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Silica-Supported Gold Catalyst Modified by Doping with Titania for Cyclohexane Oxidation

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Abstract Amorphous silica was modified by doping with titania through a surface sol–gel process and applied as the support for depositing gold. These doped silica-supported gold catalysts were tested in the selective cyclohexane oxidation to cyclohexanone and cyclohexanol using oxygen. Under the oxidation conditions of 150 °C, 1.5 MPa and 3 h, a selectivity of 91.7% for cyclohexanone and cyclohexanol could be reached over the gold catalyst, affording a cyclohexane conversion of 8.4% and a turnover frequency up to 40,133 per hour. Moreover, the catalytic activity and selectivity could be well retained in 4 recycling oxidation reactions, showing a high stability of the gold catalyst supported on titania-doped silica.

Keywords Gold catalyst · Cyclohexane oxidation · Titania · Silica

1 Introduction

The development of catalytic methods for the selectively oxidative functionalization of alkane carbon–hydrogen bonds remains a challenge in modern chemistry [1]. In particular, the partial oxidation of cyclohexane to cyclohexanone and cyclohexanol under mild conditions is of academic as well as industrial significance, as the selectively oxygenated products are key intermediates for the production of nylon-6 and nylon-6,6 polymers [2, 3]. A greater demand for these oxidation products and increased environmental concerns warrant the introduction of catalytic systems using heterogeneous catalysts as well as environmentally benign oxidants such as molecular oxygen or hydrogen peroxide [4]. In the last decade, great efforts have been made to this reaction over heterogeneous catalysts such as (Cr) MCM-41, TS-1, VPO, VMCM-41 and metal-containing AlPO redox molecular sieves [5–9]. Unfortunately, cyclohexane oxidation using hydrogen peroxide as the oxidant shows low efficiency and is, therefore, not interesting for industrial applications [10]. On the other hand, catalytic systems using oxygen as the oxidant instead resulted in three important advantages [11]: (i) the facility to separate the catalyst after the reaction, (ii) lower energy costs and (iii) a higher stability of the irreversible reaction of over-oxidation products. Therefore, the catalytic cyclohexane oxidation over solid catalysts using oxygen should be in great need of the development.

More recently, an increasing interest has been directed to the potentials of gold catalysts for the selective oxidation reactions [12–16]. Particularly, the partial liquid-phase cyclohexane oxidation using gold catalysts including Au/ZSM-5, Au/MCM-41 and hybrid Au/SBA-15 makes gold even more attractive [17–20]. Unfortunately, as for the Au/ZSM-5 catalyst, the leaching of gold nanoparticles from the support is quite serious [21]. The Au/MCM-41 catalyst gradually lost its catalytic activity and selectivity [18]. With respect to Hybrid Au/SBA-15 catalyst, no expeimental data were given to show the stability of the catalyst. In fact, gold particles are found to be extremely mobile on silica surface and readily form large unreactive particles when treated at high temperatures [22]. As a result, the traditional deposition-precipitation (DP) or co-precipitation (CP) methods of catalyst preparation fail to achieve high dispersion of gold, leading to poor activity as observed in CO oxidation [23].

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However, silica is an important catalyst support material due to large surface area, high thermal stability, mechanical strength and low price. In particular, mildly acidic SiO_2 is relatively resistant to the acidic medium formed in cyclohexane oxidation under the harsh reaction conditions, compared with other metal oxides such as Al_2O_3, CeO_2 and Fe_2O_3. Therefore, SiO_2 is especially an ideal catalyst support material for cyclohexane oxidation. The key point for preparing silica-supported gold catalyst is to load and stabilize gold on SiO_2. One possible solution is to modify the silica surface with organic bifunctional materials prior to doping with gold nanoparticles [19]. Unfortunately, the catalyst preparation was troublesome and expensive. On the other hand, gold can be readily loaded on the support via the conventional DP or CP methods by doping silica with reducible metal oxides [24]. Recently, a surface sol–gel process (SSG) originally developed by Kunitake and co-workers facilitates fabrication of metal oxide thin films over solid substrate with thickness control to molecular precision [25]. Moreover, this technique has been well explored to modify the surface of silica for loading gold nanoparticles by Yan et al. [26, 27]. Titania belongs to the class of the reducible and n-type semiconductor oxide. Gold nanoparticles supported on TiO_2 and mixed oxides of TiO_2 and SiO_2 supports have been well studied for CO oxidation [28–32]. To our knowledge, amorphous silica-supported Au catalyst with TiO_2 modification has not been attempted for the selective cyclohexane oxidation yet. Therefore, we decided to modify the amorphous silica by doping with TiO_2 and then use the doped silica to support gold by the convenient DP method. In our earlier work, a very high catalytic activity was observed over alumina-supported gold catalyst with a low gold loading of 0.2% [33]. Gold catalysis is generally believed to be very sensitive to the size of gold. Therefore, in the present work, we kept all the nominal gold loadings of the catalysts below 0.5% in order that the effect of gold size could be excluded and the effect of titania modification could be distinguished.

The objective of this work is to report an amorphous silica-supported Au catalyst modified by doping with TiO_2 of very low metal loadings and the effect of titania modification on the catalytic performance for the selective cyclohexane oxidation to cyclohexanone and cyclohexanol using molecular oxygen.

2 Experimental

$HAuCl_4 \cdot 4H_2O$ (47.8% Au), butyl titanate (98.0%), anhydrous toluene (99.5%) and anhydrous methanol (99.5%) were purchased from Sinopharm Chemical Reagent Company, Ltd. (SCRC) and used as received. Amorphous silica gel (100–200 mesh, 402 m^2/g) was purified by stirring in 0.1 M HCl solution for 24 h at 90 °C, fully washing with deionized water and finally drying at 110 °C for 2 h. This treatment could regenerate the surface hydroxyl group to a theoretical concentration of about 8 $\mu mol/m^2$ and remove most of the metal impurities from silica.

The amorphous silica-supported Au catalyst modified by TiO_2 doping with a nominal gold loading of 0.5% and varied TiO_2 contents were prepared as follows. (i) Surface modification of SiO_2 with TiO_2 through the surface sol–gel process [26]. Briefly, 2 g of the pre-treated amorphous silica was loaded into a homemade flask reactor sealed with a rubber stopper. The reactor was connected to N_2 source at one end and a vacuum system at the other end. The loaded sample was evacuated for 4 h at 60 °C, then the vacuum system was closed and the reactor was purged with N_2. Subsequently, 5.4 ml of butyl titanate in a mixture of 10 ml of anhydrous toluene and 10 ml of anhydrous methanol was transferred into the reactor through a syringe. After 30 min of reaction at ambient temperature, the organic liquid was removed via the vacuum system. Then, 20 ml of anhydrous methanol was injected into the reactor to wash off the unreacted butyl titanate. This washing procedure was conducted twice before a suitable amount of deionized water was injected into the flask to hydrolyze the adsorbed butyl titanate on the support. The final product can be washed thoroughly with anhydrous methanol and vacuum-dried again for the next cycle of the surface modification of the support. Finally, the silica with TiO_2 doping was dried in air for 2 h at 110 °C and the resulting product was labeled TiO_2/SiO_2-x (x = 1, 2 and 3, cycles of TiO_2 doping), respectively. (ii) Loading gold on the TiO_2/SiO_2-x support by the deposition-precipitation procedure. 2 g of the TiO_2/SiO_2-x support obtained was stirred in 100 ml of 0.5 mM $HAuCl_4$ aqueous solution for 1 h at 60 °C. The pH of the slurry was kept at 8.5 adjusted with 0.1 M NaOH solution. The deposition-precipitation operation was carried out in the dark because TiO_2 is able to photoreduce oxidic Au to metallic Au, which can lead to poor reproducibility of the catalyst synthesis [28]. After filtration, the resulting solid was first washed with 15 ml of 4 M ammonia liquor and then washed twice using 20 ml of deionized water for each wash to remove Cl^- ion. Finally, the resulting solid was dried for 4 h at 80 °C and calcined in air for 3 h at 200 °C. Following the procedure, the amorphous silica support was surface-modified with titania for 1, 2 and 3 times, and the corresponding supported gold catalysts were obtained, labeled as $Au/TiO_2/SiO_2$-1, 2 and 3, respectively. As a reference, silica-supported gold catalyst (Au/SiO_2) in the absence of titania doping was also prepared under the same conditions.

The chemical compositions of the samples were determined by ICP-AES (IRIS Intrepid II XSP). 0.1 g of the solid samples was leached by 4 mL of aqua regia for 4 h and the leaching liquid was collected for determining gold and titania. Powder X-ray Diffraction (XRD) patterns were collected on a D/max-RA diffractometer operated at 40 mA and 80 kV. The step size was 0.02 degree and the step time one second. Transmission electron microscopy (TEM) images were obtained on a JEM-200CX at 160 kV. The samples were dispersed in ethanol and then dropped on carbon-coated grid. The gold particle size distribution was obtained by measuring the diameter of metal particles.

In a typical oxidation reaction, 20 mL cyclohexane and 50 mg catalyst were magnetically stirred in a 100 mL autoclave lined with polytetrafluoroethylene (PTFE) under the conditions of 150 °C, 3 h and a pressure of 1.5 MPa controlled by O_2. After reaction, a suitable quantity of acetone was added into the cold reactor to dissolve all the reactants and products. The liquid samples were analyzed by gas chromatography (GC) with a SE-54 capillary column (30 m × 0.25 mm) and a FID. The identity of the components was verified by GC-MS analysis. As cyclohexyl hydroperoxide (CHHP) partially decomposes upon injection to form some cyclohexanone and cyclohexanol, it is essential that the samples are doubly analyzed by GC, before and after reducing cyclohexyl hydroperoxide to cyclohexanol with triphyl phosphine [34].

3 Results and Discussion

3.1 Catalyst Charaterization

Table 1 shows the chemical composition and the average gold diameters of the calcined samples. As shown in Table 1, the maximal loading of gold is only 0.1% for all the calcined catalysts, about one fifth of the nominal value. The conventional DP method for gold catalyst preparation is generally carried out in a pH of 8~10. Under such pH range, amorphous silica support tends to disslove, especially at a high DP temperature of depositing gold. The doped silica support with titania modification should be unstable and a majority of titania on the surface of silica was lost during the catalyst preparation. Therefore, neither surface-doped TiO_2/SiO_2-*x* nor SiO_2 support is effective enough to loading gold by the conventional DP method. In addition, within 3 cycles of doping silica support with titania, the gold loadings of the corresponding catalysts increased almost in direct proportion to the titania doping concentrations of the supports. It is interesting that all the weight ratios of gold to titania for the doped silica-supported gold catalysts are around 0.2, suggesting that an intimate contact between gold and titania could exist. This should be studied in the further work.

Table 1 Chemical compositions of the supported gold catalysts[a]

Entry	Catalyst	Au (wt.%)	TiO_2 (wt.%)	Mass ratio of Au to TiO_2
1	Au/SiO_2	0.02	0.005	–
2	$Au/TiO_2/SiO_2$-1	0.05	0.26	0.19
3	$Au/TiO_2/SiO_2$-2	0.10	0.41	0.23
4	$Au/TiO_2/SiO_2$-3	0.04	0.24	0.18

[a] Elemental analysis was conducted by ICP-AES

Figure 1a and b show the typical TEM images of silica-supported Au/SiO_2 and doped silica-supported $Au/TiO_2/SiO_2$-2 catalyst, respectively. The black round dots in the images are gold particles. As the gold loading of Au/SiO_2 catalyst is as low as 0.02%, the tiny black dots standing for gold particles in Fig. 1a are almost indistinguishable from the background due to the resolution limitation of the microscope. The gold sizes of the Au/SiO_2 catalyst are mostly less than 5 nm. On the other hand, under the same magnification of the microscope, the gold particles of the doped silica-supported $Au/TiO_2/SiO_2$-2 catalyst are obvious in the image as the gold loading is the highest among all the prepared gold catalysts. The size of the gold particles is in the range of 3~8 nm.

Figure 2 gives the XRD patterns of the calcined Au/SiO_2, $Au/TiO_2/SiO_2$-1, $Au/TiO_2/SiO_2$-2, $Au/TiO_2/SiO_2$-3 and TiO_2/SiO_2-2, respectively. No typical signals of gold at 38.19° and 44.42° were observed in Figure 2 (1)~(4). This is due to the very low gold loadings of all the catalysts, which is out of detection limit for the diffractioner. However, broad peaks at 25.24° and 37.76° ascribed to anatase phase of titania are noticeable for $Au/TiO_2/SiO_2$-2, $Au/TiO_2/SiO_2$-3 and TiO_2/SiO_2-2 with the surface modification twice. In particular, $Au/TiO_2/SiO_2$-3 shows much stronger signals of anatase phase of titania than those of the $Au/TiO_2/SiO_2$-1 sample. However, according to Table 1, these two catalysts possess almost the same loadings of gold and titania, respectively. We believe that some pore blockage of the $Au/TiO_2/SiO_2$-3 catalysts occurred during the calcination treatment of the samples. Therefore, in sample preparation for ICP-AES analysis, some titania inside the blockaged pores was inaccessible to dissolve in aqua regia and thus not detected.

3.2 Catalytic Oxidation of Cyclohexane

Cyclohexane oxidation using molecular oxygen as the oxidant was conducted over the silica support and supported gold catalysts in the absence of solvent, and the results are given in Table 2. Silica of MCM-41 and SBA-15 types is catalytically inactive in cyclohexane oxidation

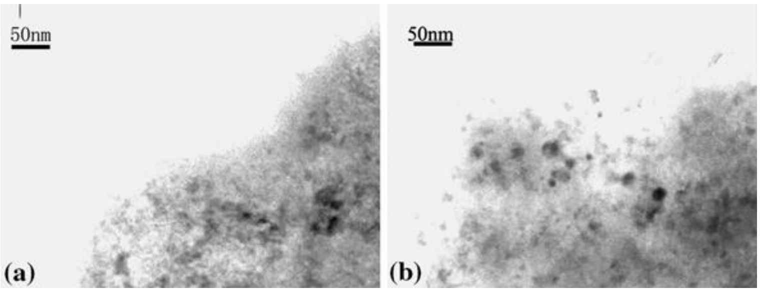

Fig. 1 Typical TEM images of silica-supported Au/SiO_2 and doped silica-supported Au/TiO_2/SiO_2-2 catalyst

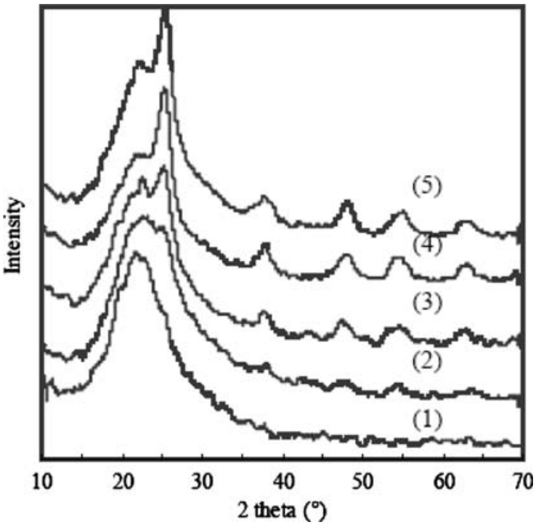

Fig. 2 XRD patterns of the calcined Au/SiO_2 (1), Au/TiO_2/SiO_2-1 (2), Au/TiO_2/SiO_2-2 (3), Au/TiO_2/SiO_2-3 (4) and TiO_2/SiO_2-2 support (5)

[18, 19]. To evaluate the catalytic effect of the reactor wall as well as the amorphous silica support with acid treatment, two blank cyclohexane oxidation were conducted. The results (Table 1, entries 1 and 2) show that both of the reactor wall and silica support are catalytically inert in cyclohexane oxidation under the conditions of 150 °C, 1.5 MPa and 1 h.

In the first set of experiments, the catalytic performances of the silica-supported gold catalyst and doped silica-supported gold catalysts were tested in a reaction time of 1 h. The Au/SiO_2 catalyst shows a noticeable conversion of 0.9%. To compare, the Au/TiO_2/SiO_2-1 catalyst affords a conversion of 3.2% with higher selectivities of cyclohexanone and cyclohexanol. This means a small quantity of titania doping can significantly increase the catalytic performance of the silica-supported gold catalyst. Under almost the same conditions, no oxidation reaction occurs over Au/ZSM-5 catalyst with a gold loading of 1.30% [17]. This means the catalytic activities of supported gold catalysts are strongly dependent on the size of gold particles. As the reaction time increases to 3 h, the silica-supported Au/SiO_2 catalyst shows the best activity among the gold catalysts tested, affording a conversion of 9.2%, although the selectivity to cyclohexanone and cyclohexanol is as low as 82.6%. On the other hand, the Au/TiO_2/SiO_2-1 catalyst gives a comparable conversion, affording a high selectivity of cyclohexanone and cyclohexanol up to 91.7%. Therefore, a small quantity of titania doping can significantly enhance the catalytic property of silica-supported gold catalyst for cyclohexane oxidation. Moreover, all the three doped silica-supported gold catalysts show similar catalytic activities with the selectivities of about 90%. This suggests that slight doping silica-supported gold catalyst with titania can result in higher selectivity while maintaining the catalytic activity compared with silica-supported catalyst. It is well established that the activation of molecular oxygen is a rate-determing step in aerobic cyclohexane oxidation. We believe these small gold particles of around 5 nm should be very effective in activating molecular oxygen under the reaction condition. Therefore, the high activities of these supported gold catalyts are evitably ascribed to the nano-sized effect of gold.

The stability of a catalyst is an important consideration for the industrial application. As the Au/TiO_2/SiO_2-2 possesses the highest gold loading among the doped silica-supported catalysts, it was used for the recycling test to evaluate the stability of the catalyst. After reaction, the Au/TiO_2/SiO_2-2 catalyst was filtered, washed with acetone for three times and finally dried at 80 °C for 4 h before the next run of the recycling test. As shown in Table 3, there is only a slight decrease of conversion as well as the selectivities to cyclohexnaone and cyclohexanol after the first run. Moreover, the activity and the selectivity were well retained in the subsequent three reactions. This suggests that the silica-supported gold catalyst with titania modification is very stable under the reaction conditions.

In summary, the silica-supported gold catalyst of very low gold loading and titania doping concentration has been shown to be highly efficient for cyclohexane oxidation to cyclohexanone and cyclohexanol using molecular oxygen. The high activity of the gold catalyst is ascribed to the

Table 2 Results of cyclohexane oxidation over supports and supported Au catalysts[a]

Entry	Support or catalyst	Time (h)	Conversion (mol.%)	Selectivity[b] (mol.%)				TOF[c] (h^{-1})
				-ol	-one	CHHP	-one + -ol	
1	None	1	No reaction					
2	SiO_2	1	No reaction					
3	Au/SiO_2	1	0.9	31.6	15.7	52.7	47.2	33745
4	Au/TiO_2/SiO_2-1	1	3.2	36.6	19.0	44.4	55.6	45719
5	Au/TiO_2/SiO_2-2	1	1.3	32.0	21.6	46.4	53.6	9723
6	Au/SiO_2	3	9.2	47.2	35.5	1.7	82.6	113201
7	Au/TiO_2/SiO_2-1	3	8.4	54.3	37.4	2.4	91.7	40133
8	Au/TiO_2/SiO_2-2	3	8.2	52.7	37.2	1.9	89.9	20903
9	Au/TiO_2/SiO_2-3	3	8.7	51.5	37.3	1.7	88.8	49059
10	Au/ZSM–5 (1.3%)[d]	1	No reaction					

[a] Reaction conditions: cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa; PTFE-lined reactor

[b] -ol and -one stand for cyclohexanol and cyclohexanone, respectively

[c] Calculated by moles of cyclohexane converted per mole of Au per hour

[d] Reaction conditions of refernce 17: cyclohexane 2 ml, catalyst 5 mg; 150 °C, 1.0 Mpa O_2

Table 3 Recycling test of Au/TiO_2/SiO_2-2 catalyst in cyclohexane oxidation[a]

Cycles	Conversion (mol.%)	Selectivity[b] (mol.%)			
		-ol	-one	CHHP	-one + -ol
1	8.2	52.7	37.2	1.9	89.9
2	7.3	54.0	33.6	2.1	87.6
3	7.8	54.5	32.6	2.6	87.1
4	7.5	52.1	35.5	2.7	87.6

[a] Reaction conditions: cyclohexane 20 ml, catalyst 50 mg; 150 °C, 1.5 MPa, 3 h

[b] -ol, and -one stand for cyclohexanol and cyclohexanone, respectively

nanometer effect of gold which should be very effective for activating oxygen in cyclohexane oxidation.

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