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Synthesis and characterization of gold nanoparticles supported on thiol

functionalized chitosan for solvent-free oxidation of cyclohexene with

molecular oxygen

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Abstract: The selective liquid phase oxidation of cyclohexene to 2-cyclohexe-1-one and 1,2-cyclohexanediol has been investigated over gold nanoparticles (GNPs) with molecular oxygen in a solvent-free condition. The gold nanoparticles were immobilized on thiolated chitosan derivative (TChD), by grafting thiol groups on the support. The catalyst was characterized by XPS, N₂ adsorption/desorption, TEM, FT-IR and UV-Visible spectroscopy. TEM results show that the majority of Au particles have diameters in the range of 3-6 nm. X-ray photoelectron spectroscopy (XPS) revealed the coexistence of both oxidized and metallic gold species on the surface of TChD. The results show that the catalytic performance of GNPs/TChD is quite remarkable and the catalytic activity over recycled catalyst remains at a high level after at least 4 cycles. Activity tests were carried out in an autoclave at 80 °C without any solvent. In order to obtain maximum conversion, the reaction parameters such as reaction temperature and time were optimized. Under optimized conditions, a maximum of 87% conversion and 70% selectivity was achieved with the GNPs/TChD catalyst.

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Key words: Gold nanoparticles, modified chitosan, cyclohexene, oxidation, solvent free.

1. Introduction

Gold nanoparticles (GNPs), particularly with dimension less than 8 nm [1-5], have been widely used to catalyze many chemical transformations such as selective oxidation of alcohols and hydrocarbons, hydrogenation, dehydrogenation and redox reactions [6-11]. The unique catalytic properties of GNPs in comparison with bulk gold are closely related to their particle size and morphology which provide large surface to volume ratio with respect to the bulk system. However, GNPs are nearly unstable and difficult to separate from the reaction medium when they are used as a catalyst. By immobilizing them on a solid support, the nanoparticles can be effectively protected from aggregation and as a result of this strategy, improvement in selectivity and stability were obtained for many important chemical reactions such as, low temperature oxidation of CO [9, 12-15], oxidation of alcohols [9, 16-19], direct oxidation of hydrogen to hydrogen peroxide [20, 21], epoxidation of alkenes [9, 12, 22-24], oxidation of olefins [4, 9, 25], oxidation of alkanes [9, 26, 27], oxidation of cyclohexane and cyclohexene [9, 27-35]. Extensive studies on the oxidation of cyclohexene have been carried out due to the potential uses of the products, including 2-cyclohexene-1-ol, 2-cyclohexene-1-one and many other chemical intermediates [36]. Cyclohexene oxidation over the Au/C catalyst with oxygen gave a good conversion (approximately 50%) along with many notable products [34]. To improve the conversion and selectivity of Au as catalyst, choice of a support with good physicochemical properties and affinities is very important and plays

crucial role for the overall stability of the supported catalyst. Therefore, we chose modified chitosan (MCh) to improve **the** efficiency of the gold catalyst for cyclohexene oxidation using oxygen as oxidant, and **to** explore the effect of composition of catalysts on oxidation of cyclohexene.

The Chitosan biopolymer (Ch) and its derivatives are nowadays widely used for different purposes. As a naturally-occurring biopolymer, chitosan has many advantages, such as biocompatibility, biodegradability, non-toxicity, etc., which make it an environmental friendly substrate [37, 38]. Various chemical groups of Ch especially its amino groups which can be grafted by different ligands are responsible for siteselective chemical modification, such as Schiff base formation, N-acylation and reductive alkylation [39-41]. These modifications favor the continuous growth of Ch derivatives for various applications fields [40].

One of the chemical modifications of Ch involves grafting thiol groups in the polymer structure. Sulfur-containing covalent and noncovalent linkers (in particular, thiol, -SH) **have attracted** individual attention. Thiol groups due to the soft character of -SH group [42] that lead to the high affinity to gold [42-46], were successfully employed as a linker for anchoring GNPs to the support.

In this paper, we are reporting a new MCh which was synthesized by N-alkylation of Ch with methyl acrylate in the first step, and successively by 1,2-ethanedithiol. We have shown that the synthesized thiolated chitosan derivative (TChD) is a very effective **ligand for anchoring GNPs**. The resulting GNPs/TChD catalyst was compared with GNPs/Ch. The GNPs/TChD catalyst showed a better catalytic performance than

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GNPs/Ch and its related conversion was the highest reported conversion in solvent-free condition and using molecular oxygen as a cheap oxidant for oxidation of cyclohexene.

2. Experimental Section

2.1. Materials and physical measurements

All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. Chitosan (Sigma Aldrich medium molecular weight, 75-85% deacetylated) was used as the polymeric component. Methyl acrylate (MA), auric chloride (AuCl₃) and 1,2-ethanedithiol were purchased from Merck chemical company.

The Fourier transform infrared spectroscopy (FT-IR) analysis was performed using a Fourier transform infrared spectrometer (Jasco FT/IR-680 plus spectrophotometer). The powders were blended with IR-grade KBr in an agate mortar and pressed into tablets. The electronic spectra of solid samples were taken on a JASCO V-550 UV–vis spectrophotometer in the range of 200 to 800 nm, using the diffuse reflectance technique (DR UV–vis spectroscopy).

Particle size and morphology were evaluated from the transmission electron microscopy (TEM) images obtained in a JEM 2100F microscope operated with an accelerating voltage of 200 kV. The standard procedure involved dispersing 4 mg of the sample in ethanol in an ultrasonic bath for 15 min. The sample was then placed on a Cu carbon grid where the liquid phase was evaporated. The average diameter was calculated by measuring the diameters of no less than 500 randomly selected metal particles.

XP spectra were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer (constant pass energy of 50 eV) and a nonmonochromatic (hv = 1253.6 eV) X-ray source, powered at 120 W. Wide scan data were collected using pass energy of 100 eV whereas high energy resolution spectra were recorded using pass energy of 20 eV. As the samples experienced variable degrees of charging the binding energy scale was referenced to adventitious carbon contamination using the C1s line at 284.8 eV. The samples were analyzed after a base pressure of 2 x 10⁻⁹ mbar was reached within the analysis camber. Data processing was performed with the "*XPS peak*" software. The spectra were decomposed with the least squares fitting routine provided with the software, with Gauss/Lorentz lines (90G/10L) and after subtracting a Shirley background. Atomic ratios were calculated from the peak areas using sensitivity factors provided with the data system [47].

Elemental CHNS analysis was performed on a Perkin Elmer Carbon Hydrogen Nitrogen (CHN), 2400 Series II Elemental Analyzer.

The nitrogen adsorption isotherm recorded at -196 °C using a Quantasorb (Quantachrome, USA) equipment. Before nitrogen adsorption, the samples were degassed at 110 °C for 3 h to a residual vacuum of 10⁻³ mbar. The specific areas were calculated by the Brunauer–Emmett–Teller (BET) method using a value of 0.162 nm² for the cross section of adsorbed nitrogen molecule.

2.2. Reaction of methyl acrylate with Ch

Firstly, N-carboxyethyl chitosan methyl ester (CChME) was prepared successfully by the Michael addition as depicted by Scheme 1(A). Briefly, chitosan (2 g) was added to 50 mL methanol, and it was stirred overnight at 50 °C to be dispersed completely. The mixture was transferred to a 100 mL three-necked round-bottom flask fitted with a dropping funnel. Methyl acrylate (48 mmol; 4.3 mL) was dissolved in methanol (5 mL), and added to the reaction mixture dropwise over 10 min through dropping funnel under nitrogen atmosphere. The reaction was monitored using FT-IR spectroscopy. The unreacted methyl acrylate in the reaction mixture was removed completely by washing with methanol in a Soxhlet apparatus.

2.3. Grafting dithioethane to CChME

Once prepared, CChME was grafted with dithioethane. The procedure consisted in dispersing CChME in chloroform in a round bottom flask that was equipped with a reflux condenser. 1,2-ethanedithiol (36 mmol; 3 mL) was added to the reaction mixture, which was refluxed for a period of 24 h. After the completion of the reaction, the product was rinsed several times with pure ethanol to remove unreacted 1,2ethanedithiol and dried under vacuum at 30 °C overnight to obtain thiolated chitosan derivative (TChD) (Scheme 1(B)). The results of the CHNS analysis, FT-IR and XPS spectroscopy (sections 3.1.1, 3.1.2 and 3.1.4, respectively) confirmed the presence of the thiol groups on the support.

2.4. Synthesis of GNPs on TChD

Next step consisted in the preparation of GNPs deposited on the TChD substrate. In a typical experiment, 2 g of the TChD were dispersed into 500 mL of distillated water (containing 2 wt% acetic acid), to which 5 mL of 10⁻² M aqueous solution of AuCl₃ was added in 10 steps to the suspension during 24 h, under vigorous stirring for loading of 0.5 wt% of Au (III). The resulting product was separated via centrifugation, and washed few times with distilled water. The product was dried under vacuum at room temperature before characterization and catalytic activity measurements. In order to prepare 1 wt% of Au (III), 10 mL of aqueous solution of AuCl₃ (10⁻² M) was added to suspension and all of the above processes was repeated again. To obtain the GNPs on the support, after addition of a given amount of aqueous metal salt (AuCl₃) to the suspension, an aqueous NaBH₄ solution (molar ratio of NaBH₄:Au = 10:1) was slowly added under vigorous stirring at room temperature, and left overnight; a bright red color was observed immediately after addition of reductant to the solution. Then the catalyst was separated by filtration, washed with distilled water, left overnight at room temperature and dried in oven at 90 °C.

Chemical reduction of Au (III) loaded on TChD with excess NaBH₄ results in formation of interdendrite-Au clusters (Scheme 1(C)) on TChD. Evidence for this reduction comes from the immediate change in solution color. It is noteworthy to mention that the same procedure was followed for Ch as a support without any modification to compare its catalytic activity with the new synthesized catalyst. The importance of modifying Ch on trapping the Au ions will be discussed in the section 3.1.3.

2.5. The selective oxidation of cyclohexene by molecular oxygen

In a typical experiment, 20 mL of cyclohexene and 50 mg of the solid catalyst were **loaded in** a titanium batch reactor. Proper pressure was provided with oxygen capsule (99.98%) and desired temperature selected and applied to the reaction mixture. After purging with O_2 , the reactor was heated to 80 °C and the O_2 pressure was adjusted to **10 bar**. After a **desired time** (8 or 16 h), the reactor was cooled down to 30 °C and the reaction mixture was separated from the catalyst by centrifugation and analyzed by gas chromatography (Trace GC Ultra) which was fitted with a HP-5 capillary column (25 m×0.32 mm) and a flame ionization detector (FID). Initial temperature = 60 °C, 1 min; final temperature = 250 °C, heating rate = 10 °C/min, temperature of injector = 200 °C, temperature of detector = 280 °C.

The reaction products of oxidation were determined by a GC–MS QP5050 SHIMADZU with CBP20 (25m) capillary column and a FID detector. **The conversion and selectivity** were determined using undecane as an internal standard in all reactions.

3. Results and Discussion

3.1. Characterization of the synthesized catalyst

3.1.1. Elemental analysis data and calculation of deacetylation degree of Ch

There are many methods to determine the degree of deacetylation (DD) of Ch such as FT-IR, titration, ¹H-NMR, elemental analysis, etc [48-50]. The elemental analysis results of original Ch and TChD are shown in Table 1, in which the theoretical values are calculated according to the molecular formula under the condition of 85 % deacetylation. Through the elemental analysis data and according to the following equation (1) [50] the 85 % DD value of Ch was obtained.



Scheme 1. Preparation process for synthesis of catalyst. A) Reaction of methyl acrylate with Ch. B) Grafting dithioethane to CChME C) Formation of interdendrite-Au clusters on TChD.

The carbon/nitrogen ratio (C/N, w/w) would vary from 5.145 to 6.861 for completely Ndeacetylated chitosan and fully N-acetylated chitin, respectively. The experimental data of CHNS analysis is more similar to A $[C_6H_9O_4 (NC_{10}S_4H_{18}O_2)_{0.85} (NHCOCH_3)_{0.15}]$ than B $[C_6H_9O_4 (NHC_5S_2H_9O)_{0.85} (NHCOCH_3)_{0.15}]$. B is the product when the amino groups of Ch reacted with methyl acrylate just once while A is the product obtained when doubly Michael addition of amino group with methyl acrylate occurred. Therefore, according to Scheme 1, nearly all of the deacetylated groups (amine-free groups) in the polymer were to a large extent doubly reacted with methyl acrylate.

Table 1.

	Experimental value				Theoretical value									
Compound					Molecu	ular for	mula A	L	Mole	cular fo	ormula	В	CA	DD0/
	С%	N%	Н%	S%	С%	N%	Н%	S%	С%	N%	Н%	S%	C/N	DD%
Ch	45.19	8.37	6.75	7		-	-	-	-	-	-	-	5.4	85
TChD	42.28	3.02	5.79	26.1	42.39	3.34	5.94	26	43.2	4.8	6.17	18.55	-	-

Elemental analysis (wt. %) of Ch and TChD.

3.1.2. FT- IR data of the synthesized catalyst

Infrared wave numbers (cm⁻¹) of significant stretching vibrations are helpful for identification of the synthesized catalyst (Fig. 1). In Fig. 1(a), **Ch spectrum, the broad band in the region of 3200-3500 cm⁻¹** is attributed to inter- and intra- molecular hydrogen bonded –NH and –OH stretching vibrations. The characteristic peaks at 1654, 1597 and 1375 cm⁻¹ were assigned to the amine and amide groups [40, 46], the key

absorption bands of Ch, respectively. The absorption band at 1152 cm⁻¹ was attributed to the asymmetric stretching of the C–O–C bridges. Bands at 1075 and 1030 cm⁻¹ were assigned to the skeletal vibration of C–O stretching. The increasing intensity of the peak at 2890 cm⁻¹ which is ascribed to C-H stretching, confirms the alkylation of the Ch backbone (Fig. 1b). Compared with the Ch spectrum, CChME in Fig. 1(b) shows strong absorption band at 1729 cm⁻¹ due to the stretching vibration of the ester groups which were formed by the Michael addition reaction of Ch with methyl acrylate. The new peak at 2567 cm⁻¹ in Fig. 1(c), was attributed to the thiol stretching vibration [51-53] in TChD, which confirms the presence of the thiol groups in the MCh.

The appearance of GNPs on TChD could be detected from FT-IR spectroscopy through disappearance of the –SH vibration at 2567 cm⁻¹ as a consequence of the reaction between sulfur and gold nanoparticles (Fig. 1(d)). Other characterization techniques such as UV-Vis spectroscopy and TEM that will be discussed in the next sections were used to detect the appearance of GNPs on the support.

3.1.3. DR UV-Vis spectroscopy and Specific surface area

UV-vis spectra were recorded with aim to reveal changes in the chemical structure of chitosan upon modification and also to provide further evidence on the morphology of Au species. Two absorption bands in the wavelength regions 200-380 nm (zone I) and 400-600 nm (zone II) can be distinguished (Figure 2). In zone I (Fig. 2(a)), Ch shows a strong absorption around 290 nm together with a shoulder at about 370 nm. TChD sample displays a similar bands structure, although it is more intense (Fig. 2(b)). The absorption spectrum for the Au loaded GNP/TChD appears

at 519 nm (Fig. 2(c)) that is quite similar to its Au-free TChD counterpart, except that the shoulder at about 370 nm became more intense. It is likely that the increase in intensity of the shoulder at 370 nm is



Fig 1. FT-IR spectra of a) Ch, b) CChME, c) TChD, d) GNPs prepared on the TChD, the zoomed region is related to the thiol S-H stretching vibrations (pink color) on TChD and elimination of it (red color) as a **result** of the reaction between sulfur and gold nanoparticles in GNP/TChD.

responsible for the the presence of small Au_n clusters (1 < n < 10) [54]. Moreover, the wide band in zone II is usually attributed to the surface plasmon resonance (SPR) of gold nanoparticles which has been proven to be very sensitive to the size, shape, composition and dielectric environment of metal nanoparticles [55-56]. SPR is the optical phenomenon which was observed in transmission when the collective oscillation of conduction electrons (free electrons) on the surface of metal nanoparticles was stimulated by incident light. At the frequency of incident photons, these electrons are set into resonant oscillation. SPR in nanostructures is called localized surface plasmon resonance (LSPR) [58-60]. The color change from yellow in the bulk to red in the nanometer range (13 nm spherical GNPs with bright red color [61]) is the striking evidence for this optical phenomenon The position and intensity of the plasmon peak is affected by the dielectric constant of the surrounding environment [57,58, 62].

According to **bibliography**, GNPs were produced in the presence of Ch by two methods. The method that produces a more uniform distribution of GNPs **consisted in adding the** gold chloride to Ch solution and used excess of NaBH₄ as the **reductant**. In the other method for producing GNPs, Ch itself was used as a **reductant** at high **temperature [63-68]**.

As reported in the literature [69,70], the rate of the nucleation can be affected considerably by the presence of thiols or polymeric thiols. It means that nanoparticle nucleation is accelerated by the presence of polar polymeric thiols, yielding more small particles rather than fewer large ones. Also with larger thiol/gold mole ratio, smaller average core sizes were resulted. With knowledge to this point that TChD consist of a thiol groups which bind tightly to surface of gold

particles can concluded that TChD could be as a controller of nucleation as well as stabilizer. By adding NaBH₄ as a reducing agent, colloidal nucleation is achieved and begins to grow. The solution changed to a bright red color due to the formation of GNPs. After centrifugation, the resultant precipitate was washed several times with deionized water and dried in oven overnight at 100 °C.



Wavelenght [nm]

Fig 2. UV-Vis spectra of a) Ch, b) TChD, c) GNP/TChD.

The specific surface area was determined using Brunauer-Emmett-Teller (BET) method. The surface area of the TChD was determined and compared to Ch. The surface area of Ch was 3 m²/g. After modification of Ch, its surface area did not change significantly and became 2.8 m²/g. After loading metal on TChD, the surface area decreased drastically to $0.4 \text{ m}^2/\text{g}$.

3.1.4. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Successful preparation of the GNPs is evidenced by TEM images (Figures 3a-3d). Fig. 3(a) shows the image of the modified polymeric support before adding gold (III) chloride solution to it. As shown in Fig. 3(b) after adding Au (III) salt to the support, the image **does** not show any particle in a nanometric size which probably means that Au (III) ions were distributed in the polymeric matrix as Au (III) complexes coordinated by different ligands, and they could not be seen because of their atomic size. By adding the reducing agent ie., NaBH₄, metal ions appear to be reduced and start aggregating to some extent. The presence of GNPs on the surface of the polymer was evidenced by detection of dark spots (Fig.3(c)) in comparison with the previous images (Figs 3(a) and 3(b)). In general, the particles were spherical in shape and no aggregation could be identified by TEM images. According to the Fig. 4 the average particle size of the gold nanoparticles was 5.5 ± 2.3 nm and more than 70% of them were in the range of 3-6 nm. In Fig. 3(d), TEM image of the catalyst after the reaction shows aggregation of the nanoparticles that occurred in some regions while in the other regions small nanoparticles still remained.

The surface composition and oxidation states of the metal catalyst were investigated by XPS. Figure 5(a) shows the **Au 4f** core-level spectrum of the GNPs/TChD sample. Each component of the **Au 4f** doublet is asymmetric on the high binding energy side indicating the presence of two different electronic environments of **than 3-4 nm [72, 73]**. Because only 29% of Au particles show sizes above ca. 5 nm, in which no final state effects are expected to appear, and the most intense peak (Au 4f_{7/2} component) of the Au 4f doublet

appears at a BE of 84.5 eV, **This BE value can be associated to** metallic Au species. On the basis of the above reasoning, ionic Au (III) species [74,75] are considered to be responsible for the binding energy of the **Au 4f**_{7/2} **component of the less intense doublet** at 86.0 eV in Fig. 5(a).



Fig 3. TEM images of a) TChD, b) Au(III) on the TChD, c) GNP/TChD, d) GNP/TChD after reaction.



Fig 4. Size distribution of GNP found in the TChD.

Photoelectron spectroscopy also confirmed the presence of S-C bonds of the $HS-C_2H_5$ moieties. The high resolution S 2p of the sample is shown in Fig. 6. This spectrum



Fig. 5. **A4f core-level spectra of**: a) GNPs/TChD b) GNPs/Ch.

shows the most intense S $2p_{3/2}$ component of the S 2p doublet (spin-orbit splitting of 1.2 eV) at a binding energy of 163.4 eV. Although there are claims in literature that the interaction between the mercapto group and gold colloids is through a true chemical bond [76], the binding energy of S $2p_{3/2}$ peak recorded here at 163.4 eV is indicative of the presence of covalent C-S bond of the grafting ethanethiol molecule but in no case originated from S-Au linkages [77-79]. Notwithstanding, as the ethanethiol molecule still remain adsorbed on the catalyst surface under the ultrahigh vacuum conditions under which the electron spectrometer operates during analysis, it can be inferred that the thiol group interacts strongly chemisorbed on the surface. It is interesting to note that by impregnating the Au (III) ions on the unmodified Ch and reducing them by NaBH₄, the catalyst contains only Au (0) as revealed by the binding energy of Au $4f_{7/2}$ component of the Au 4f doublet at 84.0 eV. According to Fig. 5(b), the observed binding energy of Au $4f_{7/2}$ component of the Au 4f doublet at metallic gold species on the Ch without any modifying group at 84.0 eV is conclusive that metallic gold is the only Au species.



Fig. 6. S2p core-level spectrum of the GNP/TChD.

Table 2 compiles the surface atomic ratios of gold-based samples. These data indicate that surface composition changes markedly upon Ch modification. At a first glance, it is clear that the value of S/C ratio is much higher for the TChD than for the non-modified Ch counterpart. The extent of Au loading on the surface of TChD has become nearly 6 times more than while using Ch alone as a support. This result suggests that catalytic performance of support will increase in parallel by modifying it with the thiol ligands. As opposite, the atomic ratio of N/C in Au/TChD decreased as a consequence of increasing C backbone over the surface of Ch upon modification with methyl acrylate and 1,2-ethanethiol. Similar reasoning applies for the decreasing O/C atomic ratio in the Au/TChD sample.

Table 2.

Entry	sample	O/C at	S/C at	N/C at	Au/C at
1	Ch-Au	0.381	0.004	0.061	0.0020
2	TChD-Au	0.205	0.357	0.026	0.0117

Surface atomic ratios of gold-based samples

3.2. Catalytic performances

3.2.1. Effect of catalyst composition and temperature

Oxidation of cyclohexene was carried out over different Au-loaded catalysts. The results summarized in Table 3 indicate that the conversion of cyclohexene oxidation with the catalyst containing 1 wt% Au(III) was higher than with the one containing 0.5 wt % Au (III) although no significant changes were observed in the selectivity of the two catalysts.

The effect of different oxidation states of Au on the performance is also shown in Table 3. Au (0) displayed 16 % higher cyclohexene conversion than Au (III) (entries 5, 6). However, if the higher conversion of Au(0) is not considered, at 80 °C the Au(III) catalyst showed better selectivity. As the extent of Au adsorption on the surface of TChD was higher than on Ch (Table 2), one would expect a higher activity for GNPs/TChD catalyst than for the Au/Ch one. Such a trend on the oxidation of cyclohexene is confirmed with data collected in Table 3. The conversion of cyclohexene on GNPs/TChD (Table 3, entry 6) was about 1.5 times higher than on the GNPs/Ch catalyst (Table 3, entry 3). Moreover, a blank experiment with the Au-

free TChD sample revealed negligible conversion of cyclohexene (Table 3, entry 2). The influence of the reaction temperature on the catalytic performance of GNPs on TChD was also studied. Table 3 summarizes results of the cyclohexene oxidation at 60, 80, 100 and 120 °C (entries 6-10).

Table 3.

Entry	Catalyst	Temperature	Conversion	Selectivity (%)		b)
		(°C)	(%)	ketone	diol	others
1	Blank	80	No reaction	-		
2	TChD without Au ^a	80	6.2	68	2	30
3	1% wt Au(0)/Ch ^b	80	57	69	1	30
4	0.5 % wt Au(III)/TChD ^b	80	51	57	28	15
5	1 % wt Au(III)/TChD ^b	80	64	65	27	8
6	1 % wt Au(0)/TChD ^b	80	80	70	14	18
7	1 % wtAu(0)/TChD ^b	60	67	66	11	23
9	1 % wt Au(0)/TChD ^b	100	57	62	33	5
10	1 % wt Au(0)/TChD ^b	120	38	33	37	30

Effect of the type of catalyst and temperature on the oxidation of cyclohexene

^a reaction condition: 0.05 g of catalyst, 20 mL of cyclohexene, **P**₀₂: 10 bar, reaction time: 16 h.

^b reaction condition: 0.05 g of catalyst, 20 mL of cyclohexene, P_{02} : 10 bar, reaction time: 8 h.

The reaction temperature has a great impact on both activity and selectivity. By increasing the reaction temperature to 80 °C, selectivity and conversion increased significantly, however if the reaction is performed at higher temperature (>80°C), both the conversion and selectivity decreased slightly. These results suggest that at higher

temperatures, the Au nanoparticles tend to aggregate on the surface of TChD. This inference is supported by a TEM image of GNPs on TChD (Figure 7).



Fig 7. TEM image of GNPs on TChD after performing the reaction at 120°C.

3.2.2. Effect of oxygen pressure

The optimal operation pressure has been identified. As shown in Fig. 8, the increase of oxygen pressure increased the conversion of cyclohexene, and such increase of the conversion occurred in the range of oxygen pressure 5-10 bar with of GNPs/TChD catalyst. Product distribution did not change more and it remained nearly constant upon increasing oxygen pressure.



Fig 8. Effect of the oxygen pressure on the oxidation of cyclohexene. Reaction conditions: amount of catalyst: 50 mg, reaction temperature: 80°C, reaction time: 8 h under the solvent free condition.

3.2.3. Effect of reaction time

Fig. 9 shows the effect of time on the cyclohexene oxidation with molecular oxygen over the GNPs/TChD catalyst. By increasing the time of the reaction from 4 to 8 h, the cyclohexene conversion and selectivity to 2-cyclohexene-1-one was increased, and almost kept unchanged after this time.

3.2.4. Effect of amount of catalyst and solvent effect

To study the effect of amount of **GNPs/TChD**, the oxidation reaction was carried out at 80 °C, oxygen pressure: 17 bar and the reaction time of 8 h. **From** the results

summarized in Table 4, it is seen that catalyst loading of 50 mg is appropriated to run the reaction. With increasing the amount of the catalyst a slight decrease in the conversion was observed.



Fig 9. Effect of the reaction time on the oxidation of cyclohexene. Reaction conditions: amount of catalyst: 50 mg, reaction temperature: 80°C, oxygen pressure: **17 bar** under the solvent free condition.

The solvent effect was studied with 1,2-dichloroethane because we demonstrated in our previous work [80] 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.

Table 4.

Entry	Amount of catalyst (mg)	Conversion (%)	Selectivity (%)		
			Ketone	Diol	others
1	10	65	65	23	12
2	30	77	69	28	3
3	50	87	70	27	3
4	100	40	45	21	24

Effect of the amount of the catalyst on the oxidation of cyclohexene.^a

^a All reactions were done with 20 mL cyclohexene, at 80 °C, reaction time = 8 h, and the pressure of oxygen was **17 bar**.

3.3. 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 5. Data showed that the selectivity of the reused 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. [81]. 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.

Schiff-base metal complexes supported on polymeric material such as chloromethylated polystyrene supported tridentate Schiff-base metal complexes (PS–DA–M) ($M=Cu^{2+}$, Co^{2+} , Ni^{2+} and Mn^{+2}) [31], PAMAMSA-Mn (II) metallodendrimers based on polyamidoamine (PAMAM) [82], CrMCM-41 [32], Au/HNTs [29] and Au/La-OMS-2 [30] are some examples of catalysts **which** have been used for oxidation of cyclohexene under solvent-free condition with molecular oxygen. The data in Table 5 compares the results obtained over GNPs/TChD and other catalysts used for this reaction. As shown in Table 5, the catalyst used in the present study might be one of the best catalysts in respect of oxidation of cyclohexene to 2-cyclohexene-1-one.

4. Conclusion

In this research, we have successfully prepared TChD as a new support for stabilizing of GNPs and preventing their aggregation. The size of these nanoparticles was in the range of 5.5 ± 2.3 nm. These particles were well dispersed and had an excellent activity toward the oxidation of cyclohexene. The conversion and selectivity of this reaction were 87% and 70% at the optimum conditions under the solvent free condition with molecular oxygen.

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Table 5.

Catalytic activities of GNPs/TChD and some previously reported catalysts in the cyclohexene oxidation.

Cycles	Catalyst	P_{O2} (bar)	Temperature	Reaction	Conversion	Ketone	Ref
			(°C)	time (h)	(%)	selectivity (%)	
1	GNPs/TChD ^a	17	80	8	87	70	This work
2	GNPs/TChD ^a	17	80	8	87	70	This work
3	GNPs/TChD ^a	17	80	8	87	70	This work
4	GNPs/TChD ^a	17	80	8	85	69	This work
5	GNPs/TChD ^a	17	80	8	73	65	This work
6	GNPs/TChD ^a	17	80	8	72	63	This work
7	GNPs/TChD ^a	17	80	8	72	62	This work
1	Au/HNTs ^b	4	80	12	29.5	49	29
4	Au/HNTs ^b	4	80	12	29.5	49	29
1	Au/La-OMS-2 ^c	4	80	24	48	44	30
4	Au/La-OMS-2 ^c	4	80	24	44	49	30
1	PS-DA-Cu ^d	1	70	10	51.9	40.9	31
5	PS-DA-Cu ^d	1	70	10	41.6	32.5	32
1	CrMCM-41 ^f	1	70	24	52.2	71.2	32
4	CrMCM-41 ^f	1	70	24	41.5	74.2	32

^a Reaction was done with 50 mg of catalyst and 20 mL of cyclohexene.

^b Reaction was done with 200 mg of catalyst and 20 mL of cyclohexene.

^c Reaction was done with 200 mg of catalyst and 20 mL of cyclohexene.

^d Reaction was done with 2 mg of catalyst and 2 mL of cyclohexene.

^fReaction was done with 20 mg of catalyst and 1 g of cyclohexene.

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Highlights

▶ gold nanoparticles supported on thiol functionalized chitosan. ▶ Liquid phase oxidation of cyclohexene to 2-cyclohexene-1-one and 1,2-cyclohexanediol. ▶ The highest conversion and highest selectivity to 2-cyclohexene-1-one reported. ▶ TEM images show that the immobilized gold nanoparticles have diameter around 3-6 nm.

Graphical abstract

