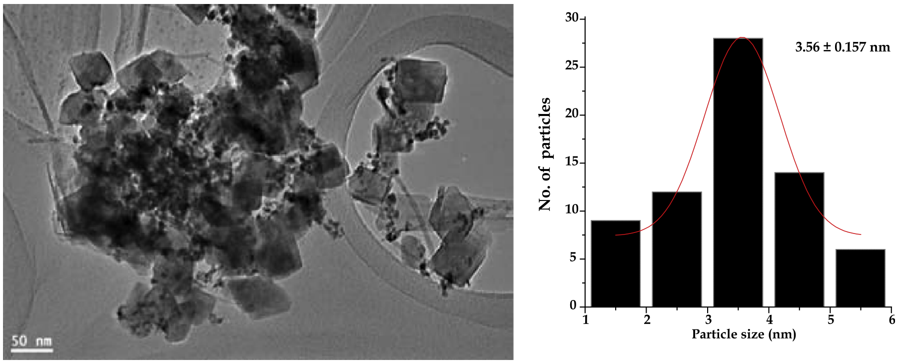

Figure 3 TEM image of 5% Ag–MnO_2–5% Au catalyst calcined at 400 °C.

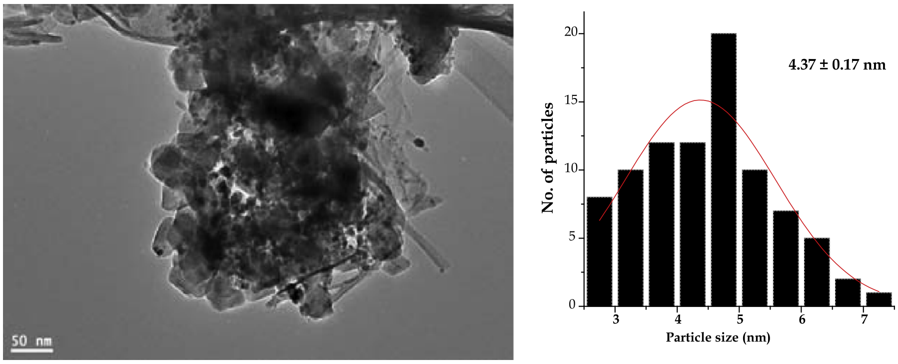

Figure 4 TEM image of 5% Ag–MnO_2–5% Au catalyst calcined at 500 °C.

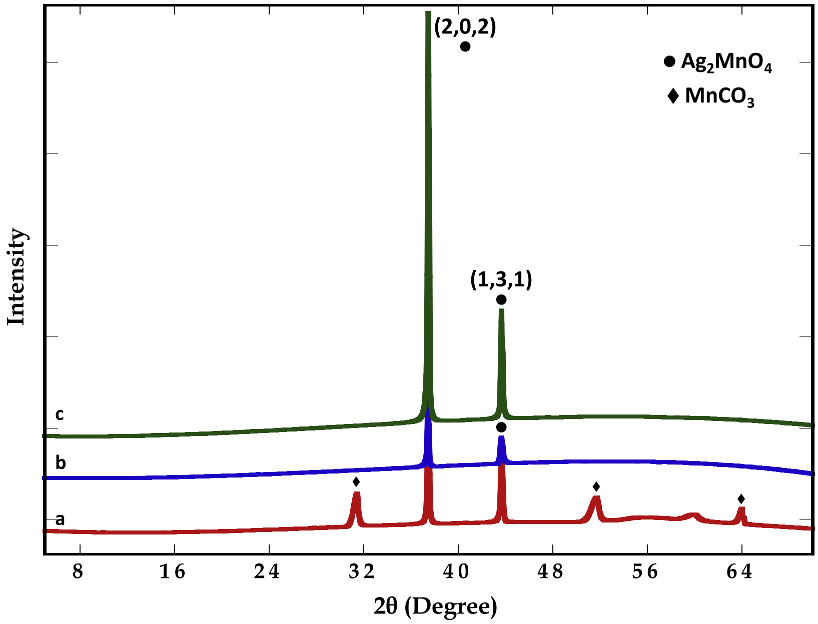

Figure 5 XRD pattern of the 5% Ag–MnO_2–5% Au catalyst calcined at different temperatures (a) 300 °C, (b) 400 °C, (c) 500 °C.

Table 1 Effect of calcination temperature on the catalytic properties of 5% Ag–MnO_2–5% Au catalyst.

Entry	Catalyst	Temperature (°C)	SA ($m^2 g^{-1}$)	Conversion (%)	Selectivity (%)
1	5% Ag–MnO_2	400	31.101	77.31	>99
2	5% Ag–MnO_2–5% Au	300	26.8278	69.51	>99
3	5% Ag–MnO_2–5% Au	400	86.9088	100	>99
4	5% Ag–MnO_2–5% Au	500	48.9591	19.90	>99

Reaction conditions: amount of catalyst-300 mg; reaction temperature-100 °C; oxygen flow rate-20 mL min^{-1}; benzyl alcohol-2 mmol; toluene-10 mL, reaction time-90 min.

the peaks at 31.353°, 56.26°, 59.69°, and 63.93° in 2θ. The indices (202) and (131) are attributed to the orthorhombic arrangement which are identical to silver manganate. The XRD pattern shows well defined diffraction features characteristic to nano crystalline with crystallite size about 7.74 nm calculated by the Debye–Scherrer equation (Fig. 5). The BET surface area analysis is given in Table 1, it can be observed that the surface area is 26.82, 86.90 and 48.95 $m^2 g^{-1}$ for the catalyst calcined at 300, 400, 500 °C, respectively.

The surface area of the catalyst calcined at different temperatures was obtained by BET analysis and it was observed that the catalyst calcined at 400 °C was found to possess highest surface area with 86.90 $m^2 g^{-1}$, while the catalyst calcined at 300, 500 °C, was found to possess surface area of 26.82, and 48.95 $m^2 g^{-1}$, respectively. The results are summarized in Table 1.

3.2. Thermal Stability

The TGA thermogram of the synthesized catalyst is shown in Fig. 6. It was observed from the thermogram of the catalyst calcined at 300 °C that the catalyst is stable up to 415 °C with a very little loss of weight i.e. < 10%, when heating is continued there is a sudden loss of weight by about 25% in the temperature range of about 425–500 °C. The total loss of wt.% observed was about 32% when the catalyst was heated up to 800 °C. This weight loss may be because calcination at 300 °C does not convert the hydroxide and hydroxy carbonate formed by precipitation of the mixed salt into oxide and this substantial weight loss is due to the conversion of hydroxide or hydroxyl carbonate species to metal oxides. In the case of the catalyst calcined at 400 °C, a maximum percentage weight loss of about 14% when heated up to 800 °C was observed, while the catalyst calcined at 500 °C showed a minimum weight loss of about 20%.

3.3. Catalytic evaluation

To investigate the catalytic oxidation properties, the prepared catalyst 5% Ag–MnO_2–5% Au was dried at 70 °C overnight and later calcined at different temperatures such as 300, 400 and 500 °C for 24 h. These catalysts were employed for oxidation of benzyl alcohol carried out in the presence of the synthesized catalyst calcined at different temperatures with toluene as solvent and O_2 gas as a source of oxygen and their effect of the kinetics of the reaction was studied. The reaction was carried out at 80 °C. It was observed that the catalyst 5% Ag–MnO_2–5% Au calcined at 300 and 500 °C displayed lesser catalytic activity than that exhibited by the catalyst calcined at 400 °C. A 100% conversion of benzyl alcohol to benzaldehyde

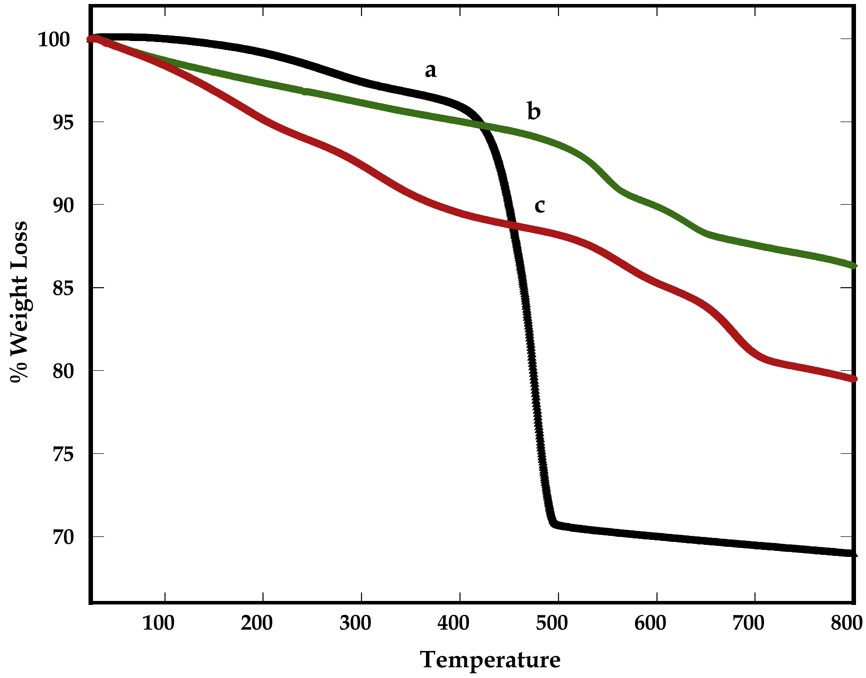

Figure 6 Thermal stability pattern of the 5% Ag–MnO_2–5% Au catalyst calcined at different temperatures (a) 300 °C, (b) 400 °C, (c) 500 °C.

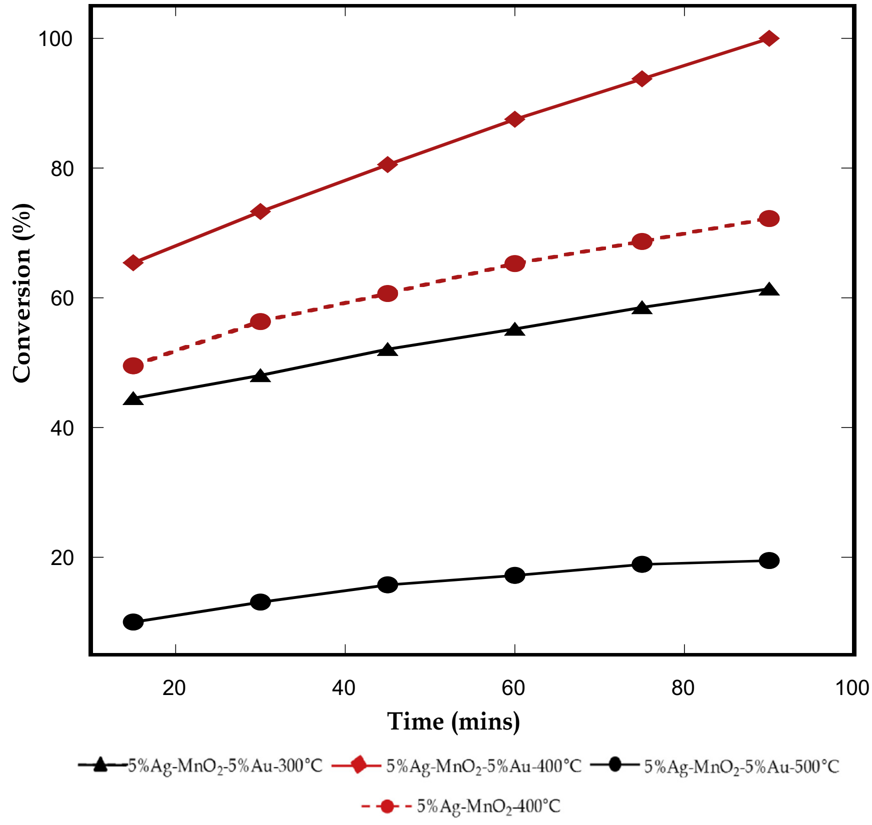

Figure 7 Graphical representation of time on line vs conversion (%).

was observed in the case of the catalyst calcined at 400 °C while catalysts calcined at 300 and 500 °C gave a conversion of 69.51% and 19.9%, respectively under similar conditions.

This catalytic performance result obtained correlated to the surface area values obtained from the BET analysis of the sample. The catalyst with the highest surface area among the synthesized 5% Ag–MnO_2–5% Au catalyst was the one calcined at 400 °C, it yielded a 100% conversion product. While the catalyst calcined at 300 °C and 500 °C have a lower surface area and yield a lower conversion product. Hence it can be understood that the calcination temperature of the catalyst has profound influence on the catalytic performance. Interestingly, the result obtained was compared with the earlier results reported by our group wherein the 5% Ag–MnO_2 is employed as a catalyst for the oxidation of benzyl alcohol. It gave a 77.31% conversion product, from which it can be confirmed that the addition of gold nanoparticles to the catalyst indeed enhances the catalytic performance of the synthesized catalyst. (Adil et al., 2013) The results are summarized in Table 1 and graphical illustration is given in Fig. 7.

In order to understand the effect of catalyst on the solvent used, which is toluene in the present study, a blank reaction was carried out without the substrate benzyl alcohol using 5% Ag–MnO_2–5% Au as catalyst and no oxidation product was observed under these conditions. Hence it can be concluded that the conversion product benzaldehyde obtained is from the catalytic conversion of benzyl alcohol and not from the oxidation of toluene.

4. Conclusions

A novel series of nano-gold and silver-doped manganese oxide catalyst were synthesized and were evaluated for their catalytic activity. They have displayed a very high activity giving a 100% conversion product for the oxidation of benzyl alcohol using molecular oxygen as a source of oxygen. A strong correlation between calcination temperatures and the chemical kinetics of the reaction was observed, and it was confirmed that calcination temperature plays an important role forming an active and durable catalyst. It can also be concluded that the addition of gold nanoparticles will surly increase the catalytic efficiency of the catalyst. Based on the finding of this study it can be said that the synthesized catalysts are excellent for selective oxidation of aromatic alcohols and can be taken up as a catalyst to study the oxidation reactions of various other organic compounds.

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