

Supported Gold Nanoparticles for the Oxidation of Benzyl Alcohol to Benzaldehyde

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Nano-size Au particles deposited over different oxidic supports (MgO, CaO, ZrO₂, TiO₂, and Al₂O₃) by wet impregnation method was successfully prepared. Catalysts were characterized by TGA, ICP, BET surface area, XRD, and TEM, and then their catalytic activity were evaluated for the selective oxidation of benzyl alcohol to benzaldehyde. Among all tested catalysts, TiO₂ supported Au nanoparticles exhibited the best catalytic activity with a benzyl alcohol conversion of 81% and benzaldehyde selectivity of 95 % at 140 °C and 5 bar O₂ in 4 h.

Keywords: Gold nanoparticles, Gold catalyst, Oxidation of benzyl alcohol.

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1. INTRODUCTION

Oxidation of benzyl alcohols (BA) to benzaldehyde (BAL) is one of the most important reactions because of the BAL extensive applications in different areas such as perfumery, pharmaceutical and agro-chemicals industries [1]. BAL can be commercially produced by the hydrolysis of benzal chloride or the partial oxidation of toluene [2,3]. However, these processes have some drawbacks such as poor selectivity to BAL and the presence of chlorine traces, which is not preferable in perfumery and pharmaceutical industries. Currently, liquid-phase oxidation of BA is becoming a preferable reaction method for the production of chlorine-free BAL with good yield, making it an environmentally friendly process [4]. Several studies have been reported for the oxidation of BA to BAL over different noble metals (e.g. Pt, Pd, Au, Ru etc.), using O₂ as the oxidant in the absence of solvent [5,6]. In particular, heterogeneous gold catalyst is found to be very effective catalysts for the oxidation of BA [7,8]. Therefore, our present study aims to develop a more active Au catalyst for the solvent-free BA oxidation with high conversion and selectivity. Gold nanoparticles (AuNPs) over different oxidic supports have been evaluated for their catalytic activity in this reaction.

2. EXPERIMENTAL

2.1 Materials

Tetrachloroauric acid trihydrate (HAuCl₄·3H₂O, ≥99.9% trace metal basis, Sigma-Aldrich), sodium citrate dihydrate (≥99%, FG, Aldrich), tannic acid (ACS reagent, Sigma-Aldrich), All oxidic supports were commercially available (except CaO and MgO were lab-prepared) and were used without further purification. Deionized water (18.2 MΩ.cm) was obtained from a Milli-Q water purification system (Millipore).

2.2 Catalyst Preparation

Catalyst preparation involves two steps. First step was the preparation of the colloidal AuNPs by the reduction of HAuCl₄ in aqueous solution using both of sodium citrate and tannic acid. In the second step, the resulting AuNPs sol was deposited onto a suitable oxidic support (e.g. MgO, CaO, ZrO₂, TiO₂, and Al₂O₃). After that, the resulting slurry was stirred for two h at room temperature and then the excess solvent was removed on a rotavapor. The solid thus obtained was oven dried at 120 °C for 16 h and then was calcined at 350 °C for five h in air. More details on the catalyst preparation are described elsewhere [9].

2.3 Catalyst Characterization

Thermogravimetric analysis (TGA) were performed with a TG apparatus (Shimadzu TGA-50). Catalysts of about 10 mg were heated from 20 to 900 °C at a rate of 5 °C/min and a flow rate of 25 mL/min in air atmosphere. The Au-content was determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES). The BET specific surface areas were estimated by nitrogen physisorption method at -196°C. X-ray diffraction (XRD) patterns were recorded for phase analysis on a Philips X pert pro diffractometer, operated at 40 mA and 40 kV by using CuKα radiation and a nickel filter, in the 2-theta range from 2 to 80° in steps of 0.02°, with a sampling time of one second per step. The morphology of the catalyst was explored by transmission electron microscopy (TEM, JEM-2100F JEOL). Carbon-coated copper grids were used for mounting the samples for TEM analysis.

2.4 Catalyst Evaluation

Catalytic activity tests were carried out under pressure using a 100-ml Parr autoclave. In a typical experiment, reaction vessel was charged with 0.15 g of Au catalyst and 0.29 mol BA. The autoclave was flushed

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three times with O₂ before setting the initial reaction pressure of O₂ at 5 bar, which was maintained constant during reaction through connection to O₂ cylinder. The reaction mixture was stirred (1500 rpm) at 140 °C for 4 h unless otherwise stated. At the end of the reaction, the solid catalyst was separated by centrifugation. Products were collected at different intervals and analyzed by gas chromatograph (Agilent 6890 N).

3. RESULTS AND DISCUSSIONS

3.1 Thermal Analysis

Thermogravimetric (TGA) analysis of uncalcined Au catalysts supported on different metal oxides (e.g. MgO, CaO, ZrO₂, TiO₂, Al₂O₃) are presented in Figure 1. This figure shows that the stability of Au catalyst depends on the nature of the supports used. It should be noted that the precursors of MgO and CaO are Mg(OH)₂ and Ca(OH)₂. The weight loss mainly occurs in two stages in all studied catalysts. The first stage occurs in the temperature range from R.T. to 150 °C, which is due to the loss of water molecules bound weakly to the surface. The second stage takes place between 150 and 350 °C with weight loss due to dehydroxylation and also to the decomposition of the used reducing agents. The weight loss, observed on the whole temperature range, is from 5 to ~20%, which however depends on the type of support used. Alumina supported catalyst is losing weight continuously with increasing temperature, while all others except ZrO₂ supported one shows only a marginal weight loss in the temperature range from 350 to 900 °C. The sudden weight loss observed in case of MgO supported catalyst at around 330 °C can be attributed to the conversion of Mg(OH)₂ into MgO [10]. Interestingly, CaO supported solid displayed quite stable behavior up to ca. 630 °C and then showed abruptly ca. 20% wt. loss at this temperature. This weight loss is undeniably due to transformation of Ca(OH)₂ into CaO. In addition, AuNPs supported on reducible carriers (e.g. ZrO₂, TiO₂) are found to have the lowest weight loss in the whole temperature range among all investigated samples, which is about 6 and 11 %, respectively.

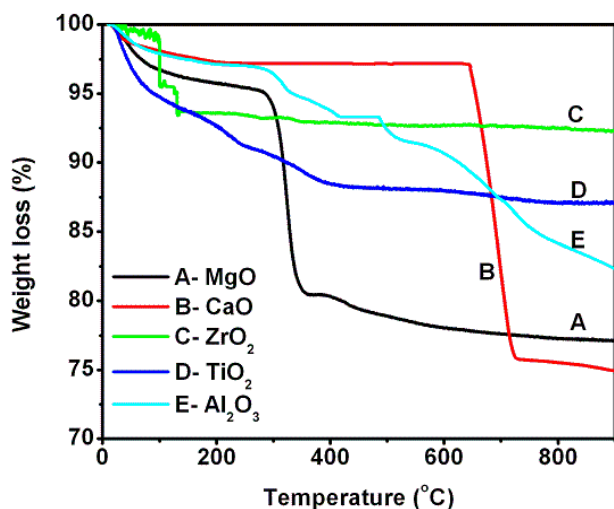


Fig. 1 – TGA profiles of Au catalysts supported on different metal oxide carrier supports (A: MgO, B: CaO, C: ZrO₂, D: TiO₂, E: Al₂O₃)

3.2 BET Surface Area

The specific surface areas and pore volumes of different pure supports and their gold supported catalysts are displayed in Table 1. The surface areas and pore volumes change notably with the nature of the support material. The surface area of most supports drastically decreased after impregnation with the AuNPs. However, in case of TiO₂ and Al₂O₃, an addition of AuNPs did not show an obvious effect on the values of BET surface areas. Such results imply that the AuNPs are highly dispersed on the support without any agglomeration effect. Such good dispersion is also confirmed by other methods such as XRD and TEM, which will be discussed in details in section 3.3 and 3.4.

Table 1 – BET surface area and pore volume of gold catalysts on various oxide supports

Catalyst	ICP	BET SA*	BET SA**
Au/MgO	0.7	59	34
Au/CaO	0.8	37	27
Au/ZrO ₂	0.9	53	39
Au/TiO ₂	0.9	47	43
Au/Al ₂ O ₃	0.8	255	261

* & **: BET surface area for pure support and catalyst, respect.

3.3 X-ray Diffraction (XRD) Analysis

XRD patterns (Fig. 2) reveal that no reflections (crystalline phases) corresponding to metallic Au could be detected over the TiO₂ and Al₂O₃ supports, which might be due to their high dispersion. TEM also indicated the formation of small gold nanoparticles in these two samples (Fig. 3a and b). However, MgO and CaO supported samples show two diffraction lines at $2\theta = 38.2^\circ$ ($d = 2.35 \text{ \AA}$) and at $2\theta = 43.4^\circ$ ($d = 2.03 \text{ \AA}$), corresponding to metallic Au phase.

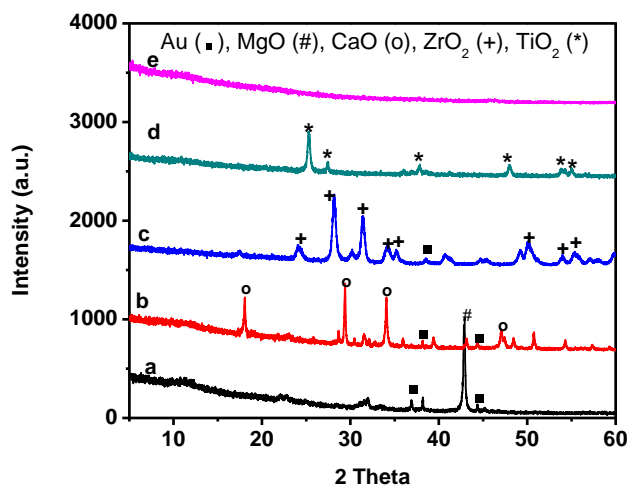


Fig. 2 – XRD patterns of fresh 1% Au catalysts over different oxidic supports (a: MgO, b: CaO, c: ZrO₂, d: TiO₂, e: Al₂O₃)

3.4 TEM Investigation

TEM studies were used to explore the size and shape of the particles since the catalytic activity of gold catalyst depends strongly on its particle size. It reported that the nature of the support can affect the size, morphology and dispersion of Au particles via metal-support interactions [11]. Representative of

selected TEM images of Au catalysts supported on different metal oxides carriers (e.g. TiO_2 , Al_2O_3) are presented in Figure 3. The Au particles have almost spherical shape and are dispersed on the supports with considerable influence of the nature of support on the Au particle size. Among all catalysts, TiO_2 and Al_2O_3 carriers resulted in particles size with a narrow size distribution in the range from 1-5 nm. However, in case of alkaline earth metal oxide supports (e.g. MgO , CaO , not shown here), there is a considerable increase in the size of Au particles, which varies in the range from 1 to 10 nm, while the morphology of the particles remained unaltered. The sequence of increasing mean Au particle size for the gold catalysts supported on different carriers is: $\text{Au/TiO}_2 < \text{Au/Al}_2\text{O}_3 < \text{Au/ZrO}_2 < \text{Au/CaO} < \text{Au/MgO}$, suggesting a dependency on the reducibility of the carrier. Nevertheless, in terms of activity, Au/TiO_2 and $\text{Au/Al}_2\text{O}_3$ are found to be the best catalysts.

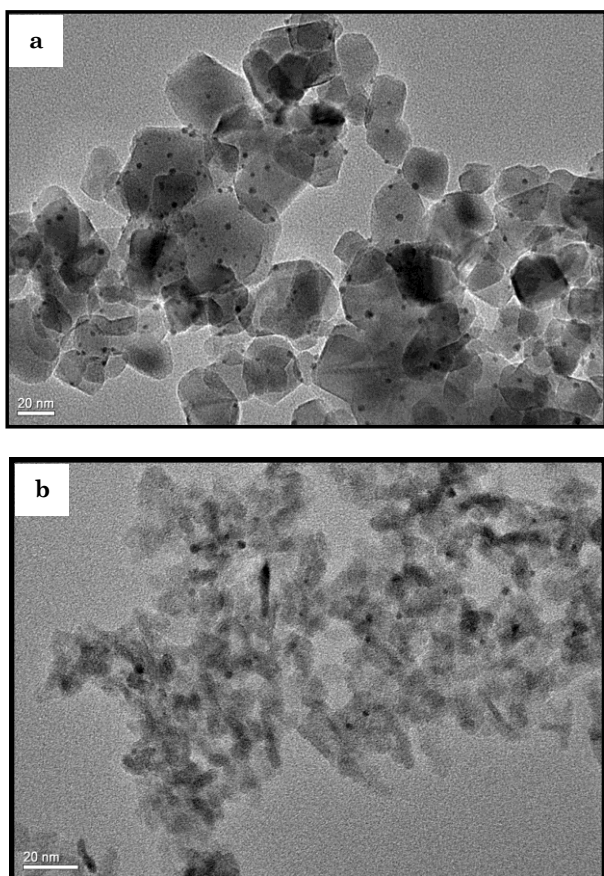


Fig. 3 – TEM images of AuNPs supported on a: TiO_2 and b: Al_2O_3

3.5. Catalytic Activity Results

Figure 4 shows the performance of Au catalysts supported on 5 different metal oxide carriers, under the solvent-free oxidation of BA, using molecular oxygen as an oxidant. The catalytic activity of Au catalysts depends strongly on the nature of the support. BA was the major product. However, some side-products such as benzyl benzoate, benzoic acid and acetal were also

observed in small amounts. The formation of benzoic acid is expected from the over-oxidation of benzaldehyde, while the formation of benzyl benzoate is due to the further esterification reaction of the benzoic acid and benzyl alcohol. On the other hand, acetal formation is expected from the reaction of unreacted benzyl alcohol and the product benzaldehyde, leading to the formation of hemiacetal, which in turn undergoes protonation and deprotonation reactions and finally forms the acetal. However, only trace amount of acetal in the product stream was detected. Among all catalysts tested, the TiO_2 supported AuNPs catalyst was highly active ($X\text{-BA} = 81\%$) and selective ($S\text{-BAI} = 95\%$), while MgO supported one was the least active ($X\text{-BA} = 16\%$ & $S\text{-BAI} = 17\%$). The higher activity and selectivity of Au/TiO_2 is undeniably due to some facts, as summarizing here: i) smaller Au size, ii) higher dispersion of Au and iii) higher surface enrichment of Au compared to other catalysts. On the other hand, the opposite is true in the case of MgO supported gold catalyst and others (e.g. Au/MgO , Au/ZrO_2). Good supporting evidence for such claims is observed from both TEM. The decreasing order of conversion of BA with changing supports is in the following order: $\text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{CaO} > \text{MgO}$.

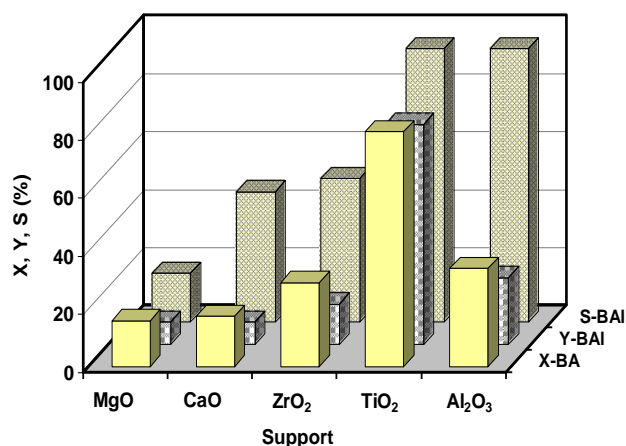


Fig. 4 – Influence of support on oxidation of benzyl alcohol to benzaldehyde over 1% Au/M catalysts (M= MgO , CaO , ZrO_2 , TiO_2 , Al_2O_3). Reaction conditions: 30 mL BA, 0.15 g catalyst, 140 °C, 5 bar O_2 , 4 h. (X = Conversion; Y = Yield; S = Selectivity)

4. CONCLUSIONS

Gold nanoparticles were successfully synthesized by a simple chemical reduction of HAuCl_4 in aqueous solution using 1% tannic acid and 1% sodium citrate, as reductants, followed by impregnation of the prepared AuNPs sol onto MgO , CaO , ZrO_2 , TiO_2 , Al_2O_3 .

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