A highly efficient catalyst Au/MCM-41 for selective oxidation cyclohexane using oxygen

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The liquid-phase highly efficient selective oxidation cyclohexane to cyclohexanol and cyclohexanone over Au/MCM-41 catalyst was carried out in a solvent-free system, which oxygen as the only oxidant and the reaction conditions are very moderate. The Au/MCM-41 was characterized by XRD, N_2 adsorption/desorption, UV–Vis, XPS, and ICP-AES.

KEY WORDS: cyclohexane; selective oxidation; gold; MCM-41 molecular sieve.

1. Introduction

Selective oxidation of cyclohexane with air or oxidation using heterogeneous catalysts is of growing consequence for the modern chemical industry [1]. The oxidation products of cyclohexane, via, cyclohexanol and cyclohexanone, are important intermediates in the manufacture of nylon-6 and nylon-66 polymers. In addition, they are also used as solvents for lacquers, shellacs and varnishes as well as stabilizers and homogenizers for soaps and synthetic detergent emulsions. Furthermore, cyclohexanol ester, *viz*., cyclohexyl phthalate, is widely used as a plasticizer as well as in the surface-coating industry. Other uses of cyclohexanone are as starting material in the synthesis of insecticides, herbicides and pharmaceuticals [2–5]. In general, both cyclohexanol and cyclohexanone are produced on an industrial scale by the oxidation of cyclohexane or hydrogenation of phenol [6]. The present commercial process for cyclohexane oxidation is carried out around 150 °C and 1–2 MPa pressure affording ~4% conversion and 70–85% selectivity to cyclohexanone and cyclohexanol over metal cobalt salt or metal-boric acid. During these chemical engineer processes of the cyclohexane oxidation, serious pollutions, low cyclohexane conversion, expensive investment, and higher operating cost are growing more and more outstanding. Selectivity oxidation cyclohexane under mild conditions continues a challenge to chemists.

On the other hand, for the laboratory-scale reaction extensive literature was available on the selective oxidation of cyclohexane using a variety of transition metal compounds in stoichiometric amount or as homogeneous catalysts [7–16]. In the cases of the latter, the use of initiators, e.g. cyclohexane [4], cyclohexylperoxide [4], methyl ethyl ketone [11], and acetaldehyde shortened the induction period as well as enhanced the catalytic activity [17]. However, owing to the limitations of these soluble catalysts, *viz*., catalyst separation from the product and the disposal of solid/liquid wastes, which posed serious problems to the environment, in recent years attention had been focused on the development of heterogeneous catalysts with oxygen or peroxides as nonpolluting oxidants [7,8,18–26]. In the last decade, many heterogeneous catalysts that included oxides, metal cations and complexes incorporated on inorganic matrixes such as silica, alumina, zirconia, active carbon, zeolites or aluminophosphates were developed for this reaction [27]. In these experiments, oxygen as an oxidant resulted in a more selective process with three important advantages [28]:the facility to separate the catalyst after the reaction, lower energy costs and a higher stability of the irreversible reaction of over-oxidation products [29]. Other notable catalysts included titanium containing mesoporous materials such as TS-1, Ti-MCM-41, Cr-MCM-41, and metal containing VPO, AlPO redox molecular sieves, however most of them gave a low conversion and turnover number [30–32]. To development new heterogenous catalysts with good stability has been discussed critically in a recent review [33]. Furthermore, as far as environmental concerned, a greater demand for replaced reaction solvent with a more benign solvent or even without any solvent has shown more attractive in recent years. But for the oxidation of cyclohexane, the solvent, which determines the polarity of the medium in the reaction system, played an important role in the activity of catalysts [34,35]. For this opinion, solvent-free systems also urgently need to be developed.

Gold-based catalysts that were regarded as poor catalysts in the past years have received particular attention in connection with the environmental protection. Nano gold catalyst supported on various metal hydroxides, oxides or zeolites have been utilized in a

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serious of important reactions [36–40]. However, it has not been sufficiently explored for the cyclohexane oxidation. Herein we wish to report a high efficient oxidation of cyclohexane over calcined Au/MCM-41 catalyst in an environmentally benign oxidation protocol involving oxygen as oxidant in a solvent-free system including preparation and characterization of the Au/MCM-41 catalyst as well as studies on its catalytic potential at the first time.

2. Experimental

Nano-scale gold supporting MCM-41 mesoporous molecular sieve was synthesized by a novel "$S^+ X^- I^+$" self-assembly process. 3.0 g of CPBr (cetylpyridinium bromide) were combined with 32 mL of HCl acid. When the mixture became clear under magnetic stirring, 6.2 g of TEOS (tetraethylorthosilicate) was added and then introduced the $HAuCl_4/H_2O$ solution, under vigorous stirring to give a mixture with reactant composition of 1 TEOS:0–0.01 $HAuCl_4$:0.3 CPBr:6 HCl:60 H_2O. After allowing the resulting gel to age at 323 K under gentle stirring for 24 h, the solid product was filtered, washed with deionized water, and air-dried at 373 K overnight. At last, the solid power needs to be calcined in air at 823 K for 4.5 h to remove template. According to the different gold loading on the MCM-41, the catalysts were labeled as A–E, and their physical properties were confirmed by XRD, N_2 adsorption/desorption, UV–Vis, and ICP-AES.

Catalytic reaction of cyclohexane oxidations was accomplished in an autoclave using 2 mL (18.5 mmol) of cyclohexane and 5 mg of Au/MCM-41. The reaction mixture was magnetically stirred at 413–433 K and 1 MPa of oxygen for 6–8 h. After reaction, the reactants and products were directly analyzed by GC-MS and GC. A blank cyclohexane oxidation reaction over MCM-41 in oxygen was also carried out under same reaction conditions.

3. Results and discussion

The chemical composition of the samples, the BET surface area and the pore volume were shown in Table 1. The loading of gold had the modest effect on the surface area of the support and the pore diameter. Taking the MCM-41 sample as a reference, we evaluated the crystallinity of the Au-containing molecular sieves from the intensity of the typical peaks 100 following a usual procedure. The results showed a slight decrease in crystallinity due to the presence of Au. The decreased of the volume cell was observed for the Au/MCM-41 samples compared to the MCM-41 sample, suggesting that Au, as expected due to its big cluster volume, did not isomorphously substitute the Si^{4+} in framework position. Au was found inside the channel system or deposited on the external surface of the crystal.

Au nanoparticles due to their surface plasmon vibration, have a characteristic absorption in the visible region of the electromagnetic spectrum at around 500–600 nm, which is responsible for the striking violet to pink rang of colors of the nanoparticles depending upon the particle size [41]. Figure 1 depicted the DRUV-Vis patterns of varied supported nanoAu/MCM-41. For the MCM-41 supported gold catalysts prepared by sol–gel and hydrothermal method, the spectra in figure 1 revealed the expected trend that the bandwidth increases with the decreasing of Au loading. From the literatures published otherwise [42–44], this bandwidth in the XRD pattern displayed the sizes of Au decreasing dramatically with the loading the Au on the supports.

The conversion of cyclohexane oxidation and the selectivity of cyclohexanone were up to ~16% and ~76%, respectively. To the best of our knowledge, it is the first time to report such excellent conversion and selectivity for cyclohexane oxidation under such reaction system. Table 2 also showed the effect of Au content on the reaction. It can been seen from the table 2, Au content had a little effect on the cyclohexane conversion but the selectivity increased with the Au content increase. Figure 2 depicted the effect of reaction time over calcined Au/MCM-41. It could be seen from the figure that the conversion increase with time, while the cyclohexanol selectivity decreases and the cyclohexanone selectivity increase. Figure 3 showed the in influence of reaction temperature, and it was clear showed from the figure that both the substrate conversion and the cyclohexanone selectivity increase with reaction temperature. At higher reaction temperature, the activity increase, but the by-product selectivity

Table 1
ICP-AES Data and BET surface area of various Au/MCM-41

Catalyst	Au content (wt%)	d_{100} (Å)	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore Size (nm)
A	1.21	36.5	839	0.97	3.8
B	0.76	36.5	670	1.01	5.2
C	0.40	37.1	624	1.01	5.7
D	0.25	35.9	723	0.93	4.4
E	0.13	35.0	799	1.01	4.2
MCM-41	–	32.9	732	0.66	3.6

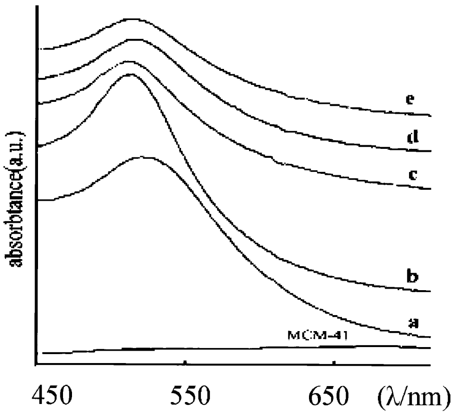

Figure 1. DRUV-vis patterns of varied supported Au/MCM-41 with different Au loading. ((a) 1.21 wt%; (b) 0.76 wt%; (c) 0.40 wt%; (d) 0.25 wt%, (e) 0.13 wt%).

Table 2
Results of cyclohexane oxidation over different Au content catalysts[a]

Catalyst	Au content (wt%)	Cov.	Sel.(%)		Others (%)	TON[b] (h^{-1})
			~ol	~one		
MCM-41[c]	–	–	–	–	–	–
A	1.21	19	21	73	6	1907
B	0.76	17	16	76	8	3091
C	0.40	15	17	75	8	4550
D	0.25	13	27	68	5	6317
E	0.13	12	37	60	3	11,214

[a] cyclohexane 2 mL (18.5 mmol), catalyst 5 mg, O_2 1 MPa, 150 °C, stirrer, reaction time 6 h.

[b] TON:moles of substrate converted per mole of metal (Au) in the catalyst per hour.

[c] Cyclohexane oxidation was performed at the same reaction conditions using pure silicon MCM-41 as catalyst.

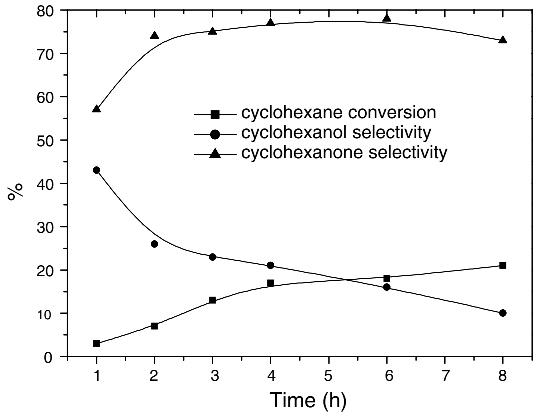

Figure 2. Effect of reaction time on the conversion and selectivity over Au/MCM-41(A).

increased. The suitable reaction conditions of selective oxidation cyclohexane over Au/MCM-41 were 413–433 K, 4–6 h, respectively from Figures 2 and 3.

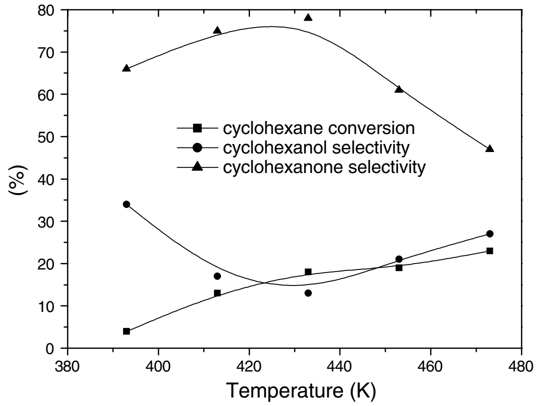

Figure 3. Effect of reaction temperature on the conversion and selectivity over Au/MCM-41(A).

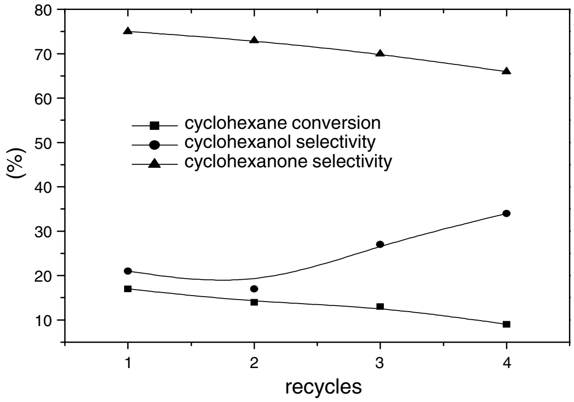

Figure 4. Results of catalyst reused four times over Au/MCM-41(A).

Recycling tests with repeated use of Au/MCM-41 (A) in four consecutive reactions were carried out. The catalyst was removed from the reaction system after 6 h by filtration, washed with acetone, dried at 373 K for 6 h and subjected to the next catalytic run, using the same molar ratio substrate:oxidant:catalyst. Figure 4 illustrated that Au/MCM-41 can be recycled three times without obviously activity loosing.

In summary, a calcined Au/MCM-41 catalyst is found to be a very efficient catalyst for the quantitative oxidation of cyclohexane using oxygen as oxidant in a solvent-free system. The catalyst can be used repeatedly for at least three times without obviously conversion and selectivity losing. The preliminary experimental results showed that Au/MCM-41 as a novel environmentally friendly catalyst is not only possible but also quite satisfactory. Further study is still ongoing.

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