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Supported Gold Nanoparticles Catalysts for Solvent-free Selective Oxidation of Benzylic Compounds into Ketones at 1 atm O_2

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Abstract Supported gold nanoparticles catalyst (Au/TiO_2) was investigated for the oxidation of benzylic compounds into corresponding ketones without any organic solvent at 1 atm O_2 under mild reaction conditions (≤100 °C). For instance, indan was oxidized with conversion of 46% and 1-indanone selectivity of 90% at 90 °C for 24 h. Effect of various reaction parameters viz., temperature, time, and effect of a range of supports was studied for the oxidation of indan. The conversion of indan and selectivity of 1-indanone over recycled catalyst remains almost same.

Keywords Supported gold nanoparticles · Solvent-free oxidation · Benzylic oxidation · Molecular oxygen · Heterogeneous catalyst

1 Introduction

Benzylic oxidations are industrially vital synthetic processes owing to their broad application in the synthesis of pharmaceuticals and fine chemicals [1–3]. Conventionally, stoichiometric amount of oxidants such as manganese dioxide, selenium dioxide or chromium trioxide and homogeneous catalytic methods are employed for these transformations [1–6]. Yet, excessive use of these reagents, along with difficult work-up of the hazardous metal residues and lack of recyclability of homogeneous catalytic systems makes such procedures environmentally objectionable. As a consequence, many effective and recyclable transition metal based heterogeneous catalytic systems have been studied for the liquid phase oxidation of benzylic compounds [7–11]. However, these catalytic systems are generally performed in volatile and/or toxic organic solvents such as dichloromethane [7], chlorobenzene [8, 10, 11], methanol [9] etc., in combination with hydroperoxide-based oxidants and are often prone to leaching of metal ions leading to homogeneous processes. The product separation and catalyst recovery is also difficult.

In view of above, to make these oxidation reactions more environmentally friendly, it is essential to carry out them without any organic solvents. This could be the best approach from an ecological point of view offering considerable synthetic advantages in terms of yield, selectivity, and most importantly simplicity of the reaction procedure [12]. In addition, the replacement of hydroperoxide-based oxidants with H_2O_2 or molecular oxygen is also highly advantageous. A solvent-free/molecular oxygen system can help to suppress the leaching.

Pioneering work of Haruta et al. [13] and Hutchings [14] have stimulated a rapid growth in catalytic properties of gold for a variety of heterogeneous reactions such as hydrogenation [15], CO oxidation [13, 16], alcohol oxidation [17], hydrocarbon oxidation e.g., oxidation of cyclohexene, *cis*-cyclooctene [18], oxidation of cyclohexane [19–21], and epoxidation of propene [22]. Among the various reactions, selective oxidation of alcohols with or without solvents with supported gold nanoparticles has grabbed considerable

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attention due to their higher selectivity and lower susceptibility to leaching [23–28]. Moreover, it has been shown that the choice of a suitable metal oxide as support plays a crucial role in determining the catalytic activity and selectivity of the gold catalysts [29]. Recently, we also reported the exceptional catalytic properties of supported gold nanoparticle (Au/TiO_2) catalyst for oxidation of various alcohols in supercritical carbon dioxide solvent [30].

To our knowledge, supported gold nanoparticles catalyst has not been attempted for the selective oxidation of benzylic methylene group compounds into their benzylic ketones. Hence, the current work was undertaken with the objective of investigating supported gold nanoparticles catalysts for oxidation of benzylic compounds in the absence of solvent at 1 atm O_2.

2 Experimental Section

2.1 Catalyst Preparation and Characterization

The supported gold catalysts were prepared by deposition–precipitation (DP) method [31, 32]. In a typical preparation, titania P25 (Nippon Aerosil) was used as support and $HAuCl_4$ (99.9%, Aldrich) as a gold precursor. 800 mL of $HAuCl_4$ aqueous solution (2.1×10^{-3} M) was heated up to 70 °C. The gold concentration in the solution corresponds to the theoretical Au loading of 4 wt% in case of a complete DP. The pH was adjusted to the desired value by a dropwise addition of 0.5 M NaOH aqueous solution, and then 8 g of TiO_2 support was added with vigorous stirring at 70 °C for 2 h. The pH value was maintained by NaOH solution. After cooling to room temperature, the suspension was filtered. The resulting solid was washed several times with deionised water to remove residual chloride ion and Au species which were not deposited on the support. The solid was dried at 100 °C overnight and calcined in air at 300 °C for 4 h. For comparison, the rest of the supports (Al_2O_3, CeO_2, MgO, and activated carbon) were prepared at pH = 8 and calcined at 300 °C for 4 h [30]. All catalysts were used for catalytic experiments directly after calcinations.

The average nano Au particle size was determined by transmission electron microscopy (TEM, TECNAI-20ST, operating at 200 kV). The gold content was analyzed by Inductive coupled plasma-atomic emission spectroscopy (ICP-AES, SPS 7800 Plasma spectrometer, Seiko Instruments Japan).

2.2 General Procedure for Oxidation of Benzylic Compounds

The catalytic experiments were carried out in a glass reactor (HIPER GLASTOR Taiatsu Techno. Corp.; Capacity = 50 cm^3, pressure maximum 1 MPa) equipped with molecular oxygen balloon.

In a typical experiment, 1 g substrate and 50 mg catalyst was placed inside the glass reactor. The reactor was closed and then fluxed two times with molecular oxygen. The reactor was next heated to the desired reaction temperature in oil bath under constant stirring. Stirring was achieved by means of a magnetic stirrer. After completion of the reaction, the reactor was cooled to room temperature and reaction products filtered through Millipore (syringe driven) filter unit. Following the first reaction run, the catalyst was recovered and dried at 80 °C for 12 h. The recovered catalyst was used for recycling studies.

2.3 Product Analysis

The reaction products were analyzed by capillary gas chromatography using a FID (Chromatograph: Varian CP 3800, column: HP-5, 30 m (length) × 0.32 mm (inner diameter) × 0.5 μm (film thickness)). The identity of the products was first established by using authenticated standards and their individual response factors were determined by using a suitable internal standard phenylacetonitrile by the calibration method. Reaction products were also identified by GC-MS (Varian CP 3800, 1200L Quadrupole MS/MS, column: HP-1). It is known that alkyl hydroperoxide is the initial intermediate of the oxidation of benzylic compounds [8]. However, its yield cannot be measured directly by GC analysis because of its thermolability. We measured its concentration by ^{1}H-NMR. ^{1}H-NMR of reaction mixture (without purification) was measured on Varian Unity INOVA-500.

3 Results and Discussion

3.1 Physical Parameter and Average Particle Size of Supported Gold Nanoparticles Catalyst

Table 1 shows pH value, Au contents, deposition efficiency and average particle size of supported gold nanoparticles catalyst. To illustrate the effect of pH of solution on gold deposition efficiency, Au/TiO_2 catalyst was prepared at three different pH values of 6, 8, and 9, respectively. Our preliminary result shows that by increasing pH from 6 to 9, gold deposition efficiency decreases from 60 to 20%. Moreau et al. [32] has studied the influence of pH on the gold deposition on TiO_2. They reported similar observation, although in their study they achieved higher gold deposition efficiency of about 60–70% at pH 9. In addition, average gold particle size also decreases from 3.6 to 2.6 nm. For rest supports viz. Al_2O_3, CeO_2, MgO and C, gold deposition efficiency was determined at pH 8. A very

Table 1 pH value, Au content, deposition efficiency and average particle size of supported gold nanoparticles catalyst

Catalyst	pH	Au content/ wt (%)[a]	Au deposition efficiency (%)[b]	Average Au particle size (nm)[c]
Au/TiO_2	6	2.42	60	3.6
Au/TiO_2	8	1.06	26	2.7
Au/TiO_2	9	0.83	21	2.6
Au/MgO	8	0.58	15	6.0
Au/Al_2O_3	8	0.29	7	5.0
Au/CeO_2	8	1.61	40	7.0
Au/C	8	0.79	20	10.0

[a] Au content determined by ICP-AES

[b] Au deposition efficiency = [(Au content determined by ICP-AES/theoretical Au content) × 100]

[c] d_{Au} determined by TEM after calcination at 300 °C for 4 h

low amount of gold deposited on Al_2O_3 support. But for MgO, C, CeO_2 supports, gold deposition of 15, 20, 40%, respectively was obtained. The average size of gold particles deposited on Al_2O_3, CeO_2, MgO and C supports was in the range of 5–10 nm, relatively higher than Au/TiO_2.

3.2 Effect of Supports

In order to understand the product distribution of benzylic compound oxidation, firstly, we investigated the solvent-free oxidation of indan at 1 atm O_2. We also studied the influence of various metal oxide supports containing gold nanoparticles for the oxidation of indan and results are shown in Table 2. It is known that catalytic oxidation of indan gives initial product 1-indan hydroperoxide (1-InHP) and it further decomposes into 1-indanone (1-InOne) and 1-indanol (1-InOl) (Scheme 1) [8]. It can be seen from Table 2 that without catalyst, the conversion was only 5% and 1-indan hydroperoxide was the major product (entry 1). In presence of Au/TiO_2 catalyst, conversion of indan was significantly increased to 46% with high 1-indanone selectivity of 90 and 10% selectivity of 1-indanol (entry 2). This implies that Au/TiO_2 is not only effective for decomposition of 1-indan hydroperoxide into 1-indanone and 1-indanol (Scheme 1, step II and III) but also for dehydrogenative oxidation of 1-indanol to 1-indanone (Scheme 1, step IV). To verify the effectiveness of Au/TiO_2 for the dehydrogenative oxidation route, we carried out the oxidation of 1-indanol over Au/TiO_2 under identical reaction conditions. We found catalyst was active and highly selective towards ketone product (see Table 3, entry 2). Therefore we obtained a high selectivity of 1-indanone in the presence of this catalytic system. It is noteworthy to mention here that no 1-indan hydroperoxide was observed under these reaction conditions.

In succession, we have carried out the oxidation of indan with gold catalyst supported on various supports to know their influence on decomposition of 1-indan hydroperoxide. Similar to Au/TiO_2, Au/MgO and Au/Al_2O_3 was also effective for the decomposition of 1-indan hydroperoxide into 1-indanone and 1-indanol (entries 3 and 4). However, selectivity of 1-indanone was approximately 10–14% lower as compared to Au/TiO_2 owing to the formation of more amount of 1-indanol. Furthermore, Au/CeO_2 showed good indan conversion of 32 and 88% of selectivity of 1-indanone (entry 5). However, Au/C showed lower conversion of indan as well as 1-indanone selectivity as compared to the gold nanoparticles catalyst supported on metal oxide (entry 6). The different structure of the activated carbon

Table 2 Solvent-free oxidation of indan with various supported gold nanoparticles catalyst at 1 atm O_2

Entry	Support	Conversion (%)[a]	Product selectivity (%)[a]		
			1-InOne[b]	1-InOl[c]	1-InHP[d]
1	Blank	5	17	13	70
2	TiO_2	46	90	10	0.0
3	MgO	50	84	16	0.0
4	Al_2O_3	48	80	20	0.0
5	CeO_2	32	88	12	0.0
6	C	19	70	30	0.0

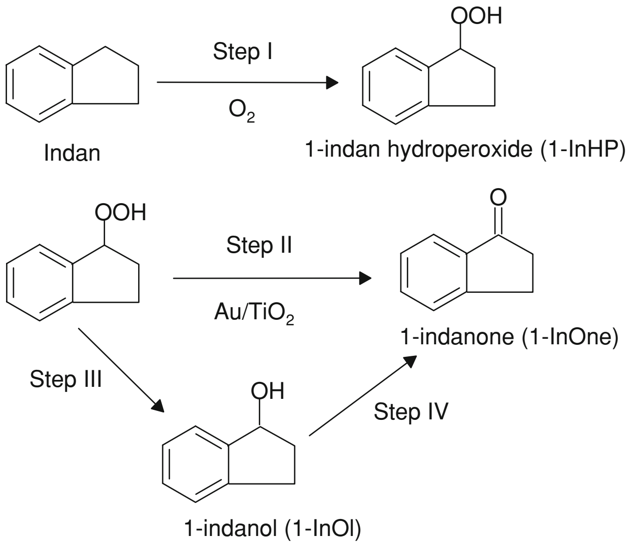
Reaction conditions: m(indan) = 1 g; m(catalyst) = 50 mg; t = 24 h; T = 90 °C

[a] The data was obtained by GC analysis using phenylacetonitrile as an internal standard

[b] 1-indanone (1-InOne)

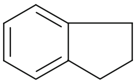
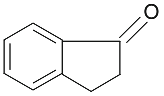
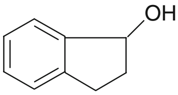
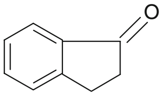
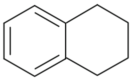
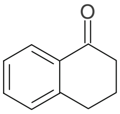
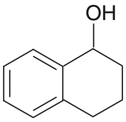
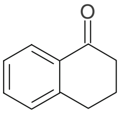
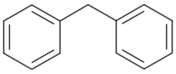
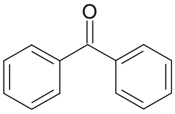
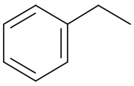
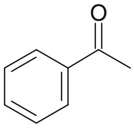
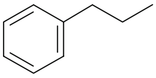
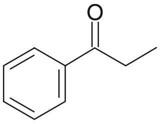
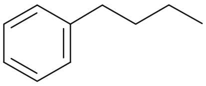
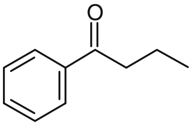
[c] 1-indanol (1-InOl)

[d] 1-indan hydroperoxide (1-InHP)



Scheme 1 Catalytic oxidation of indan at 1 atm O_2

Table 3 Results of solvent-free oxidation of various benzylic compounds with Au/TiO_2 at 1 atm O_2

Entry	Substrate	Conversion(%)	Ketone product	Selectivity of ketone(%)	Yield of ketone(%)
1		46		90	41.4
2		45		100	45.0
3		32		85	27.2
4		65		100	65.0
5		25		95	23.8
6		26		85	22.1
7		18		90	16.2
8		12		92	11.0

Reaction conditions: *m*(substrate) = 1 g; *m*(Au/TiO_2) = 50 mg; *t* = 24 h; entries (1–4,6,7), *T* = 90 °C; entries (5,8), *T* = 100 °C

and large crystalline size of gold nanoparticles ($d_{Au} \approx$ 10 nm) may be responsible for low catalytic activity. It is observed that all the studied supports have some effect on the conversion of indan as well as selectivity of 1-indanone and 1-indanol. On the other hand, there is small influence of gold content and/or gold deposition efficiency on the catalytic activity (see Tables 1, 2).

Figure 1 shows the recycling of Au/TiO_2 catalyst under similar reaction conditions. It can be seen from figure that from fresh to first cycle, slight drop in conversion from 46

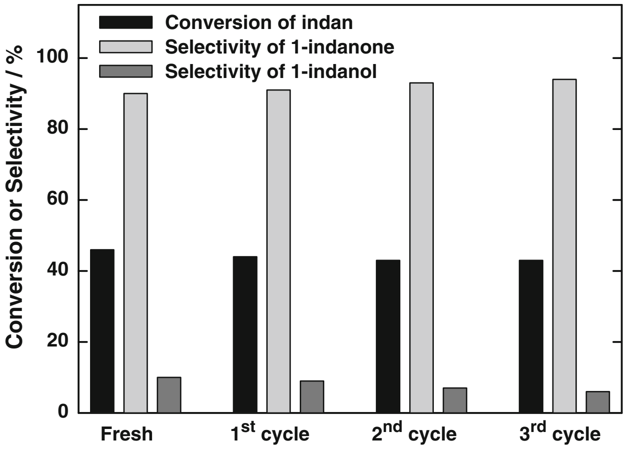


Fig. 1 Recycling of Au/TiO_2. (Reaction conditions: *m*(indan) = 1 g; *m*(Au/TiO_2) = 50 mg; *T* = 90 °C)

to 44% was noticed. But from first cycle to third cycle, conversion remains almost same. The analysis of solution by ICP-AES does not detect gold, indicating that catalyst is stable under present reaction conditions. Upon recycling selectivity of 1-indanone was increased from 90 to 94%. A selectivity of 1-indanol decreases from 10 to 6%. There could be two possible reasons either 1-indan hydroperoxide decomposes more selectively to 1-indanone and/or further oxidation of 1-indanol occurs during recycling (Scheme 1, step II and IV). Furthermore, average gold particle size remains within the same range (d_{Au} = 3 nm) after the reaction (see Supplementary Information).

3.3 Effect of Reaction Time

To understand the reaction pathways, we studied the effect of reaction time on the conversion of indan and the product selectivity. Figure 2 shows the effect of reaction time on the conversion of indan and product selectivity with Au/TiO_2 at 1 atm O_2. As expected, with increase in reaction time from 4 to 48 h, the conversion increases from 15 to 50%. During initial hours of reaction, a mixture of 1-indanone and 1-indanol was obtained. As the reaction time increases from 4 to 48 h selectivity of 1-indanone also increases from 53 to 92% and simultaneously selectivity of 1-indanol decreases form 47 to 8%. This indicates parallel decomposition of 1-indan hydroperoxide and dehydrogenative oxidation of 1-indanol occurs in the presence of catalyst (Scheme 1, step IV).

3.4 Effect of Reaction Temperature

Figure 3 shows the effect of reaction temperature on the conversion of indan and product selectivity with Au/TiO_2 at 1 atm O_2. As expected, with increasing reaction temperature from 70 to 120 °C, conversion increases from 25 to 75%. Furthermore, selectivity of 1-indanone also increases from 81 to 95% and selectivity of 1-indanol decreases. This indicates dehydrogenative oxidation of 1-indanol to 1-indanone (Scheme 1, step IV). At 120 °C, 71% yield of 1-indanone was obtained. However, it is important to mention here that at high reaction temperature gold leaching was observed. Note that at <70 °C, undecomposed 1-indanhydroperoxide along with 1-indanone and 1-indanol was observed in product distribution. Hence in accordance catalytic experiments were carried out at reaction temperature of 90 °C, where complete decomposition of 1-indan hydroperoxide occurred and negligible gold leaching was noticed.

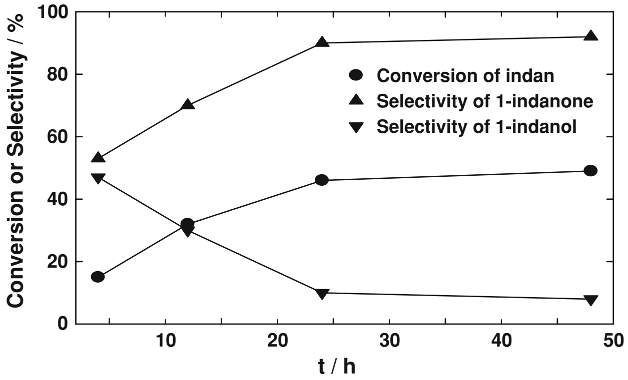


Fig. 2 Effect of reaction time on solvent-free oxidation of indan with Au/TiO_2 at 1 atm O_2. (Reaction conditions: *m*(indan) = 1 g; *m*(Au/TiO_2) = 50 mg; *T* = 90 °C)

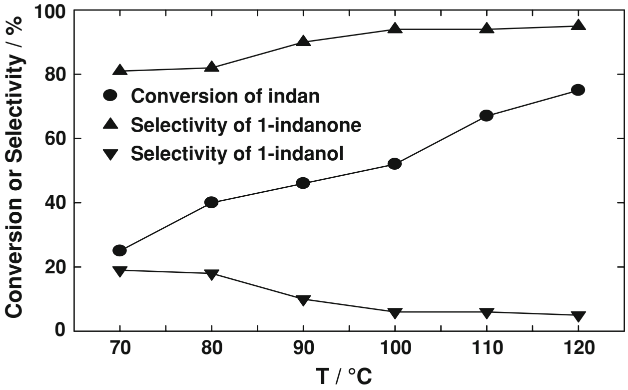


Fig. 3 Effect of reaction temperature on solvent-free oxidation of indan with Au/TiO_2 at 1 atm O_2. (Reaction conditions: *m*(indan) = 1 g; *m*(Au/TiO_2) = 50 mg; *t* = 24 h)

3.5 Solvent-free Oxidation of Various Benzylic Compounds

Solvent-free oxidation of various benzylic compounds was examined with Au/TiO_2 at 1 atm O_2 and the reaction results are shown in Table 3. Benzylic alcohol of indan, 1-indanol was effectively oxidized with conversion of 45% into corresponding 1-indanone (entry 2). Tetralin was likewise oxidized with 32% conversion and 85% selectivity of 1-tetralone (entry 3). Similarly, 1-tetralol was oxidized with 65% of conversion and 100% selectivity of 1-tetralone (entry 4). Meanwhile, diphenylmethane was oxidized with 25% conversion 95% selectivity of benzophenone (entry 5).

Alkylbenzenes (C_2 to C_4) were oxidized to their corresponding phenones with poor yields (entries 6–8). For instance, ethylbenzene and propylbenzene gave 26 and 18% of conversion and 85 and 90% selectivity of acetophenone and propiophenone, respectively. Likewise, butylbenzene was poorly oxidized with 12% conversion and 92% selectivity of butylphenone. We also observed that the oxidation rate decreases with increasing alkyl chain length of benzyl compounds. The reason could be the less preference of the catalyst for adsorption of longer alkyl chain. In all cases, a high selectivity (85–100%) and a good ketone yield (11–64%) was obtained.

4 Conclusion

A high selectivity and a good yield of benzylic ketones were obtained by oxidation of benzylic compounds with supported gold nanoparticles catalyst without any organic solvents at 1 atm O_2. This catalyst could be an alternative for the transition metal catalysts generally used for these transformations.

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