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Synthesis and characterization of Au nanocatalyst on Modifed Bentonite and Silica and Their Applications for Solvent Free Oxidation of Cyclohexene with Molecular Oxygen

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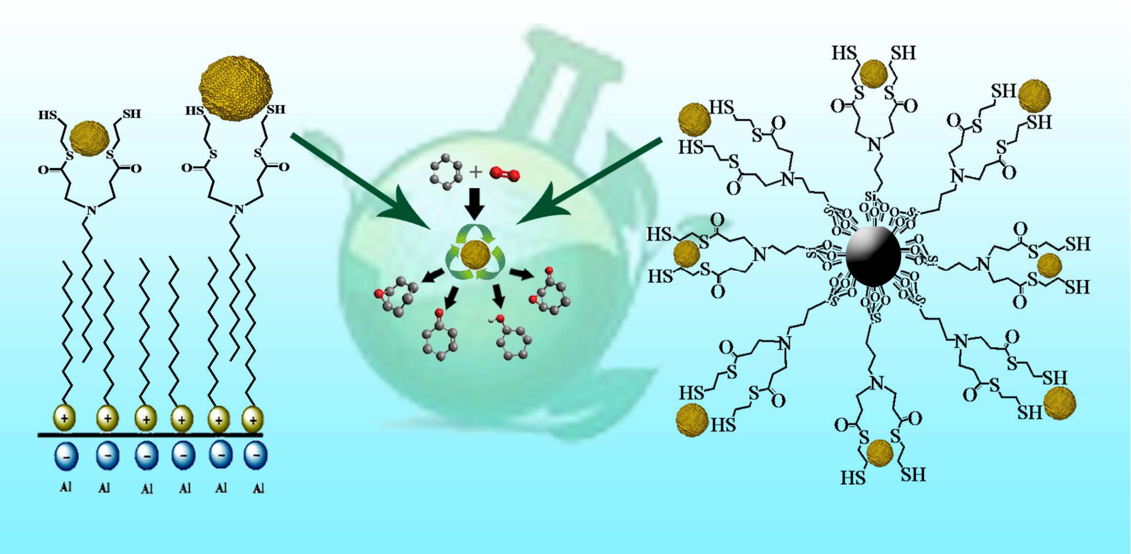
Graphical Abstract



Highlights

- ► gold nanoparticles supported on modified bentonite and modified silica.
- ► Liquid phase oxidation of cyclohexene mainly to 2-cyclohexene-1-one and 2-Cyclohexene-1-ol.
- ► A high conversion (92%) and a high selectivity (97%) to 2-cyclohexene-1-one was obtained.
- ► TEM images show that the immobilized gold nanoparticles on modified silica have diameter around 5-10 nm.

Abstract: In the present work, the selective liquid phase oxidation of cyclohexene mainly to 2-cyclohexe-1-one has been investigated over gold nanoparticles (GNPs) with molecular oxygen in a solvent-free condition. Gold nanoparticles were synthesised on two modified supports of silica and bentonite. In this respect the surface of silica and bentonite was modified with organic ligands consist of thiol and thioester groups. The catalysts were characterized by TEM, XPS, N_2 adsorption/desorption, FT-IR, and CHNS techniques. TEM images show that the gold nanoparticles over modified bentonite and silica have diameters in the range 0f 50 and less than 10 nm, respectively. The results show that the catalytic activity of gold nanoparticles over modified silica, SiO_2-pA-Acrylate-Thioamide-Au (0), is much better than the gold nanoparticles immobilized on the modified bentonite, MEDPT@CP-bentonite-Au (0). The catalytic activity over SiO_2-pA-Acrylate-Thioamide-Au (0) recycled catalyst remained at a satisfactory state after at least 4 cycles. Activity tests were carried out in an autoclave under solvent-free conditions. In order to obtain maximum conversion, the reaction parameters such as reaction temperature and time were optimized. Under optimized conditions, a maximum of 92% conversion and 97% selectivity was achieved with the SiO_2-pA-Acrylate-Thioamide-Au (0) catalyst.

Keywords : Nanogold catalyst; Cyclohexene oxidation; Molecular Oxygen; Heterogeneous Catalysis.

1. Introduction

The catalytic aerobic transformation of alkenes into value-added oxygenated derivatives is still a challenge in the modern chemistry and industry world [1-4]. In particular, the oxidation of cyclohexene is often inefficient as there is a C=C bond and four állylic-H atoms in the cyclohexene molecule. Oxidation of cyclohexene is an important organic reaction for the synthesis of chemical intermediates like 2-cyclohexene-1-ol and 2-cyclohexene-1-one used in the manufacture of high-value pharmaceuticals [5]. A greater demand for these oxidation products and increased environmental concerns warrant the introduction of catalytic systems using heterogeneous catalysts and the environmentally friendly oxidants such as molecular oxygen or hydrogen peroxide [6-8]. The use of H_2O_2 is really appreciated because the only by-product is water, but the relatively high cost of H_2O_2 severely hinders its wide application in catalytic oxidation [9]. On the other hand, catalytic systems using heterogeneous catalysts and molecular oxygen as the oxidant resulted in three important advantages: the facility to separate the catalyst after the reaction, lower energy costs and a higher stability of the irreversible reaction over oxidation products [10,11]. In this research, supported gold nanoparticles over modified bentonite and modified silica have been used. Bentonite has long been used as catalyst [8] and as support for many catalysts, because it is a green support, chemically inert and thermally stable. The silica-supported metal catalysts have advantages over the other heterogeneous catalysts, since they show excellent properties such as high stability (chemically and thermally), good accessibility, and also due to the fact that organic groups can be literally anchored to the surface to provide catalytic centers [9-12]. Herein, and in continuation of our previous works [13,14], we wish to report the activity of two new catalysts and compare their preference in this important reaction.

In recent years, an increasing interest has been directed to the catalytic potential of gold catalysts. Gold nanoparticles are excellent catalyst for oxidation of hydrocarbons and when its particles are small enough they are so hectic that can perform the oxidation process by using molecular oxygen. According to many different studies, the catalytic activity and selectivity of supported gold nanoparticles depend upon the support and preparation method. Among the various techniques for obtaining supported gold catalysts, co-precipitation, deposition-precipitation, vapor-phase deposition, co-sputtering are the most important and applicable ones. In this work, the gold nanoparticles were synthesized in an efficient and gentle condition. In the first stage, the surface of bentonite and silica was modified by a new pincer-type ligand; this organic ligand consists of thiol and thioester groups. Clearly, we have modified the surface of bentonite and silica by different methods but the pincer! parts of the two ligands are identical, so that one would expect that the gold nanoparticles are trapped in comparable environment. Advantages of this method are: (1) a very mild condition (pressure and temperature) has applied during the synthesis of nanoparticles. (2) By increasing or decreasing the molar ratio of the ligand on the surface of the support, it is possible to control the size of provided nanoparticles. (3) Bonds between thiol and thioester groups with gold nanoparticles are probably coordination bonds which causes gold nanoparticles to have a very stable attachment to the support. In this work, we have investigated the activity of the synthesized gold nanoparticles in the oxidation of cyclohexene. The reactions were conducted in the solvent-free conditions by using molecular oxygen as a cheap and green oxidant. One of the catalysts has shown a desirable activity and selectivity that will be discussed in the following sections.

2. Experimental Section

2.1. Materials

The parent bentonite had the following chemical composition (in wt%): SiO_2 (65.04), Fe_2O_3 (1.67), MgO (1.87), Al_2O_3 (13.61), CaO (2.01), TiO_2 (0.19), Na_2O (2.26), K_2O (0.75). It was obtained from Salafchegan mine (Salafchegan, Iran). SiO_2 (400 mesh), n-cetyl pyridinium bromide (CP), methyl acrylate, dodecylamine, and ethanedithiol were purchased from Merck and used as received. The metal precursor $AuCl_3$ (99%) was obtained from Aldrich. All other chemicals used this study were of analytical grade.

2.2. Characterization techniques

Transmission electron microscopy (TEM) was carried out on the powder samples with a Tecnai F30TEM operating at an accelerating voltage of 300 kV.

BET surface area and pore size distribution were measured on a Micromeritics Digisorb 2600 system at −196 °C using N_2 as adsorbate. Before measurements, the samples were degassed at 450 °C.

FTIR spectra of the catalyst were recorded on a JASCO FTIR 680 plus spectrometer with the KBr pellet method.

BEIFEN 3420 gas chromatograph equipped with a FID detector was used to identify the reaction products. The column was a 30 m HP-FFAP with 0.32 mm i.d. and 0.5μm film thickness. The initial temperature was 170 °C for 5 min. The GC was then ramped at 10 °C/min to 280 °C, and hold for 1 min at that temperature. The products of the oxidation of cyclohexene were confirmed by GC/MS (Fisons Instruments 8060, USA).

2.3. General procedures

2.3.1. Purification of the raw bentonite

Since SEM and XRD analysis revealed the presence of significant amounts of quartz and feldspar, the raw material (Salafchegan bentonite) was purified using the following procedure. Bentonite slurry (5 wt %) in water was prepared and swollen at room temperature under continuous stirring. After 5 h, the suspension was diluted to 2 wt % by the addition of 1 mol/dm^3 NaCl solution. The suspension was stirred overnight and then decanted. This ion-exchange procedure was repeated three times with fresh NaCl solution. Finally, the solid was washed free of chloride ions. In the last washing, stirring was stopped and the particles contained in the suspension were separated from the quartz and feldspar precipitates and centrifuged. The resulting cake was dried at room temperature. The cation-exchange capacity (CEC) of the Na-bentonite was 0.7 mequiv/g, as measured using the Ming and Dixon method [15]. The specific surface area of the unmodified Na-bentonite, as determined by N_2 adsorption (single point method), was 63 m^2/g. Purification increased this value to 124 m^2/g.

2.3.2. Preparation of monolayer bentonite

To obtain bentonite with monolayer surfactant coverage (organobentonite), the purified Na-bentonite was modified with n-cetyl pyridinium bromide (CPB) solution (cmc; critical micelle concentration = 10^{-3} mol/dm^3) with a concentration below the cmc (5×10^{-4} mol/dm^3). Thus, 2 g of Na-bentonite was dispersed in 100 mL of CPB solution (20% w/w ethanol−water, pH 6) and the resulting dispersion was shaken for 48 h and centrifuged. The solid was washed with water to remove excess of the surfactant and surfactant loosely attached to the bentonite particles, then dried at room temperature. The specific surface area of the monolayer bentonite, as determined by N_2 adsorption (single point method) was 26 m^2/g.

2.3.3. Synthesis of s,s′-bis(2-mercaptoethyl)-3,3′-(dodecylazanediyl) dipropanethioate (MEDPT)

For modification of the monolayer bentonite we have used MEDPT. This compound was prepared as mentioned below. In the first step, 5.4 g (29.1 mmol) dodecyl amine and 15 g (174.2 mmol) methyl acrylate were refluxed in 30 mL methanol under a nitrogen atmosphere for 24 h. Subsequently, 2.2 mL (26.2 mmol) ethanedithiol was added to the mixture which was then refluxed for 2 days under N_2 atmosphere. The product s,s′-bis(2-mercaptoethyl)-3,3′-(dodecylazanediyl) dipropanethioate (MEDPT) was separated and purified by column chromatography. IR (KBr): v_{max}/cm^{-1}, 2852(s), 2559(m), 1638(m). Elemental analysis % calculated for $C_{22}H_{43}NS_4O_2$, C = 54.89, H = 8.94, N = 2.91, S = 26.61 and observed % was C = 55.22, H = 9.17, N = 2.73 and S = 26.97. Mass (m/z): 481 (Scheme 1).

2.3.4. Preparation of bilayer bentonite (MEDPT@CP-bentonite)

To obtain the bentonite with bilayer surfactant coverage, the monolayer bentonite was modified using MEDPT solution (cmc = 10^{-3} mol/dm^3) with a concentration below the cmc (5×10^{-4} mol/dm^3). Thus, 0.1 g of the monolayer modified bentonite was dispersed in 20 mL of MEDPT solution (20% w/w ethanol−water, pH 6). The resulting dispersion was shaken for 48 h and centrifuged. The solid was then washed with water to remove excess surfactant and surfactant loosely attached to the bentonite particles, then dried at room temperature. The specific surface area of the bilayer bentonite, as determined by N_2 adsorption (single point method) was found to be 25 m^2/g

2.3.5. Preparation of immobilized gold (0) on modified bentonite (MEDPT@CP-bentonite-Au (0))

To prepare this catalyst, 0.05 g MEDPT@CP-bentonite was completely suspended in 100 mL n-hexane for 24 hours on a magnetic stirrer, then 290 µl $AuCl_3$ solution ($1x10^{-2}$ M) was added very slowly (10 µl each time) to the mixture during 12 hours. During this period, the solution was shaken with constant speed. MEDPT-Bentonite that now contains golden nanoparticles was isolated and dried at ambient temperature, and in the next step by passing hydrogen gas over the catalyst in a fixed bed reactor set for 3 hours and at 230 °C, Au(III) was reduced to Au (0).

2.3.6. Preparation of immobilized gold (0) on modified silica catalyst (SiO_2-pA-Acrylate-Thioamide-Au (0))*:*

The silica (400 mesh) was refluxed in EtOH with trimethoxysilyl propylamine for 24 h and was soxhlted for removing the unreacted materials. Afterward the modification of support was done by the refluxing it with methyl acrylate in MeOH for 24 h. Then ethandithiol was added, and the mixture was refluxed for another 24 h. At the final step the gold nanoparticles was immobilized on the modified silica using the procedure explained above for preparation of Au nanoparticles on modified bentonite.

2.3.5. General procedure for oxidation of cyclohexene

In order to perform cyclohexene oxidation, a reaction was designed as follows: 10 mL cyclohexene with 0.05 mg of the catalyst was transferred to a steel reactor and the substrate was oxidized by oxygen by modifying the reaction parameters such as temperature, oxygen pressure, reaction time and amount of the catalyst. It should be mentioned that after separating the catalyst, the reaction mixture was diluted in methanol and injected to the GC. The products were analyzed using GC-MS (Shimadzu QP5000; DB1 column). Identification of products was done by comparing the GC retention times of expected products with those of standard samples.

3. Results and Discussion

As a general view, we have modified two hydrophilic supports with organic moieties, and investigated the cyclohexene oxidation on the prepared catalysts with molecular oxygen in solvent-free conditions, or in other words, in non-polar conditions. Polanski et al. [16] investigated oxidation of cyclohexene on Au nanoparticles supported on different supports in water as media, and discussed the influence of support wettability on conversion and selectivity of the reaction. In the present work, by modifying the two supports, i.e., silica and bentonite, by organic moieties they would be able to suspend very well in solvent-free conditions. Therefore, the observed activity of the catalysts should be largely due to wettability of the catalysts by the substrate and molecular oxygen as oxidizing agent.

3.1. Modification of bentonite

s,s′-bis(2-mercaptoethyl)-3,3′-(dodecylazanediyl) dipropanethioate (MEDPT) was immobilized on a modified bentonite starting from Na-bentonite with monolayer n-cetyl pyridinium cation coverage (CP-bentonite). The scheme of the process is shown in Scheme 2. Immobilization of MEDPT proceeded smoothly on the monolayer modified bentonite. MEDPT surfactant consists of a 12 carbon chain and is able to put its alkyl chain part between hydrophobic chains of the CP-surfactants. In fact, we could imagine that its stabilizing factor is hydrophobic interactions of the alkyl chain of the MEDPT and hydrophobic part of the CP-surfactants. From the CHNS analysis (Supplementary data), it was estimated that the final modified bentonite, i.e., MEDPT@CP-bentonite, contained 0.57

mmol CP-surfactant and 0.24 mmol MEDPT surfactant per gram of the final solid. The final modified bentonite was designated as MEDPT@CP-bentonite as mentioned before.

The specific surface area of the catalysts was investigated in different steps by BET technique. According to the data of Table 1, by comparing the surface area of the parent bentonite with the surface area of the modified bentonite, i.e., CP-bentonite, it clearly shows that the surface area of the modified bentonite has decreased, as expected. After loading the MEDPT surfactant on the CP-bentonite, and immobilizing gold nanoparticles on it, the surface area has not been changed to a large extent. In fact, one would expect that when bentonite becomes bilayer by the MEDPT surfactant molecules, they should not probably occupy new spaces on the bentonite, and therefore we should not expect that the surface area changes too much.

Fig. 1 represents the FTIR spectra of several samples starting from Na-bentonite to bilayer modified bentonite. The peaks corresponding to the Si-O-Si vibration in the bentonite spectrum (Fig. 1a) appears as a strong band in the range of 1000-1100 cm^{-1}; the band at 920 cm^{-1} is due to Al-OH. The peak at 1637 cm^{-1} and the broad band at 3446 cm^{-1} were assigned to the bending and stretching modes of adsorbed water, respectively. The strong bands at around 3619 cm^{-1} are due to the lattice OH stretching modes [17]. The FTIR spectra of modified bentonites as monolayer and bilayer (Fig. 1b and 1c) display new peaks at 1473-1488, 1577, 2854-2927, and a peak at 2567 cm^{-1} was attributed to the thiol stretching vibration [18–20] which confirms the presence of the thiol groups (Supplementary data).

3.2. Modification of silica

The preparation procedure to obtain the catalyst is outlined in Scheme 3. We employed silica with mesh size 400 as the support, which was activated at 500 ºC for 3 h in oven. The resulting silica was then functionalized with 3-aminopropyltrimethoxysilane, followed by condensation with methyl acrylate and ethanedithiol, respectively, via nucleophilic substitution. Upon completion, the resulting solid was filtered off, and to remove unreacted reactants the obtained modified silica was washed with methanol for 24 h in a continuous extraction apparatus (Soxhlet) to give SiO_2-pA-Acrylate-Thioamide. The modified silica was characterized by elemental analysis (CHNS) (C 12.45%, H 2.26%, N 1.06%, S 10.28%).

The FTIR spectra of SiO_2, SiO_2-pA, SiO_2-pA-Acrylate, and SiO_2-pA-Acrylate-Thioamide are compared in Fig. 2. The FTIR spectrum of SiO_2 (Fig. 2a) exhibits strong bands in the range of 1000-500 cm^{-1}, due to the silica skeleton. The characteristic bands of Si-O and O-H are observed at 1087 and 3200-3500 cm^{-1}, respectively. In the FTIR spectrum of SiO_2-pA (Fig. 2b) the peak at 2850-3000 and 3200-3400 cm^{-1} show the existence of the aliphatic segments and NH_2 groups, respectively. Moreover, by condensation of ethanedithiol with SiO_2-pA-Acylate (Fig. 2c), the strong peak appears at 1557 cm^{-1} is attributed to the sulfamide group in SiO_2-pA-Acrylate-Thioamide.

Table 1 shows the specific surface area of the support, SiO_2-pA-Acylate, and SiO_2-pA-Acrylate-Thioamide. Modification of silica to the stage that we have synthesized SiO_2-pA-Acylate, decreased the specific surface area. Interestingly, by adding MEDPT to SiO_2-pA-Acylate the surface area increased to some extent that might be reasonable, because if we accept that MEDPT does not occupy any new space on the silica and only decreases the hydrophilic nature of the support, one should believe the slight increase in the surface area.

3.3. Immobilization of gold nanoparticles on modified bentonite and modified silica

MEDPT@CP-bentonite (0.5 g) was dispersed in dry n-hexane (100 mL) and stirred for 24 h under nitrogen. Then 300 µ*l* of aqueous solution of $AuCl_3$ (concentration = $1x10^{-2}$ M) was added to the mixture during 12 h. The mixture was stirred for another 24 h under nitrogen, and then the solid was separated by centrifugation, washed with ethanol and ether. Finally, the solid was dried at room temperature to furnish the corresponding MEDPT@CP-bentonite-Au(III) sample. Then the as-prepared sample was treated in a stream of hydrogen at 230 ºC for 3 h to yield MEDPT@CP-bentonite-Au(0) catalyst. No diffractions were detected for Au NP species from powder XRD patterns after H_2 reduction which indicates Au loading is too low or the nanoparticles are too small in the catalyst. Inductively coupled plasma/atomic emission spectroscopy (ICP-AES) analysis of the obtained catalyst showed that the Au weight percentage in the catalyst was 6.72%.

To immobilize the gold nanoparticles on the SiO_2-pA-Acrylate-Thioamide support, 1.0 g of the support was dispersed in dry n-hexane (100 mL) and stirred for 24 h at room temperature under nitrogen. Then 300 µ*l* of an aqueous solution of $AuCl_3$ (concentration =

$1x10^{-2}$ M) was added to the mixture during 12 h. The mixture was stirred for another 24 h under nitrogen, and then the solid was separated by centrifugation, washed with ethanol and ether. In this way, a new catalyst containing gold i.e., SiO_2-pA-Acrylate-Thioamide-Au (III) was prepared. Similar to the procedure used for reduction of Au(III) in MEDPT@CP-bentonite-Au(III), we treated the SiO_2-pA-Acrylate-Thioamide-Au(III) sample in a stream of H_2 at 230 ºC for 3 h to prepare SiO_2-pA-Acrylate-Thioamide-Au(0) catalyst. Inductively coupled plasma/atomic emission spectroscopy (ICP-AES) analysis of the obtained catalyst showed that the Au weight percentage in the catalyst was 1.02%.

The TEM images (Fig. 3) show the distribution of Au nanoparticles in the range of 5-10 nm size on the surface of modified silica, and in comparison with the Au nanoparticles on the modified bentonite (Fig. 4), the size of nanoparticles are smaller by at least a factor of five.

Finally, the SEM photographs of the both catalysts are shown in Fig. 5. By comparing the surface area of Na-bentonite with the surface area of modified bentonite i.e., MEDPT@CP-bentonite catalyst, it has lost about 80% of its surface. The silica by modification has lost about 20% of its surface. What could this mean? This means that for modification of bentonite more carbon is added to the bentonite than that added to silica for modification. It should also be mentioned that the organic moieties used for modification of bentonite are naturally much more hydrophobic. Therefore, one would expect that bentonite becomes more hydrophobic and fluffier!

3.4. Catalytic performances

3.4.1. Effect of catalyst and temperature

Oxidation of cyclohexene was carried out over MEDPT@CP-bentonite-Au (0), and SiO_2-pA-Acrylate-Thioamide-Au (0) catalysts. In fact cyclohexene was chosen because this molecule could be oxidized in two positions, both C=C bond and allylic positions; of course oxidation of allylic positions are more important. In this reaction we also used oxygen as a green and cheap oxidant. Moreover, because oxidation reaction was conducted in absence of solvent the importance of the reaction has doubled. The results summarized in Table 2, indicate that the conversion and selectivity of cyclohexene oxidation with the SiO_2-pA-Acrylate-Thioamide-Au (0) catalyst containing 1.02 wt% Au was much higher than that with the MEDPT@CP-bentonite-Au (0) catalyst containing 6.72 wt% Au. As an overall view, the silica supported catalyst displayed 55% higher cyclohexene oxidation than bentonite supported catalyst. As TEM images of the two catalysts show the size of nanogolds in silica supported catalyst are smaller than the nonogolds in the bentonite basis catalyst by a factor of five, and also the silica supported catalyst has a much higher surface area, and clearly these characteristic properties have a large effect on conversion and selectivity.

The reaction temperature has also an impact on both activity and selectivity especially on SiO_2-pA-Acrylate-Thioamide-Au (0) catalyst. It should be reminded that the boiling point of cyclohexene is 83 ºC at atmospheric pressure, and we have done the reaction under the pressure of oxygen (P_{O2} = 8-13 bar). Therefore, at 80 ºC one would expect that cyclohexene was in the liquid phase in the reaction conditions, and its contact with the catalyst might be in optimal condition. As a matter of fact, by increasing the reaction temperature to 80 ºC, selectivity to cyclohexene-2-one has increased to 97%. However, the MEDPT@CP-bentonite-Au (0) catalyst was not efficient in this regard! By increasing the temperature to 95 ºC we did not lose the activity of the catalyst because of high pressure of oxygen that increased the boiling point of cyclohexene. Interestingly, like our previous work in oxidation of cyclohexene [14], the optimum temperature for oxidation 80 ºC was chosen, because of energy saving!

3.4.2. Effect of oxygen pressure

The efficient operating pressure for both catalysts has been obtained. As a matter of fact, the two catalysts have different optimal pressure. The best operation pressure for SiO_2-pA-Acrylate-Thioamide-Au (0), and MEDPT@CP-bentonite-Au (0) catalysts was 13 and 8 bars, respectively. It is interesting that these two catalysts have different optimum pressure. As a matter of fact, the bentonite supported catalyst has a much lower surface area, and it will be saturated with oxygen at lower pressure, and there would be less room for substrate. Therefore, by increasing the pressure of oxygen to higher values one should expect a decrease in conversion in comparison with the silica supported catalyst (Table 3).

3.4.3. Effect of reaction time

Table 4 shows the effect of time on the cyclohexene oxidation with molecular oxygen over the two catalysts. Clearly, 8 h was chosen as the best time for the oxidation reaction over silica supported catalyst, and 10 h was the best for bentonite supported catalyst. Again this has something to do with surface area. The catalyst that has more surface area has more chance to convert the cyclohexene to products in a shorter time. Also the SiO_2-pA-Acrylate-Thioamide-Au (0) catalyst shows much more selectivity to 2-cyclohexene-1-one in different condition than the MEDPT@CP-bentonite-Au (0) catalyst.

3.4.4. Effect of amount of catalyst

To study the effect of amount of catalyst, the oxidation reaction was carried out at 80 ºC, oxygen pressure, 17 bar and the reaction time of 8 h. From the results summarized in Table 5, it is observed that catalyst loading of 50 mg is appropriated to run the reaction with SiO_2-pA-Acrylate-Thioamide-Au (0) catalyst. However, in the case of MEDPT@CP-bentonite-Au (0) catalyst by using 100 mg of the catalyst the conversion increased to some extent, but because of the low selectivity of the catalyst we did not bother to show more curiosity. We demonstrated in our previous work [13] that 1,2-dichloroethane is the best solvent for the reaction. Thus, using this solvent, conversion and selectivity to ketone reached 90% and 55%, respectively. Comparing these data with solvent-free conditions, a significant decrease in selectivity was observed under solvent condition.

3.4.5. Reusability of the catalyst

One of the main advantages of heterogeneous catalysts over homogeneous is that the former can be recovered and reused. The GNPs/TChD catalyst could be easily separated from the reaction mixture by centrifugation and then wash it with organic solvent and subsequently with water. The results of reusability are presented in Table 6. Data showed that the selectivity of their used catalyst remained unchanged after four cycles, and then the catalytic performance decreased gradually. As a matter of fact, oxidation in the liquid phase is very often subject of leaching phenomenon and the question about the true nature of the catalytic reaction (homogeneous or heterogeneous) is a matter of debate. To answer this question, the catalyst was separated from the reaction mixture and then the reaction was continued without the heterogeneous catalyst according to the method described by Sheldon et al. [21]. The results show that the amount of leached metal is very low and its contribution to the total activity of the catalyst in the cyclohexene oxidation reaction is probably negligible.

In Table 7, we have compared the result obtained over previously reported catalysts for oxidation of cyclohexene. Supporting different Schiff-base metal complexes on polymeric materials such as chloromethylated polystyrene (PS-DA-M; M = Cu2+, Co2+, Ni2+, and Mn2+) [22], polyamidoamine (PAMAM-Mn^{2+}) [23], CrMCM-41 [24], Au/HNTs [25], Au/La-OMS-2 [26], and our previously reported nanogolds over modified chitosan [14] are some examples of catalysts which have been used for oxidation of cyclohexene under solvent free conditions with molecular oxygen. As shown in the Table 7, the catalyst SiO_2-pA-Acrylate-Thioamide-Au (0), reported in this work has shown an excellent selectivity to 2-cyclohexene-1-one.

4. Conclusion

In this work we have prepared two supports with identical anchoring ligands for gold nanoparticles and compared their reactivity and selectivity for oxidation of cyclohexene under solvent-free conditions and using molecular oxygen as the greenest oxidant. The size of gold nanoparticles on the SiO_2-pA-Acrylate-Thioamide-Au (0) catalyst was in the range of 5-10 nm. These nanoparticles were well dispersed and have shown a good reactivity (92%) and selectivity (97%) to 2-Cyclohexene-1-one.

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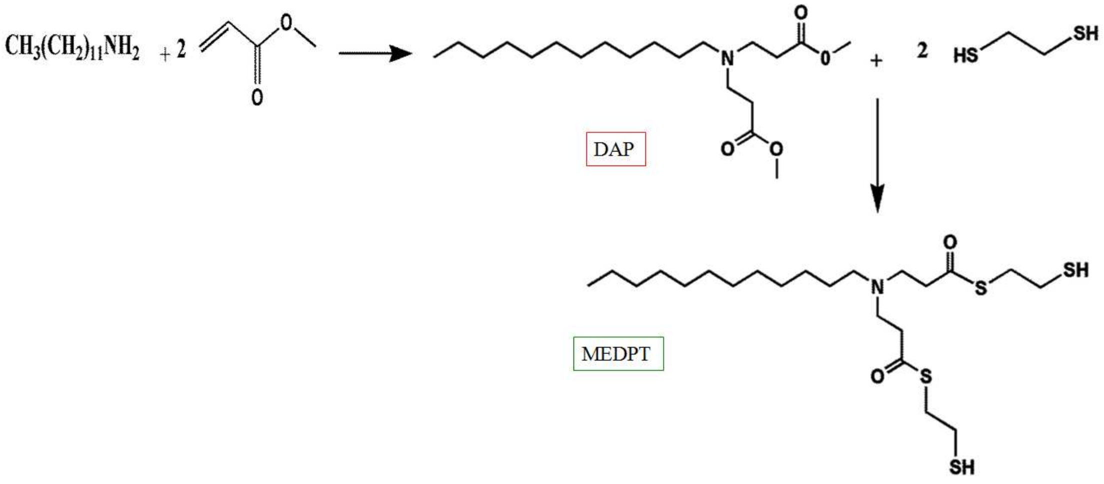
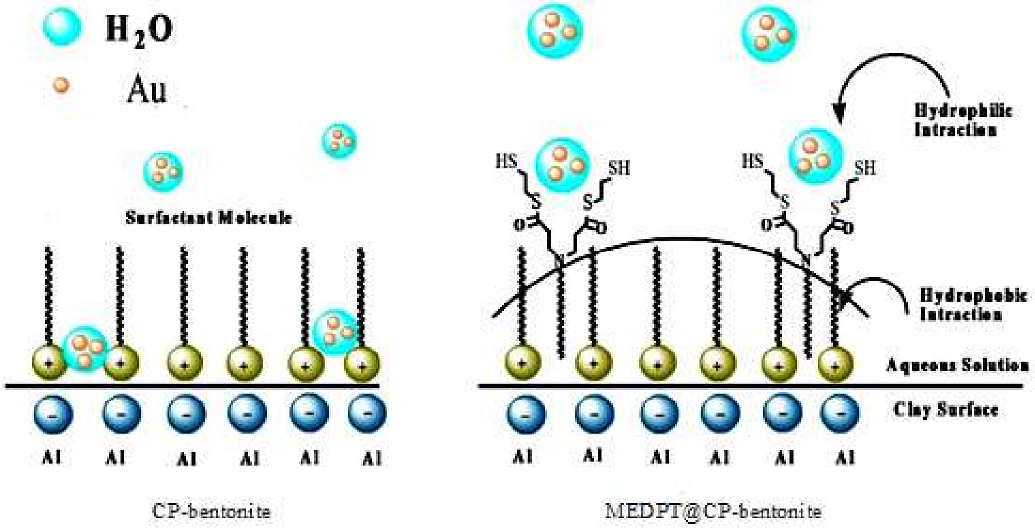
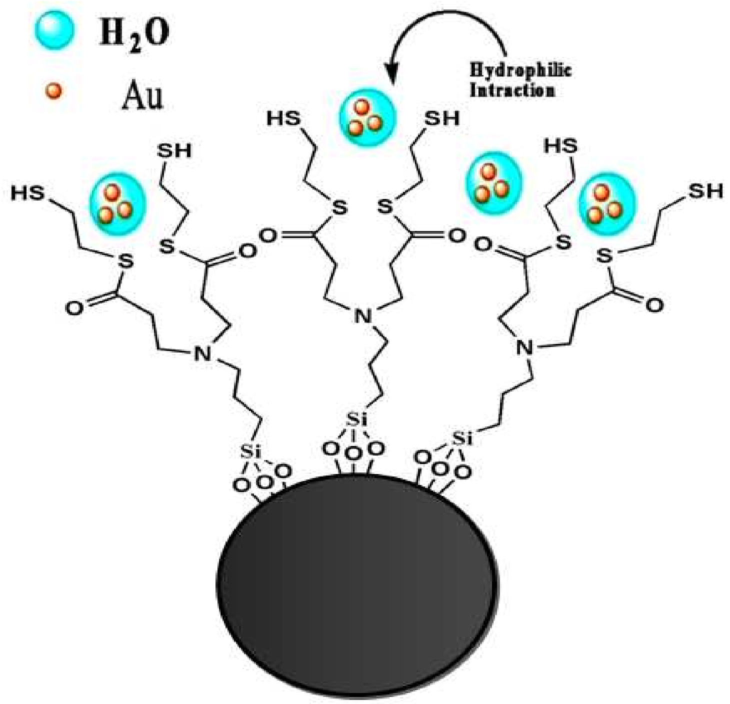
Figure Captions



Scheme 1. Synthesis of s,s′-bis(2-mercaptoethyl)-3,3′-(dodecylazanediyl) dipropanethioate (MEDPT).



Scheme 2. Model of sorption of surfactant on the clay surface, and preparation of Au nanoparticles.



Scheme 3. Modification of silica and preparation of Au nanoparticles.

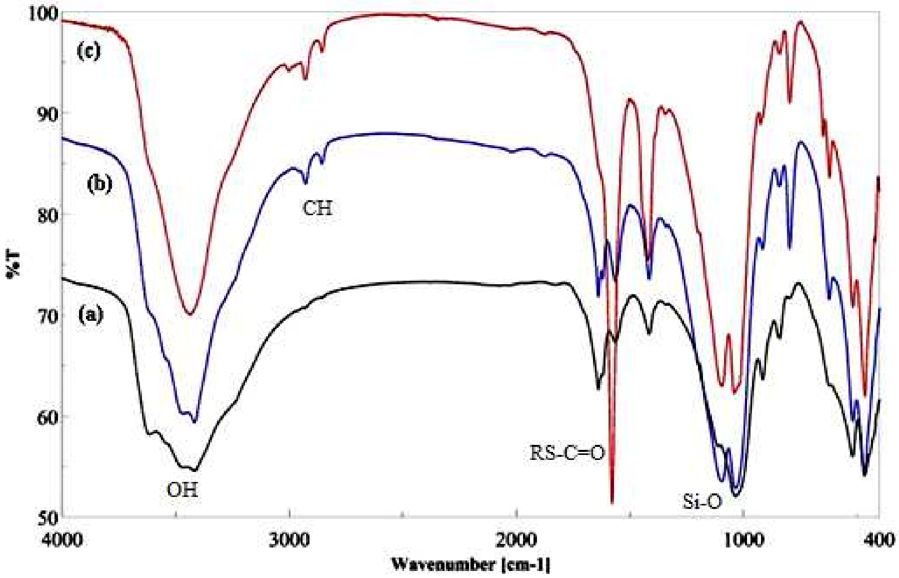


Figure 1. FT-IR spectra of bentonite (a) raw bentonite, (b) monolayer bentonite and (c) bilayer bentonite [KBr pill].

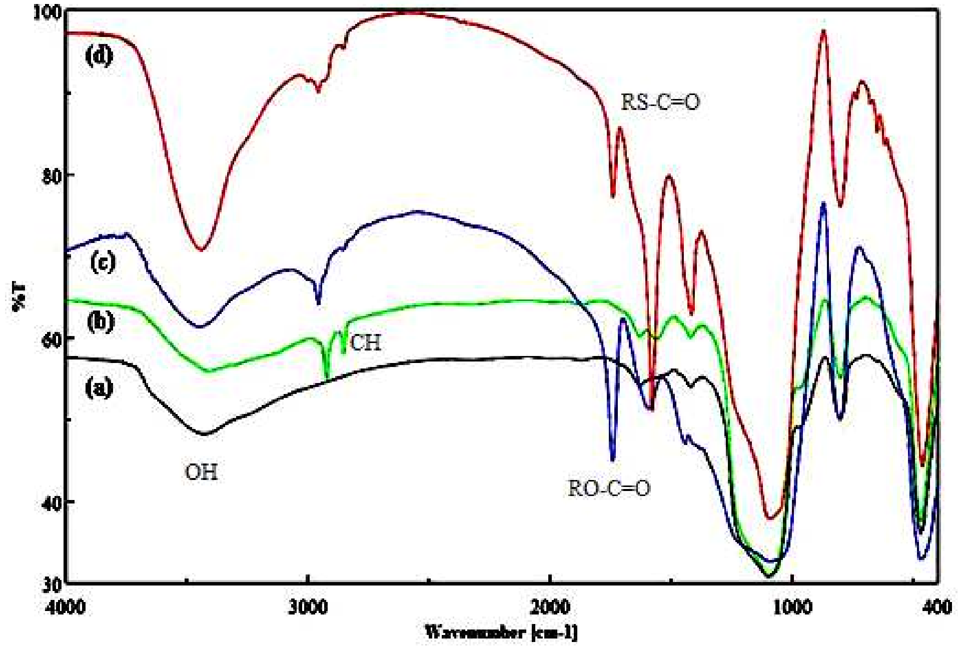


Figure 2. FT-IR spectra of (a) Silica gel, (b) SiO_2-pA, (c) SiO_2-pA-Acrylate and SiO_2-pA-Acrylate-Thioamide [KBr pill].

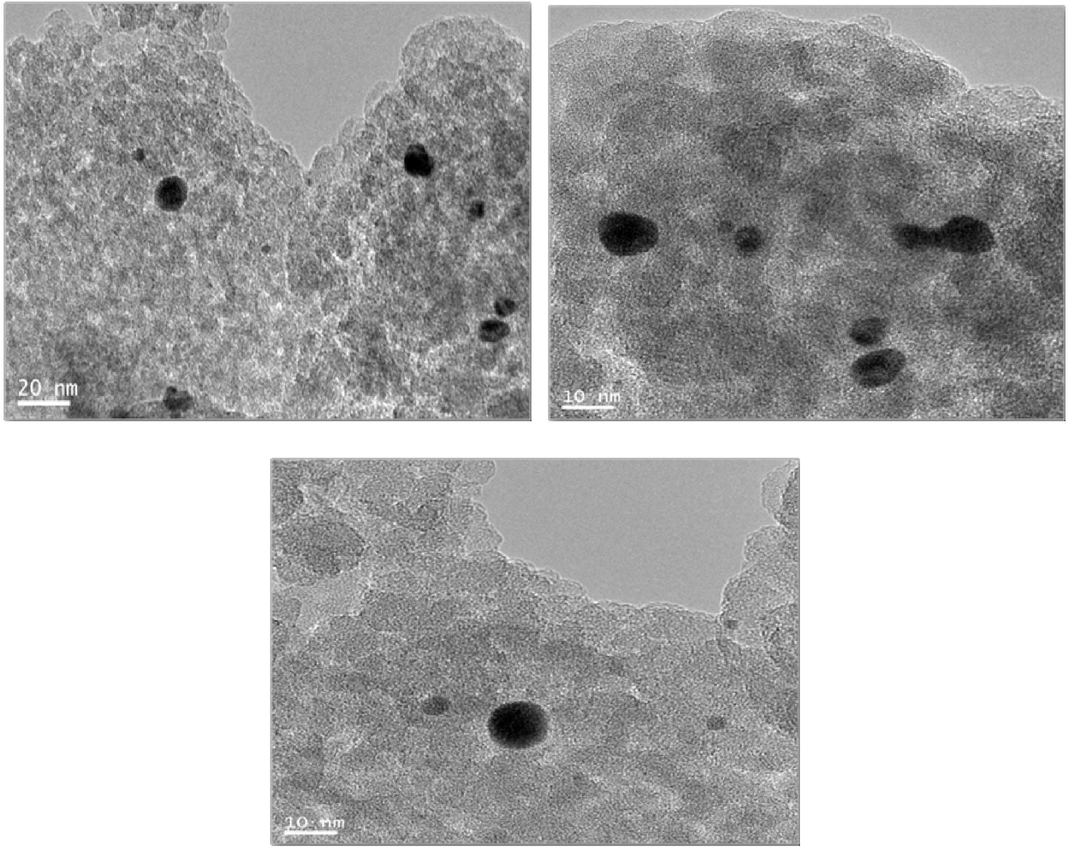


Figure 3. Gold nanoparticles immobilized on the modified silica.

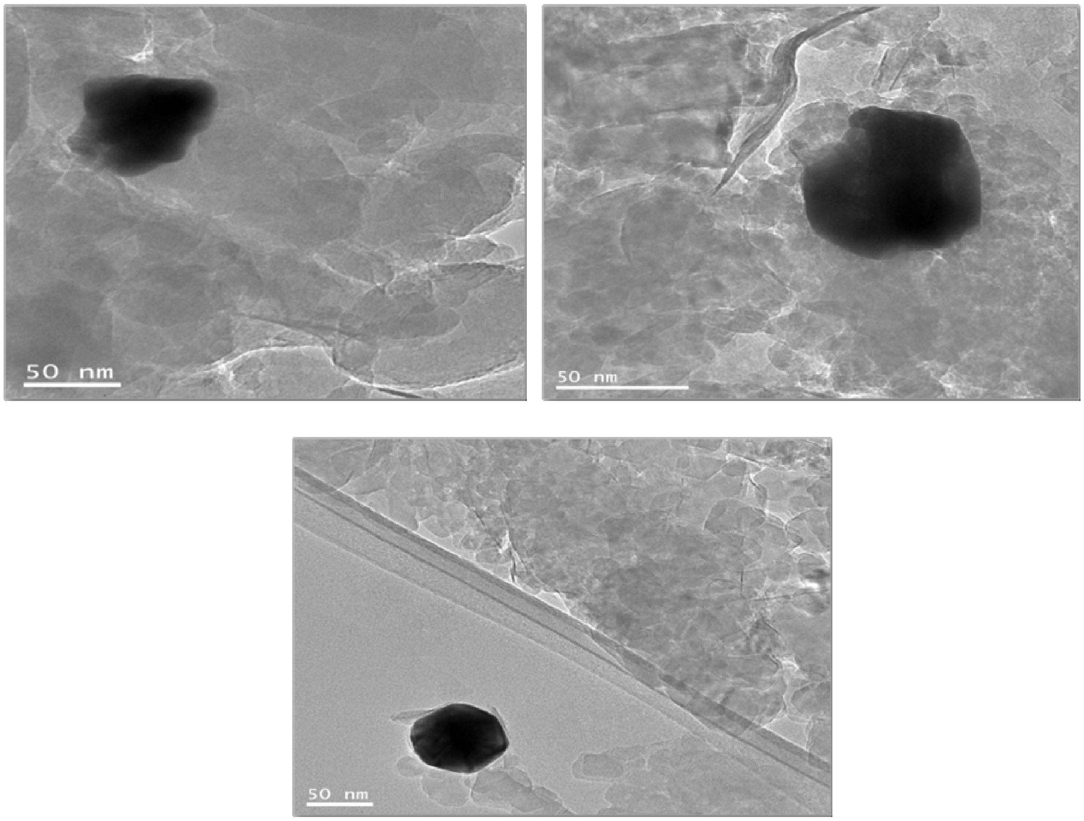


Figure 4. Gold nanoparticles immobilized on the modified bentonite.

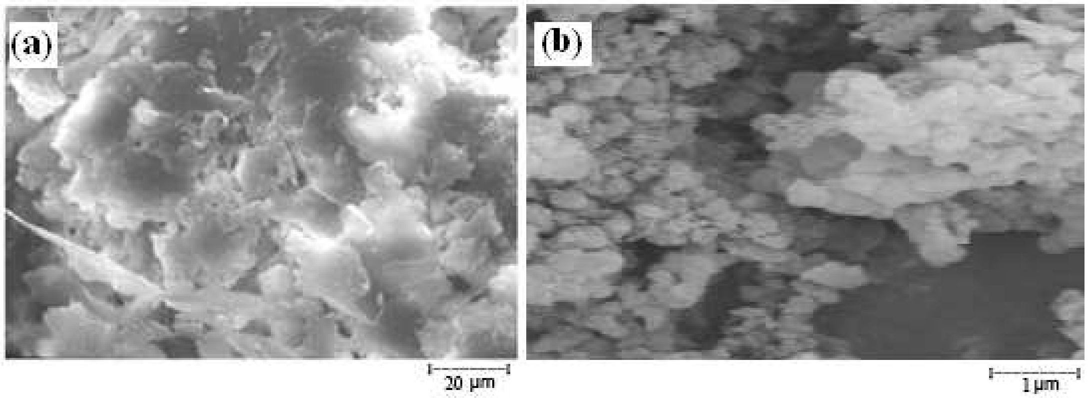


Figure 5. SEM images of (a) MEDPT@CP-bentonite-Au (0), and (b) SiO_2-pA-Acrylate-Thioamide-Au (0) catalysts.

Tables

Table 1. BET analysis for modification of different supports.

Entry	Support	Surface area (m^2/g)
1	Raw Bentonite	63
2	Na-Bentonite	124
3	CP-Bentonite	26
4	MEDPT@CP-bentonite	25
5	Silica gel	480
6	SiO_2-pA-Acrylate	375
7	SiO_2-pA-Acrylate-Thioamide	378

Table 2. Oxidation of cyclohexene over MEDPT@CP-bentonite-Au (0) and SiO_2-pA-Acrylate-Thioamide-Au (0) at various temperatures.

Entry	Catalyst	Temperature ^0C	Conversion %	selectivity Cy-one%	 Cy-ol%	 Others%
1	Au- Bentonite	95	52	51	29	20
	Au- Silica		94	78	0	22
2	Au-Bentonite	80	53	63	34	3
	Au-Silica		92	97	3	0
3	Au-Bentonite	65	37	45	39	16
	Au-Silica		87	74	10	4

Table 3. Effect of the oxygen pressure on the oxidation of cyclohexene.

Entry	Catalyst	Pressure (bar)	Conversion %	selectivity Cy-one%	 Cy-ol%	 Others%
1	Au- Bentonite	15	37	51	30	19
	Au- Silica		87	69	9	22
2	Au-Bentonite	13	38	47	28	25
	Au-Silica		90	81	7	12
3	Au-Bentonite	10	40	46	32	22
	Au-Silica		69	73	8	19
4	Au-Bentonite	8	53	63	34	3
	Au-Silica		52	58	35	7

Table 4. Effect of the reaction time on the oxidation of cyclohexene.

Entry	Catalyst	Time (h)	Conversion %	selectivity		
				Cy-one%	Cy-ol%	Others%
1	Au- Bentonite	16	56	48	31	21
	Au- Silica		93	74	9	17
2	Au-Bentonite	10	53	63	34	3
	Au-Silica		92	81	7	12
3	Au-Bentonite	8	28	52	29	19
	Au-Silica		92	97	3	0
4	Au-Bentonite	6	17	71	27	2
	Au-Silica		80	97	3	0

Reaction conditions: cyclohexene 10 mL; catalyst 0.05 g; 80 °C. Au-Bentonite in 8 bar; Au-Silica in 13 bar.

Table 5. Effect of the amount of the catalyst on the oxidation of cyclohexene.

Entry	amount of catalyst (g)	Conversion %	selectivity		
			Cy-one%	Cy-nol%	Others%
1	Without catalyst	0	0	0	0
2	MEDPT-Bentonite without gold (0.05)	5	35	28	37
	Modified – Silica without gold (0.05)	7	68	10	22
3	Au-Bentonite (0.05)	53	63	34	3
	Au-Silica (0.05)	92	97	3	0
4	Au- Bentonite (0.10)	68	54	25	21
	Au-Silica (0.03)	78	83	7	10

Reaction conditions: Cyclohexene 10 mL; Au-Bentonite, 8 bar; 10 h; 80 ^{0}C; Au- Silica, 13 bar, 8 h, 80 ^{o}C.

Table 6. Recycling of the catalysts.

Cycles	Catalyst	Conversion %	TOF	selectivity		
				Cy-one%	Cy-ol%	Others%
1	Au- Bentonite	53	$3.65*10^{3}$	63	34	3
	Au- Silica	92	$6.15*10^{3}$	97	3	0
2	Au-Bentonite	52	$3.58*10^{3}$	58	33	10
	Au-Silica	90	$6.02*10^{3}$	95	3	2
3	Au-Bentonite	50	$3.44*10^{3}$	53	35	12
	Au-Silica	90	$6.02*10^{3}$	91	4	5
4	Au- Bentonite	41	$2.83*10^{3}$	56	32	12
	Au- Silica	89	$5.95*10^{3}$	91	3	6
5	Au-Bentonite	-	-	-	-	-
	Au-Silica	85	$5.68*10^{3}$	90	2	8

Reaction conditions: Cyclohexene 10 mL; Au-Bentonite 0.05, 8 bar; 10 h; 80 ^{0}C Au-Silica 0.05, 13 bar; 8 h; 80 ^{o}C.

Table 7. Catalyst activities of Au-silica, Au-bentonite and some previously reported catalysts in the cyclohexene oxidation.

Cycles	Catalyst	P_{O2} (bar)	Temperature (ºC)	Reaction time (h)	Conversion (%)	Ketone selectivity (%)	Ref
1	GNPs/TChD[a]	17	80	8	87	70	14
2	GNPs/TChD[a]	17	80	8	72	62	14
1	Au/HNTs[b]	4	80	12	29.5	49	25
4	Au/HNTs[b]	4	80	12	29.5	49	25
1	Au/La-OMS-2[c]	4	80	24	48	44	26
4	Au/La-OMS-2[c]	4	80	24	44	49	26
1	PS-DA-Du [d]	1	70	10	51.9	40.9	22
5	PS-DA-Du [d]	1	70	10	41.6	32.5	22
1	Cr-MCM-41[e]	1	70	24	52.2	71.2	24
4	Cr-MCM-41[e]	1	70	24	41.5	74.2	24
1	Au-Bentonite [f]	8	80	10	53	63	In this work
4	Au-Bentonite [f]	8	80	10	41	56	In this work
1	Au-Silica [f]	13	80	8	92	97	In this work
5	Au-Silica [f]	13	80	8	85	90	In this work

[a] Reaction was done with 50 mg catalyst and 20 mL cyclohexene.
[b] Reaction was done with 200 mg catalyst and 20 mL cyclohexene.
[c] Reaction was done with 200 mg catalyst and 20 mL cyclohexene.
[d] Reaction was done with 2 mg catalyst and 2 mL cyclohexene.
[e] Reaction was done with 20 mg catalyst and 1 g cyclohexene.
[f] Reaction was done with 50 mg catalyst and 10 mL cyclohexene