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Synthesis of bioactive compounds, oxidation catalysts and spherical nanoparticles

NANO-GOLD SUPPORTED NICKEL MANGANESE OXIDE: SYNTHESIS, CHARACTERISATION AND EVALUATION AS OXIDATION CATALYST

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ABSTRACT

Gold nanoparticles supported on nickel manganese mixed oxide were synthesised by co-precipitation method. The catalytic properties of these materials were investigated for the oxidation of benzyl alcohol using molecular oxygen as an oxidant. It was observed that the calcination temperature and the size of the particle play an important role in the process.

Keywords: gold nanoparticles, nickel manganese mixed oxides, oxidation, benzyl alcohol.

AIMS AND BACKGROUND

Aromatic aldehydes play an important role in the synthesis of materials of fine chemicals such as fragrances or flavourings agents that are obtained either by catalytic hydrogenation of carboxylic acids into corresponding aldehydes[1–3] or by the oxidation of alcohols into corresponding aldehydes[4,5]. The hydrogenation of acids to aldehydes is an energy-consuming process and not very selective. Nevertheless, selective oxidation of alcohols to aldehydes can be environmentally friendly as this can be achieved by using molecular oxygen or hydrogen peroxide as an oxidant.

Among the plethora of oxidation catalysts, manganese complexes have been extensively used for oxidation reactions such as epoxidation of olefins[6–10], oxygenation of saturated[11] and oxidation of aromatic hydrocarbons[12], as well as oxidation of alcohols[13–15] by peroxides and other reagents[16–18]. They have been combined with different elements and have been tried as catalyst for oxidation of alcohols such as

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Co, Cr, Fe, Mg and Ni. Nickel-modified manganese oxide has been reported for the oxidation of methanol in fuel cells[19].

The present investigation deals with gold catalysts supported on nickel-manganese oxide and its evaluation for selective oxidation of benzyl alcohol to benzaldehyde.

EXPERIMENTAL

Preparation of gold supported on nickel manganese oxide. 95 ml of 0.2 M solutions of nickel nitrate and manganese nitrate were mixed in a round bottomed flask, to it were added 10 ml of 0.2 M solution of $HAuCl_4$ solution. The resulting solution was heated to 80°C, while stirring using a mechanical stirrer and 1 M solution of $NaHCO_3$ was added drop wise until the solution attained a pH = 9. The solution was continuously stirred at the same temperature for about 3 h and then left on stirring overnight at room temperature. The solution was filtered using a Buchner funnel under vacuum and dried at 70°C overnight. The product obtained was characterised using SEM, TEM and EDAX. The resulting powder was then calcined at different temperatures and was evaluated for its oxidation activity using benzyl alcohol as starting material.

Catalyst testing. In a typical reaction run, 300 mg of catalyst were loaded in a glass flask pre-charged with 0.2 ml (2 mmol) benzyl alcohol with 10 ml toluene as a solvent; the mixture was then heated to 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 analysed by gas chromatography to evaluate the conversion of the desired product by (GC, 7890A) Agilent Technologies Inc., equipped with a flame ionisation detector (FID) and a 19019S-001 HP-PONA capillary column.

Catalyst characterisation. Scanning electron microscopy (SEM) and elemental analysis (energy dispersive X-ray analysis: EDAX) were carried out using Jeol SEM model JSM 6360A (Japan) in order to determine the morphology of nanoparticles. Transmission electron microscopy (TEM) was carried out using Jeol TEM model JEM-1101 (Japan) to determine the shape and size of nanoparticles. Powder X-ray diffraction studies were carried out using an Altima IV Rigaku, X-ray diffractometer.

RESULTS AND DISCUSSION

Catalyst characterisation. The synthesised catalyst was characterised by electron microscopy to evaluate the morphology and particle size of the catalyst. The scanning electron microscopy (Figs 1–3) shows that the particles obtained are well defined and are spherical in shape. There is no effect of calcinations temperature on the catalyst morphology, except of slight increase in the size of particles with increasing calcination temperature. The TEM images show that the particles size of the gold is below 10 nm and they are uniformly dispersed on the nickel manganese oxide support and the support also is in nanometer range (Fig. 4). The powder X-ray diffraction pattern

shows the crystalline nature of the catalysts and is compared with the known oxide phases. The broad peaks in the XRD pattern further confirm the nanoparticles nature of these catalysts, which was confirmed by calculation of crystallite size using the Scherrer equation. The particles sizes were found to be 10.8, 7.2, and 2.2 nm for the catalyst calcined at 300, 400, and 500°C, respectively (Fig. 5).

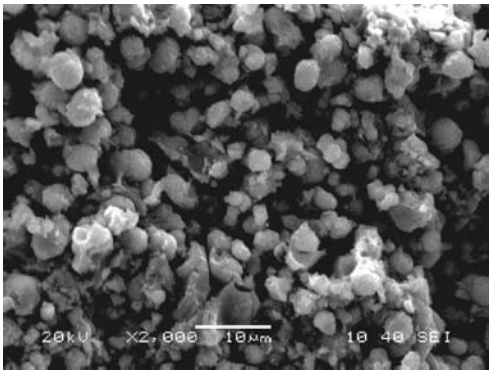

Fig. 1. SEM of the catalyst calcined at 300°C

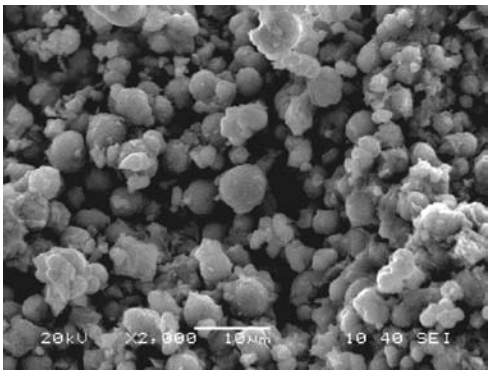

Fig. 2. SEM of the catalyst calcined at 400°C

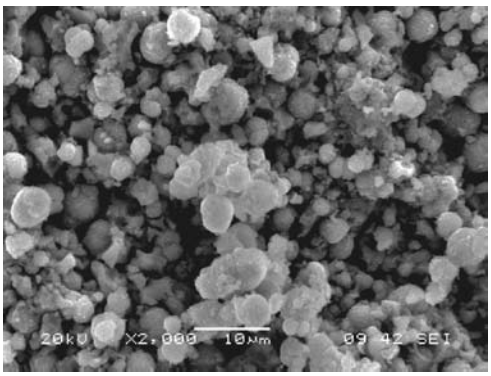

Fig. 3. SEM of the catalyst calcined at 500°C

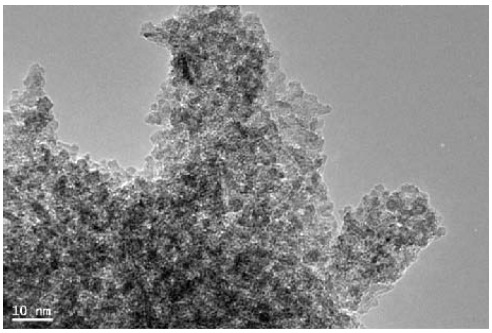

Fig. 4. TEM of the catalyst calcined at 300°C

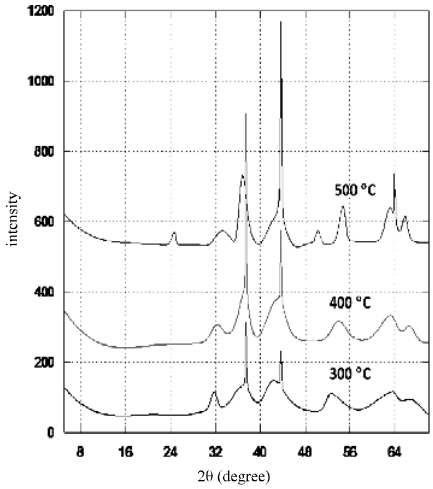

Fig. 5. XRD pattern of the catalyst at different temperatures

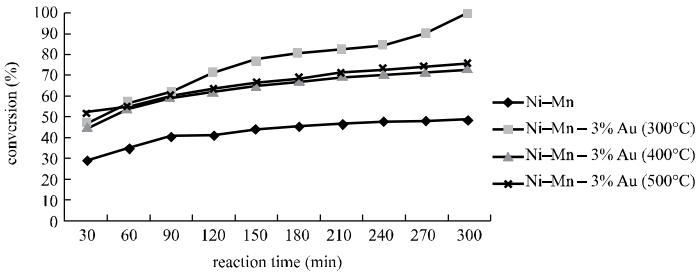

Fig. 6. Oxidation of benzyl alcohol using catalysts calcined at different temperatures depicting the kinetics of the reaction

Catalytic properties. To investigate the catalytic oxidation properties of the prepared catalysts the oxidation of benzyl alcohol was carried out in the presence of the synthesised catalyst using toluene as a solvent. The reaction was carried out at 100°C, while passing O_2 gas as a source of molecular oxygen. It was observed that there is a

decrease conversion of benzyl alcohol to benzaldehyde as the calcination temperature of the catalyst is increased. In order to confirm the role of gold acting as a promoter to the catalytic process, a reaction was carried out using Ni–Mn oxide without gold as a catalyst and it was observed that the conversion to the desired product falls drastically to 48% when compared to 100% conversion obtained by using the catalyst with gold calcined at 300°C. A conversion of 73 and 76% was observed for the catalyst calcined at 400 and 500°C, respectively.

CONCLUSIONS

Nanogold-supported nickel manganese oxide showed high activity and stability for the oxidation of benzyl alcohol using molecular oxygen as a source of oxygen. A synergistic effect 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 be assumed that this catalyst can be further used for the evaluation of its oxidative property for the synthesis of other important aromatic and aliphatic aldehydes.

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