



# Synthesis, characterization, and reactivity of Au/MCM-41 catalysts prepared by homogeneous deposition–precipitation (HDP) method for vapor phase oxidation of benzyl alcohol



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## ABSTRACT

The vapor phase oxidation of benzyl alcohol was investigated over Au/MCM-41 catalysts under aerobic conditions. The catalysts were prepared by homogeneous deposition–precipitation (HDP) method. The physico-chemical properties of the catalysts were investigated by XRD, TEM, BET surface area, CO-chemisorption, and XPS techniques. The influence of metal, nature of the support, the metal–support interactions, the catalytic activity, and stability of the Au/MCM-41 catalysts were investigated. The conversion of benzyl alcohol was increasing with decrease in the size of Au nanoparticles. Au/MCM-41 catalysts with smaller Au nanoparticles had a beneficial effect on the catalytic properties during the oxidation of benzyl alcohol.

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## 1. Introduction

The gold nanoparticles supported on mesoporous oxides are widely employed in the recent past for various oxidation reactions of alcohols to the corresponding carbonyl compounds. It is well established that the catalytic activity of supported gold nanoparticles depend on the particle size and nature of the support. Among the reactions studied, the vapor phase oxidation of benzyl alcohol (PhCH<sub>2</sub>OH) to benzaldehyde (PhCHO) is commercially of importance, since the process is environmentally benign and needs less expensive additives. Conventionally, benzaldehyde is produced as a by-product during the oxidation of toluene (PhCH<sub>3</sub>) to benzoic acid (PhCOOH) or from the hydrolysis of benzyl dichloride. These routes generate a large amount of environmentally hazardous by-products like organic chlorine or benzoic acid. Hence, this limits the usage of benzaldehyde in the cosmetics, pharmaceutical, and flavouring industries [1]. From the commercial point of view, air/molecular oxygen is the favourable choice as the primary oxidant since they produce water as only the by-product [2]. However, the use of air requires the development of newer and novel catalysts in order to achieve higher catalytic

activity under ambient reaction conditions. Many studies have been attempted on supported gold as catalyst in several catalytic applications including selective aerobic oxidation of alcohols such as benzyl alcohol [2–4] and low temperature CO oxidation [5–9]. In order to achieve a high catalytic performance, these catalysts are used in the form of nano-composites where nanoparticles of gold are loaded onto the support materials like activated carbon, metal oxides, and polymers. However, such batch reactions in liquid phase require a long period of time to reach the steady state and also require separation of catalysts from the products. From the viewpoint of atom economy and green chemistry, more emphasis has been laid on the vapor phase catalytic oxidation of benzyl alcohol to benzaldehyde [1,4,10–13] since it is solvent free continuous system and provides a high quality of benzaldehyde. Recently, Haruta et al. [3] and Yang et al. [13] have reported that gold catalysts to be more effective in the vapor phase oxidation of volatile alcohols to form the corresponding ketones and aldehydes. Metal catalysts containing supported–Pd, Cu, and Co have been studied for the title reaction. However, their catalytic activities were found to be much lower [12,13] compare to supported gold catalyst.

Among the various routes for the synthesis of Au nanoparticles, the preferred and versatile route is the homogeneous deposition–precipitation (HDP) method. This method has many advantages like usage of simple equipment, better control of pore structures,

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and the availability of higher dispersion of gold particles at lower concentration on the catalyst support [14]. Nano-sized gold particles have been reported to show a better catalytic activity [15–17] compared to the conventional catalysts. The present investigation deals with a direct correlation study between dispersion, metal area and oxidation of benzyl alcohol to benzaldehyde over supported gold nanoparticles. This work has allowed us to draw clear conclusions regarding (i) the quantitative influence of particle composition; (ii) the role of particle size; and (iii) the influence of the support on benzyl alcohol activity. The structural features of Au/MCM-41 catalysts were investigated by XRD, CO-chemisorption, BET surface area, B–J–H pore-size distribution, TEM, and XPS techniques.

## 2. Experimental

### 2.1. Synthesis of MCM-41

The mesoporous MCM-41 was prepared according to the procedure reported elsewhere [18] by using as a source of silica was tetraethylorthosilicate (TEOS, 98%, Aldrich) and cetyl trimethyl ammonium bromide (CTAB, Aldrich, 98%) as a structure-directing agent. In a typical synthesis method 1.01 g of CTAB was dissolved in 30 g of demineralized water at room temperature under vigorous stirring for 1 h. After complete dissolution, 0.34 g of NaOH was added to the above solution and the mixture was stirred for 10 min at room temperature. Following this, 5.78 g of TEOS was added dropwise with vigorous stirring till the addition was complete, then stirring was continued for 4 h. The molar ratios were investigated as 1.0:0.10:0.30:60 TEOS/CTAB/NaOH/H<sub>2</sub>O. The precipitate was aged at 100 °C for 48 h. The solid product was obtained by filtration, washed with demineralized water until the pH 7 and subsequently dried in a hot air oven at 100 °C for 10 h. Finally, the dried sample (mesoporous MCM-41) was calcined at 550 °C for 5 h at a heating rate of 1 °C/min in air to remove the surfactant template.

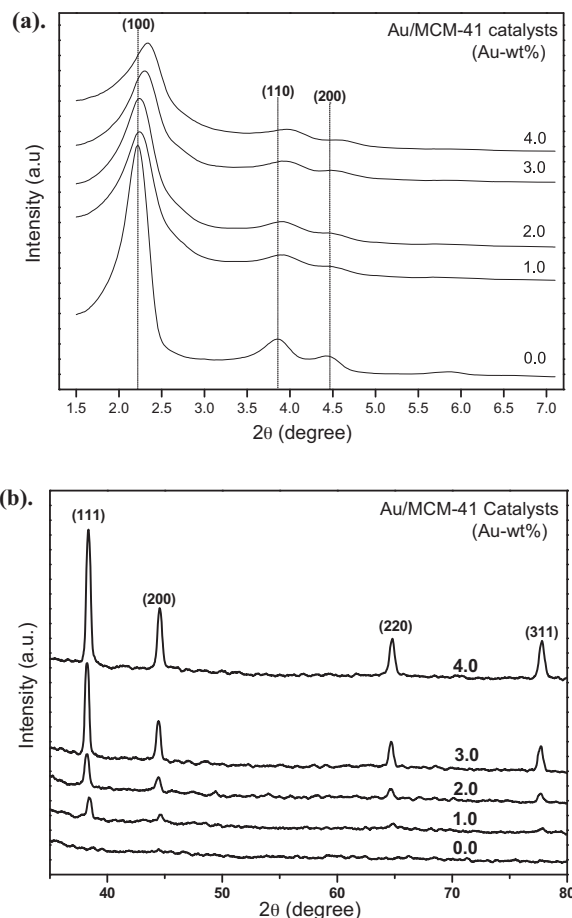
### 2.2. Synthesis of gold catalysts

The Au/MCM-41 catalyst with varying gold loadings were prepared by homogeneous deposition–precipitation (HDP) method using urea as the precipitating agent [14,19]. The mixture of an aqueous solution containing HAuCl<sub>4</sub>·3H<sub>2</sub>O (Sigma–Aldrich, 99.8%, with desired gold loading) and urea was stirred with gradual heating to a temperature upto 95 °C for 6 h. On heating, the urea decomposes to ammonia and hence the precipitation occurs in a homogeneous way in the whole bulk solution as the pH shift towards basic conditions (pH ~6–8). Subsequently, the support (mesoporous MCM-41) was added to the above solution with continuous stirring. The requisite amount of 0.1 M freshly prepared NaBH<sub>4</sub> aqueous solution [20] was added to the above solution so as to precipitate metallic gold nanoparticles on MCM-41 support. The solid product formed was filtered, washed thoroughly with deionized water until the filtrate contained no chloride ions (confirmed with AgNO<sub>3</sub> test) and subsequently dried in hot air oven at 100 °C for 5 h and finally calcined at 400 °C for 3 h in N<sub>2</sub> atmosphere. The EDAX-analysis suggests that the concentration of sodium is present in negligible amount (<0.01%).

### 2.3. Characterization

X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex (M/s. Rigaku Corporation, Japan). X-ray diffractometer using Ni filtered Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) with a scan speed of 2° min<sup>-1</sup> and a scan range of 10–80° for wide angle diffraction at 30 kV and 15 mA. The crystallite size of gold was calculated by using Debye–Scherrer

equation and phase identification with the help of the JCPDS files. The CO-chemisorption measurements were carried out on AutoChem 2910 (Micromeritics, USA) instrument. A 100 mg of the catalyst was pre-treated with helium gas for 1 h at 150 °C. The sample was subsequently cooled to 50 °C in the same He gas stream. CO uptake was determined by injecting pulses of 10% CO/He from a calibrated online sampling valve into the He gas stream passing over the samples at 80 °C. Metal area, metal dispersion and metal average particle size were calculated assuming the stoichiometric factor (CO/Au) as 1. Adsorption was deemed to be completed after three successive runs showed similar peak area. Gold content was determined by inductively coupled plasma optical emission spectrometer (ICP-OES) on a Varian 720-ES instrument. Solid samples were first digested in a mixture of HF, HCl, and HNO<sub>3</sub> in a microwave oven for 2 h and further diluted with deionized water to analyze the gold contents by ICP-OES. ICP analysis, performed on the fresh samples of Au/MCM-41 catalysts. The BET surface areas of the catalysts were obtained from N<sub>2</sub> adsorption–desorption isotherm (Autosorb I/Quantachrome instruments, USA at –196 °C). The samples were first out gassed at 300 °C to ensure a clean surface prior to construction of adsorption isotherm. The Barrett–Joyner–Halenda (B–J–H) method was used to calculate the pore-size distribution from the desorption branch of the isotherm (Autosorb I/Quantachrome, USA). Transmission electron microscopy (TEM) images of the catalysts were obtained using a Technai-12, FEI, Netherlands at an accelerating voltage of 120 kV. The specimens were prepared by dispersing the samples in methanol using an ultrasonic bath and evaporating a drop of resultant suspension onto the carbon coated



**Fig. 1.** (a) Low angle XRD patterns of MCM-41 and various Au/MCM-41 catalysts. (b) Wide angle XRD patterns of MCM-41 and various Au/MCM-41 catalysts.

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