Aerobic oxidation of cyclohexane by gold nanoparticles immobilized upon mesoporous silica

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A series of highly efficient hybrid gold nanoparticle/mesoporous-silica catalysts were synthesized and employed for the solvent-free aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone under moderate reaction conditions. The catalysts were characterized by XRD, N_2 adsorption/desorption, TEM and ICP-AES, which shows the active species are monodispersed gold nanoparticles.

KEY WORDS: gold; nanoparticles; mesoporous; silica; oxidation.

1. Introduction

Selective oxidation of cyclohexane to cyclohexanol and cyclohexanone using air/O_2 or other oxidants is the topic of many recent studies and is of particular interest because the two major products are important intermediates in the manufacturing of nylon-6 and nylon-6,6 polymers [1,2]. Additionally, cyclohexanol and cyclohexanone also find utilities as solvents for lacquers, shellacs and varnishes; stabilizers and homogenizers for soaps and synthetic detergent emulsions; and starting reagents for synthesizing insecticides, herbicides and pharmaceuticals [3,4]. The present commercial process to produce cyclohexanol and cyclohexanone on an industrial scale starting from cyclohexane and molecular oxygen is to use cobalt salt or metal-boric acid as catalysts, which gives ∼4% conversion and 70–85% selectivity to cyclohexanol and cyclohexanone at 150 °C under 1–2 MPa pressure [5,6]. As a homogenerous process, which entails handling of toxic solids and waste liquids, this process has some inherent drawbacks: low conversion, cost effectiveness, higher operating costs, as well as environmental concerns. Such disadvantages make it necessary and urgent to design and cultivate new heterogenerous catalysts, furthermore, a low-cost environmentally-benign solvent-free process would be preferable to the conventional solvent based process.

To heterogenize this process, metal cations, metal complexes and oxides doped upon silica, alumina, zirconia, active carbon, zeolite or aluminophosphates have been developed to catalyze the reaction [7]. Mesoporous materials such as TS-1, Ti–MCM-41, Cr–MCM-41, metal containing VPO and AlVPO were also found to be active for the aerobic oxidation of cyclohexane [8–12], however, in most cases these new catalytic systems resulted in either a low conversion or low turnover frequency. Very recently, Au–MCM-41 and Au–zeolite were reported as new systems and were found to be highly active and selective for the reaction. Au–MCM-41 was prepared by an *in-situ* addition of $HAuCl_4$ to the silica gel while the mesophase was forming, followed by calcination at 550 °C to remove the organic templates [13]. Au–ZSM-5 was prepared by a similar *in-situ* hydrothermal method using $HAuCl_4$ as the gold precursor, followed by calcination at 550 °C [14].

Silica is an attractive support for supporting metals because it is only mildly acidic and is relatively inert, and has good mechanical properties. However, gold particles are found to be extremely mobile on silica surfaces [15–17] and readily form very large (50+ nm) unreactive particles when treated at high temperatures [18], thus making it difficult to prepare gold nanoparticles on silica. One possible solution is to modify the silica surface prior to doping with gold nanoparticles. The conventionally used stabilizing ligands to gold nanoparticles are amine or thiol groups [19]. Mukherjee and co-workers immobilized 3-aminopropyltrimethoxysilane(APS) and 3-mercaptopropyl-triethoxysilane upon mesoporous silica to prepare monodispersed gold nanoparticles on the MCM-41 [20,21], the supported gold nanoparticles were found to be highly active for hydrogenation reactions and no leaching of gold was observed in the reaction. Furthermore, Ionic Liquids(IL) were also found to be capable of transferring gold nanoparticles from aqueous solution to Ionic Liquids through phase transformation [22], which can also be immobilized upon mesoporous silica through grafting methods [23], thus, motivating our experiments

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for enabling gold nanoparticle immobilization upon IL modified mesoporous silica.

With this background, we used three different organic groups to modify the surface of SBA-15 and immobilize gold-nanoparticles. [24] These samples were then utilized for the aerobic oxidation of cyclohexane, here, SBA-15 is selected for its larger pore diameter(5–30 nm) and high surface area, as well as the higher stability, moreover, SBA-15 possess interconnected micropores between the meso-channels [25], which facilitate the dispersion of gold upon the support and the mass transfer during both the modification and the catalytic reactions. It is unnecessary to calcine the catalysts in the preparation procedures reported herein, therefore, the gold particles sizes remain unchanged as they are prepared. The interactions between the organic groups and the nanoparticles improved the immobilization of the metals in the reactions as well as in the preparation procedures, this category of stabilized gold nanoparticles have never been explored for the oxidation of cyclohexane to the best of our knowledge.

2. Experimental details

SBA-15 was synthesized according to a published procedure [24] using the triblock co-polymer Pluronic P123 (BASF) and tetraethyl orthosilicate (TEOS, 98%, Aldrich) under acidic conditions, after aging at 95 °C for 3 days. After synthesis and template removal by calcination at 550 °C, the white powder was dried at 150 °C for 3 h in vacuum. The aminosilylation procedure was performed according to the literature method [26] with minor modification. In a typical procedure, 1 g of SBA-15 was suspended in 30 mL of toluene solution containing 1% APS and refluxed for 5 h. The resulting materials were filtered off, washed with toluene, then dried at 95 °C for 3 h to remove the remaining solvent, thus prepared samples are denoted as APS/SBA-15. Immobilized gold nanoparticles were prepared *in-situ* similarly to previously reported procedures [20,21] by adding 1.0 g of APS/SBA-15 to an aqueous solution of 250 mL 10^{-3} M $HAuCl_4$, followed by stirring at 353 K for 5 h. The mixture was filtrated and washed with copious amounts of water and acetone then dried under vacuum at room temperature. Samples thus prepared are denoted as Au–APS/SBA-15. Thiol- and chloro-modified SBA-15 were synthesized in a similar manner, using 3-mercaptopropyl-triethoxysilane and 3-chloro-triethoxysilane as starting materials, the thiol- modified SBA-15 is denoted as SH/SBA-15. The sample labeled as IL/SBA-15 was prepared by adding 50.0 mL tetra-hydrofuran(THF) and 0.15 mL 1-methylimidazole to 1.0 g chloro-modified SBA-15, and refluxing for 24 h, filtrating and washing with THF. To prepare the final product with Au immobilized on silica, 0.15 g HAuCl$_4 \cdot$ 4H$_2$O was dissolved in 250 mL H$_2$O to form a

solution, to which 1.0 g IL/SBA-15 was added, the mixture was stirred under an inert atmosphere for 5 h at room temperature, then, 0.50 mL Et$_3$N was added dropwise. After vigorously stirring for 24 h, the solids were filtrated and washed with water and ethanol, these samples are denoted as Au–IL/SBA-15. The same procedure was adopted to prepare gold nanoparticle upon SH/SBA-15, labeled as Au–SH/SBA-15.

The mesostructures were characterized by small angle X-ray diffraction (XRD) and N$_2$ adsorption/desorption. Formation of gold nanoparticles was confirmed by transmission electron microscopy (TEM) and XRD, gold content in the samples was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The aerobic catalytic oxidation of cyclohexane was conducted in an autoclave using 2 mL (18.5 mmol) of cyclohexane and 5 mg catalysts, the mixture was stirred at 150 °C under 1.5 MPa of oxygen for 6 h. The products were directly analyzed by gas-chromatography-mass-spectroscopy (GC-MS) and GC. A blank reaction using pure SBA-15 was employed as a comparison under the same reaction conditions.

3. Results and discussion

N$_2$ adsorption/desorption isotherms for initial and Au nanoparticle functionalized SBA-15 are shown in figure 1, the isotherms for all the samples show irreversible type IV adsorption isotherms with H1 hysteresis loop as defined by IUPAC. The gold nanoparticle modified samples retain the same shape of the isotherm observed for the initial sample, however, the amount of adsorbed nitrogen is decreased and the onset of the capillary condensation step shifts to relatively lower pressures. The decrease of absorption amount can be attributed to the reduction of surface area and loading of gold, which has a much higher density than silica, while the shift of the inflection point of the step to lower
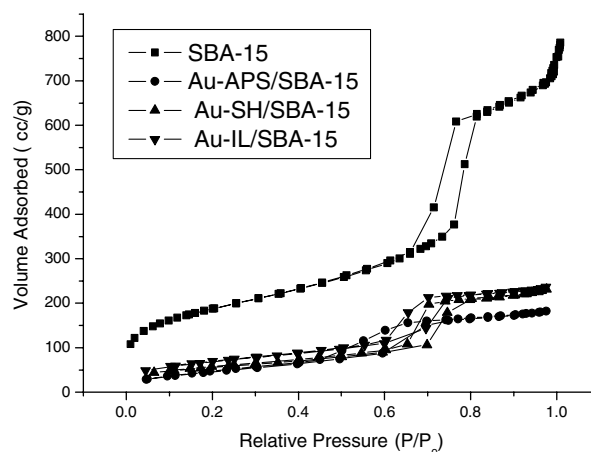

Figure 1. Nitrogen adsorption/desorption isotherms of initial SBA-15 and gold nanoparticle modified SBA-15.

Table 1
N$_2$ adsorption/desorption parameters of the support and prepared catalysts

Sample	BET surface area (m^2 g^{-1})	BJH surface area (m^2 g^{-1})	Pore volume (cc/g)	Pore diameter (nm)
SBA-15	893.5	861.9	1.27	9.4
Au–APS–SBA-15	242.2	275.2	0.306	6.0
Au–SH–SBA-15	194.0	195.2	0.349	7.7
Au–IL–SBA-15	243.2	267.2	0.366	7.7

P/P$_0$ is caused by smaller pore size. Brunauer–Emmett–Teller (BET) method was used for the calculation of all surface area data, and the Barrett–Joyner–Halenda (BJH) formula was employed to evaluate the pore characteristics by using the desorption branch of the isotherm curve, as provided in table 1. A dramatic decrease of surface area and pore volume can be discerned after the loading of gold, while there is only a small decrease of pore diameter, this can be accounted for by the sporadic dispersion of gold nanoparticles within the mesochannels of SBA-15, leaving large amounts of unaffected mesopores in the samples. Gold loading in this way can decrease the surface area and pore volume more sharply than the pore diameter.

Small angle X-ray diffraction patterns of the initial and gold loaded mesoporous silica are shown in figure 2(a), which shows XRD patterns of SBA-15, Au–APS/SBA-15, Au–SH/SBA-15 and Au–IL/SBA-15, all samples exhibit three peaks that can be indexed as characteristic (100), (110) and (200) reflections of hexagonal mesoporous SBA-15, which indicates these samples are consisting of well-ordered packed channels. Therefore, the meso-structure of SBA-15 is maintained during modification of the channel surface (the loading of gold precursors and formation of gold particles inside the channels). Wide Angle XRD(figure 2(b) shows that the (111) peak of gold nanoparticles at $2\theta = 38.2$, from which mean particle sizes of 2.8, 6.5 and 8.8 nm can be deduced for Au–APS/SBA-15, Au–SH/SBA-15 and Au–

IL/SBA-15, respectively, through application of the Debye-Sherrer Equation. Gold nanoparticle size in Au–APS/SBA-15 is the smallest among the three because the aqueous solution precursor AuCl$_3$OH$^-$ can interact strongly with the amine groups, preventing the particles from aggregating during the formation process. Accordingly, the particle size in the Au–IL/SBA-15 is the largest, which is even larger than the pore diameter, due to the weak interaction between the gold particle and the Ionic Liquid species, the bigger particles will "push" the silica wall during gold particle formation, some of the particles will consequently exceed the pore diameter in size.

Transmission electronic microscopy was employed to present intuitive evidence of the gold nanoparticles upon mesoporous silica, as shown by the Au–APS/SBA-15 and Au–SH/SBA-15 images in figure 3, the uniform mesoporosity remains unchanged after the formation of gold nanoparticles within the channels of silica demonstrating that the mesoporous silica is stable to the surface modification and gold nanoparticle formation. The small highly regular particles along the channels of the silica wall correspond to gold nanoparticles, which are around 3 and 7 nm for Au–APS/SBA-15 and Au–SH/SBA-15 respectively, and are sporadically dispersed in the silica matrix, there are no large blocks found outside the mesopores. Most particles are restricted by the pore diameter in size, thus they are larger than the gold nanoparticles previously reported inside MCM-41 (3–4 nm in diameter), this shows that the particle size of gold is influenced by using mesoporous silica with varied pore sizes in this method. Still, in the TEM images, there are some particles near or even exceeding the pore size of SBA-15, this is due to the copious inter-channel pores in SBA-15, through which the gold can migrate to form particles larger than the pore diameter, this is different from the MCM-41 supported gold nanoparticles, which has no micropores to connect the mesopores [20,21]. The gold particles in the TEM are also consistent with the XRD results.
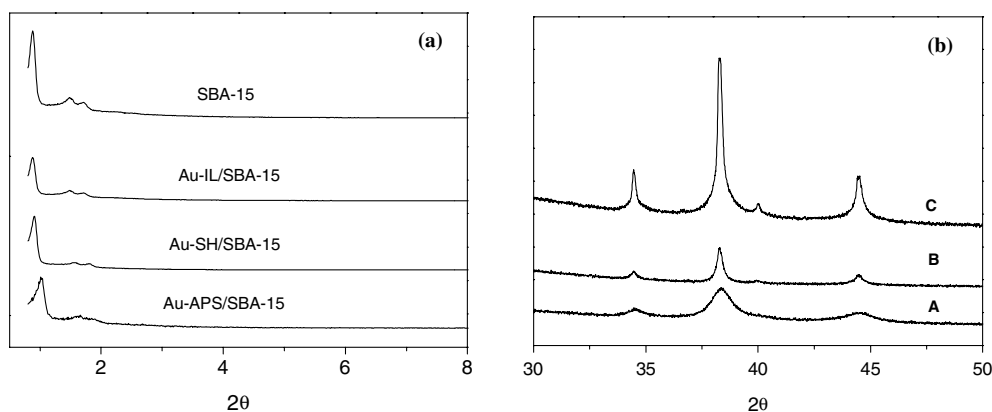

Figure 2. Small (a) and Wide (b) angle X-ray Diffraction of gold nanoparticles upon modified mesoporous silica (A)Au–APS/SBA-15, (B) Au–SH/SBA-15, (C) Au–IL/SBA-15.
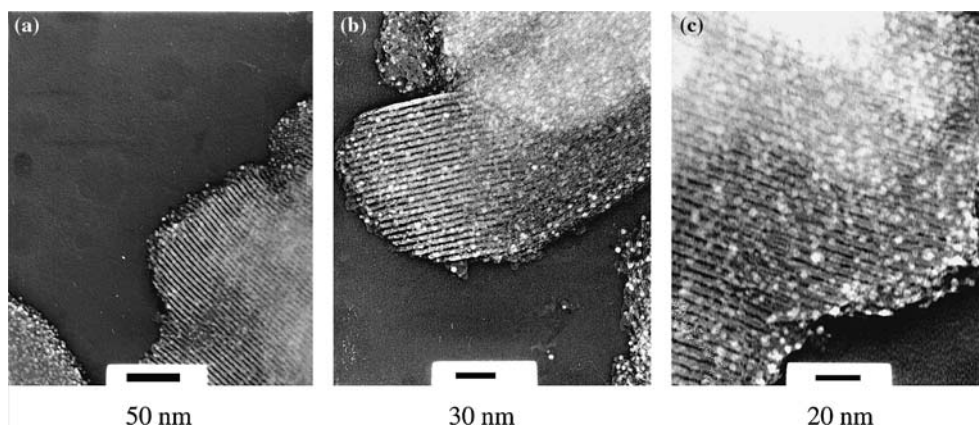
Figure 3. Representative Transmission Electronic Spectroscopy (TEM) images of Au–APS/SBA-15 (a), and Au–SH/SBA-15 with low (b) and high magnifications (c).

Table 2
Results of cyclohexane oxidation over nano-scale Au catalysts

Catalyst	Au wt%	TON h^{-1}	Conv. %	Sel. %		
				Cyclohexanone	Cyclohexanol	Others
SBA-15			0	–	–	–
APS	3.86	661	21	56	40	4
SH	4.53	858	32	62	32	6
IL	2.09	1628	28	57	37	6
Au–MCM-41[a]	1.21	1907	19	73	21	6
MnAlPO-5[b]		292	16.5	43	20	37

Reaction conditions in this work: cyclohexane 2 mL (18.5 mmol), catalyst 5 mg, O$_2$ 1.5 MPa, 150 °C, reaction time 6 h. (a) from Ref. [14] , under the same conditions as employed in this work; (b) from Ref. [11] after 24 h reaction at 130 °C in the presence of hydroquinone, TON calculated by converting to per mole of Mn.

The results of cyclohexane catalytic aerobic oxidation using the above catalysts are listed in table 2, together with the gold content and Turn Over Number(TON), which are compared with previously reported values carried out under the same reaction conditions. The best catalytic performance previously reported is Au–MCM-41 (1.21%), which has a conversion of 19% with a TON of 1907 h^{-1} (moles of substrate converted per mole of metal (Au) in the catalyst per hour), however, in this work, conversion of 21%, 32% and 28% are achieved by Au–APS/SBA-15, Au–SH/SBA-15 and Au–IL/SBA-15, respectively, as well as a good selectivity to the two major products, making this system the best performance ever reported for such a system. The TON observed for these catalysts are lower than the Au–MCM-41 series catalysts because the TON will decrease with an increase in gold content. The cause of this effect in the previously reported systems is caused by a decrease of the active surface with increasing metal particle size (as a result of calcinations), in this work, the gold content is higher than for the *in-situ* prepared Au–MCM-41 or Au–ZSM-5 [13,14] because of the absence of a calcinations step.

In conclusion, a series of organically modified mesoporous silica are used to immobilize gold nanoparticles as catalysts for the heterogenerous aerobic oxidation of cyclohexane, which show the best achievements of conversion to present. It is obvious from our characterizations and those previously reported [20,21], that gold nanoparticles prepared in this way are uniform and less likely to aggregate or leach, this is the key reason for a superior performance as compared to the calcined gold/silica systems previous reported. Our results show that well dispersed gold nanoparticles are active species for the catalytic reaction, thus suggest improvement should be made to control the particle size and surface chemistry in the preparation procedures.

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