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Solvent controlled catalysis: Synthesis of aldehyde, acid or ester by selective oxidation of benzyl alcohol with gold nanoparticles on alumina

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ABSTRACT

As shown herein, selectivity of aerobic oxidation of benzyl alcohol with gold nanoparticles dispersed on Al_2O_3 support is solvent-controlled. Using different solvents, the reaction was directed toward a variety of products: benzaldehyde, benzoic acid or benzoic esters were selectively produced from benzyl alcohol depending on the conditions. In toluene, benzaldehyde was produced with high selectivity, while quantitative conversion to benzoic acid was achieved in alkaline water. In methanol, methyl benzoate was produced with very high yield. Moreover, activity of the catalyst was dramatically improved without loss of selectivity in biphasic media; with a toluene/alkaline water system the highest TOF for benzoic acid synthesis was close to 5200 h^{-1}, selectivity being 98%.

1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds is a fundamental reaction of great industrial importance. Beside conventional stoichiometric oxidants, catalytic processes using environmentally friendly air or dioxygen are developed to reduce both costs and environmental impact [1,2]. Gold-based catalysis has become lately one of the key points of interest in this area [3–5]. Due to their catalytic properties, gold and especially supported gold nanoparticles are attracting increasing attention in a variety of transformations [6–8]. In terms of green chemistry, catalysts based on gold nanoparticles are promising in alcohol oxidation because they provide high catalytic activities and often high selectivities [9]. The oxidation of primary alcohols is especially challenging as it can yield several products. Using different gold catalysts, the production of aldehydes [10,11], carboxylic acids [12,13] or esters [14,15] is reported. Being industrially relevant compounds, a catalyst is focused and optimized for one of these oxidation products.

As reported for benzyl alcohol oxidations, majority of nano-gold catalysts in solvent free conditions favor selectivity toward benzaldehyde [11,14,16]. As shown for gold on mesoporous silica and titania, similar high selectivity toward benzaldehyde occurs also in nonpolar solvents like toluene and xylene [16,17].

Addition of water to Au/TiO_2 markedly improves the catalytic activity (TOF up to 300 h^{-1}) but reduces selectivity and as consequence only 67% selectivity to benzaldehyde is obtained [17]. Addition of base (Na_2CO_3) increases the activity of Au/TiO_2 further but the product distribution shifts and quantitative yield of ester, benzyl benzoate, is reported. Further on, performing the oxidation with Au/TiO_2 in methanol and presence of a base, methyl benzoate is produced in high yield [18]. Reports on the third appreciated product, benzoic acid are rather sparse. High to quantitative yields are obtained with polymer-stabilized nano-gold catalysts in aqueous K_2CO_3 or KOH solutions, respectively, but with low activities [12,13].

In general, the activity and selectivity of gold catalysis are considered to depend on several factors including size of the gold particles and the catalyst support. However, the marked examples above underline the sensitivity of the catalyst selectivity also to changes in reaction conditions. This opens a way to develop "one for all" catalytic system; using one catalyst at different reaction

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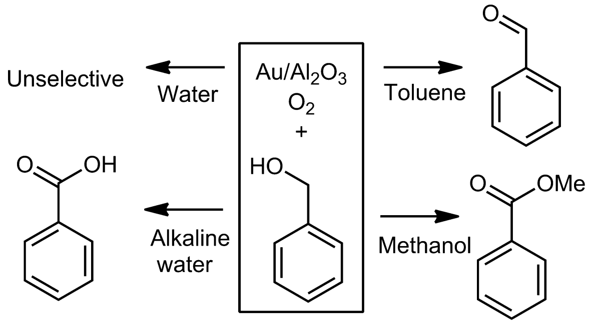

Fig. 1. Oxidation of benzyl alcohol with Au/Al_2O_3 is solvent-controlled; depending on the solvent the catalyst can produce either benzaldehyde, benzoic acid or methyl benzoate with high selectivity and activity.

conditions to selectively switch from one reaction product to another. Already known example is the epoxidation of cyclohexene with Au/C and its dependence on the solvent [19]. Inspired by this idea we focus on developing "one for all" Au/Al_2O_3 catalyst to convert benzyl alcohol selectively to corresponding aldehyde, carboxylic acid and esters (Fig. 1).

2. Experimental

According to our preliminary studies with different catalysts, the most interesting results were obtained with Au/Al_2O_3. The Au/Al_2O_3 catalyst was prepared with direct ion exchange method [20]. An aqueous solution of $HAuCl_4$ (99.9%, ABCR) of concentration 5×10^{-4} M was prepared corresponding to final Au loading of 2 wt%. The solution was heated to 70 °C and powdered Al_2O_3 (UOP, A-201, SBET = 200 m^2/g) was added. The slurry was mixed for 1 h, washed with 100 ml 4 M ammonia for 1 h, filtered, dried overnight at 70 °C and calcined in air at 300 °C for 4 h. Based on transmission electron microscopy (TEM) the average gold particle size was 1.0 ± 0.3 nm and dispersion 77% [21]. Actual gold loading of the catalyst was 1.5 wt% according to ICP determination. Detailed catalyst characterization is reported in Ref. [21].

The oxidation experiments were carried out in glass liners loaded into a pressurized steel autoclave. For a typical run, 0.97 mmol of benzyl alcohol, 0.38 mol% Au/Al_2O_3 (48 mg) and the solvents were measured into the glass liners. Additional base was added as a solid when only organic solvent was used. The autoclave was pressurized with 10 bar oxygen, heated to 100 °C and the mixtures were stirred with magnetic stirring at 1000 rpm.

After the reaction the autoclave was depressurized and the mixtures were extracted twice with ethyl acetate. After the first extraction the reaction mixtures were acidified with HCl to transfer benzoate salt to the organic phase as benzoic acid. Centrifuge (3000 rpm, 2 min) was used to separate the phases. The products were analyzed using GC (Agilent 6890N) equipped with a HP-Innowax column and a flame ionization detector. Molar selectivity and conversion were determined using acetophenone as a standard. GC-MS was used to identify the products. In control reactions without the catalyst, no oxidation occurred without added base. With 1 equiv. NaOH, 10% benzaldehyde was formed. No oxidation of toluene was observed under our reaction conditions. Turn-over frequencies (TOF) were calculated from the conversion of the substrate using shorter reaction times and higher substrate to gold ratios (total Au) than in the selectivity studies (see Table 2).

3. Results

The Au/Al_2O_3 catalyst was prepared using direct ion exchange method (DIE) which has the advantage of producing small gold particles with a narrow size distribution [21]. This type of catalyst has previously been studied, e.g., in oxidation of carbohydrates [21], hydroxymatairesinol [22] and carbon monoxide [23,24]. Herein, the Au/Al_2O_3 catalyst is studied in the oxidation of benzyl alcohol in various solvents with and without the addition of base.

Water is an attractive solvent for catalytic transformations, but first experiments with 0.38 mol% Au/Al_2O_3 showed that the oxidation of benzyl alcohol is unselective in pure water (Table 1, entry 1). Additional bases can be beneficial for the oxidation [25], so in order to improve productivity and selectivity of the catalyst, the effect of bases was studied. The addition of K_2CO_3 resulted in full conversion and the subsequent oxidation of benzaldehyde to benzoic acid (Table 1, entry 2). The optimal amount of K_2CO_3 was 50 mol%, as lower and higher amounts resulted in both decreased selectivity and conversion. Under these conditions benzoic acid was formed with 82% yield along with a significant amount of benzyl benzoate as a side product (18%). The addition of NaOH instead of K_2CO_3 had even higher positive effect on the reaction; equimolar ratio of NaOH to the alcohol gave quantitative conversion to benzoic acid in one hour (entry 3).

Along with excellent selectivity, the presence of base markedly improved the catalyst activity; the highest activity in water (TOF = 3069 h^{-1}) was achieved using NaOH (Table 2, entry 3). This is nearly 10-fold increase of the TOF value in comparison to the results in pure water. To study the differences in activity in different solvents, higher substrate to gold ratio and shorter reaction times were used for TOF value measurements (Table 2) than in the selectivity studies presented in Table 1.

When the solvent was changed from water to toluene, Au/Al_2O_3 produced benzaldehyde with 89% selectivity and with increased activity (Tables 1 and 2, entry 4 vs. 1). Similar activities were reported for gold on mesoporous silica in toluene (364 h^{-1}) and solvent-free oxidation (377 h^{-1}) [16]. The effect of alkali was studied by adding solid K_2CO_3 or NaOH to the toluene solution. Like in water, the addition of base increased the catalytic activity

Table 1
Oxidation of benzyl alcohol in different solvents with 0.38 mol% Au.

Entry	Solvent	Time (h)	Base (mol%)	Conversion (%)	Selectivity (%)		
					Benzaldehyde	Benzoic acid	Benzyl benzoate
1	Water	2	–	50	53	23	24
2	Water	2	K_2CO_3 (50)	100	0	82	18
3	Water	1	NaOH (100)	100	0	100	0
4	Toluene	2	–	86	89	9	2
5	Toluene	2	K_2CO_3 (50)	100	57	40	3
6	Toluene	1	NaOH (100)	100	29	66	5
7[a]	Biphasic	2	–	79	86	11	3
8[a]	Biphasic	2	K_2CO_3 (50)	100	0	90	10
9[a]	Biphasic	0.5	NaOH (100)	100	0	98	2

Reaction conditions: 0.97 mmol benzyl alcohol, 100 °C, 10 bar O_2, 0.38 mol% Au/Al_2O_3 (48 mg), 2 ml solvent.

[a] 1 ml toluene and 1 ml water.