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Self-assembly preparation of Au/SiO_2 catalyst and its catalysis for cyclohexane oxidation with air

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Abstract Au/SiO_2 catalysts were prepared by self-assembly technique and characterized by EDS, XRD, XPS, AAS and N_2 adsorption/desorption. They were found to be very efficient catalysts for the selective oxidation of cyclohexane with air in the absence of any solvent or promoter. The influences of Au loading, reaction temperature, reaction pressure and reaction time on the catalytic activity were explored in detail. Under suitable reaction conditions, the conversion of cyclohexane and total selectivity of cyclohexanone and cyclohexanol were up to ~ 10 and $\sim 92\%$, respectively.

Keywords Self-assembly · Au/SiO_2 · Air · Oxidation · Cyclohexane

Introduction

For a long time, gold was considered to be a poor catalyst due to its electronic configuration of noble metal, which is usually accompanied by very low activity [1]. However, the study of catalysis by gold has attracted increasing interest since

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Haruta et al. [2] reported that CO oxidation could be achieved at room temperature over gold catalysts when very small gold nanoparticles were dispersed on suitable oxide supports. So far, the catalytic activity of gold has been recognized for a variety of reactions, such as epoxidation of propylene, NO_x reduction, the water–gas shift, selective hydrogenation of acetylene, and reactions involving halogens [3–5].

Oxidation of cyclohexane is one of the most important commercial reactions among the liquid phase oxidation of alkanes, owing to the large demand for its oxidized products, cyclohexanone and cyclohexanol. They are important raw materials for the production of adipic acid and caprolactam finally used in the manufacture of nylon-6 and nylon-66 polymers [6, 7]. Furthermore, they are also very useful as stabilizers, homogenizers, solvents and in the synthesis of various pharmaceuticals, insecticides, and herbicides [8, 9]. Traditional oxidants consist of NaClO, H_2O_2, PhIO and alkyl hydroperoxides, but the use of molecular oxygen, which is the most inexpensive, abundant and readily available oxidant, provides a better option for replacing oxygen donors because of its economic and environmental virtues. Unfortunately, the technology with which cyclohexane is oxidized by molecular oxygen to produce cyclohexanone and cyclohexanol has not been improved very well up to now, especially not with the use of air. In recent years, supported gold catalysts, including Au/MCM-41, Au/SBA-15, Au/ZSM-5 and Au/Al_2O_3, have shown high activity in performing the selective cyclohexane oxidation using molecular oxygen [10–15], though their performance still needs to be improved.

Many approaches have been developed to prepare supported gold catalysts, such as impregnation [16], coprecipitation [17], precipitation-deposition [18], ion exchange [19], microemulsion [20] and so on [21–23]. The former three are the most commonly used methods. However, various parameters, for example the Au precursor, the nature of the support, the reaction conditions, particularly the preparation method and the size of gold particles, have already been considered as crucial factors influencing the structure and catalytic activity of gold containing systems [24–28]. From this point of view, developing a new preparation method of supported gold catalyst to better activate the reaction between molecular oxygen and cyclohexane continues to be of far-reaching significance.

The present work is aimed at preparing active Au/SiO_2 catalysts by using gold nanoparticles and nanosilica supports functionalized with sulfhydryl groups. Compared with known preparation methods, this self-assembly technique shows outstanding advantages in controlling the size, loading and dispersion of the Au active component. In addition, this catalyst exhibits a relatively high activity for cyclohexane oxidation using air, without any addition of solvent, initiator, reductant or co-catalyst.

Experimental

Catalyst preparation

All the reagents with A.R. grade were directly used in the preparation of catalysts and the oxidation of cyclohexane without further purification. SiO_2 supports with a particle size of ~70 nm were synthesized according to the literature method [29]. Spherical gold colloidal nanoparticles with an average diameter of about 6 nm were prepared following a published procedure [30].

Seven mg nanosilica was stirred in the mixed solution of 100 mL toluene and 5 mL 3-mercaptopropyltrimethoxysilane (MPTMS). The slurry was refluxed for 24 h to get thiol-terminated nanosilica. After that, the as-prepared powder was collected and rinsed with copious amounts of toluene and methanol. Note that it is very important to remove the excess of MPTMS from the modified silica to prevent gold particle aggregation during the next step. According to the Au loading, 0.1 g thiol-terminated nanosilica was added in some amount of the gold colloidal suspension with stirring overnight. Then, the solid was filtered, washed with distilled water until free from Cl^- against $AgNO_3$ solution, dried under vacuum at 50 °C for 8 h, and finally calcined in air at 500 °C for 2 h.

Characterization techniques

The elemental analysis of samples were measured by a scanning electron microscope (SEM, Hitachi S-570) equipped with X-ray energy dispersive spectrometer (EDS). The phase compositions of the obtained samples were examined by X-ray diffraction (XRD) patterns on a Bruker D8 Advance diffractometer with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) measurement was performed in a VG Scientific ESCALAB Mark instrument. The C(1s) level was used as an internal reference at 284.6 eV. The amounts of Au loaded on SiO_2 were analyzed by atomic absorption spectroscopy (AAS, Varian 240FS). N_2 adsorption/desorption isotherms were obtained at −196 °C on an Omnisorp 100CX instrument, and pore size distributions were determined from desorption branch of the isotherms with the Barrett–Joyner–Halenda (BJH) method.

Cyclohexane oxidation with air

All cyclohexane oxidations were carried out according to the following procedures: 0.01 g Au/SiO$_2$ and 4 mL cyclohexane were put into a 100 mL autoclave reactor. Then the mixture was stirred and heated to the reaction temperature after having been sealed up. Once the temperature had equilibrated, air was pumped into the system continuously and the pressure was kept at a certain value. After the reaction, the autoclave was cooled to room temperature and slowly depressurized. Product samples were identified and quantified immediately by gas chromatography (GC) with the internal standard method using chlorobenzene as the standard substance [31]. Blank cyclohexane oxidation reactions without catalyst and over pure SiO$_2$ supports were also carried out. To study the reuse of the as-prepared Au/SiO$_2$ catalyst, the most recently used catalyst was separated from the reaction mixture, washed with alcohol, dried at ambient temperature, and then put into the next catalytic cyclohexane oxidation.

Results and discussion

Catalyst characterization

EDS study

Fig. 1 shows the EDS spectrums of original SiO_2 supports (a), MPTMS functionalized SiO_2 supports (b), MPTMS/SiO_2-supported Au compound (c), and Au/SiO_2 catalyst after calcination at 500 °C (d). It is obvious that sulfur element in sample b originates from MPTMS. Even though Au nanoparticles have been assembled on the MPTMS functionalized SiO_2 supports, the sulfur element is still present. The high temperature curing process basically removes the sulfur element, and pure Au/SiO_2 catalyst is finally obtained. Digital photographs of MPTMS functionalized SiO_2 supports (a) and MPTMS/SiO_2-supported Au compound (b) are given in Fig. 2. It can be seen that MPTMS/SiO_2 is light gray before reacting, but its color becomes deep red after immobilizing Au nanoparticles. On the basis of the above data, we can conclude that in our system, Au nanoparticles are really immobilized on the surface of thiol-functionalized silica through the strong Au–S bonds. Their existence has been confirmed by many previous works, where the bonding of thiols to gold surfaces was exploited [32–36]. The procedure for preparing Au/SiO_2 catalyst is shown in Scheme 1.

XRD characterization

Fig. 3 shows the XRD patterns of the Au/SiO_2 catalysts prepared with different Au loadings. When the Au loading is below or equal to 4%, the XRD pattern only exhibits a diffraction in 15–30° in 2θ, which corresponds to the amorphous SiO_2. A possible reason is that gold particles with smaller size uniformly disperse on the supports, leading to the highly dispersed Au diffraction peak. However, when the Au loading is raised to 5%, the XRD pattern shows two wider diffraction peaks of gold. At this time, the Au particle size is about 6.3 nm estimated by the Scherrer formula.

This result indicates that Au nanocrystals are highly dispersed on the SiO_2 supports without any significant agglomeration or sintering to bigger particles. Therefore, this kind of Au/SiO_2 catalyst should be beneficial for cyclohexane oxidation according to the previous literatures, which reported that gold can be catalytically active on inactive supports only when it is at a highly dispersed state [37], and only the methods that able to produce small gold particles on oxide supports can lead to performing catalysts [24, 38].

XPS measurement

XPS spectra of Au/SiO_2 were performed and shown in Fig. 4. The peaks of Au4$f_{7/2}$ and Au4$f_{5/2}$ on Au/SiO_2 are centered at 83.5 and 87.2 eV, respectively, which is associated with metallic gold species [39].

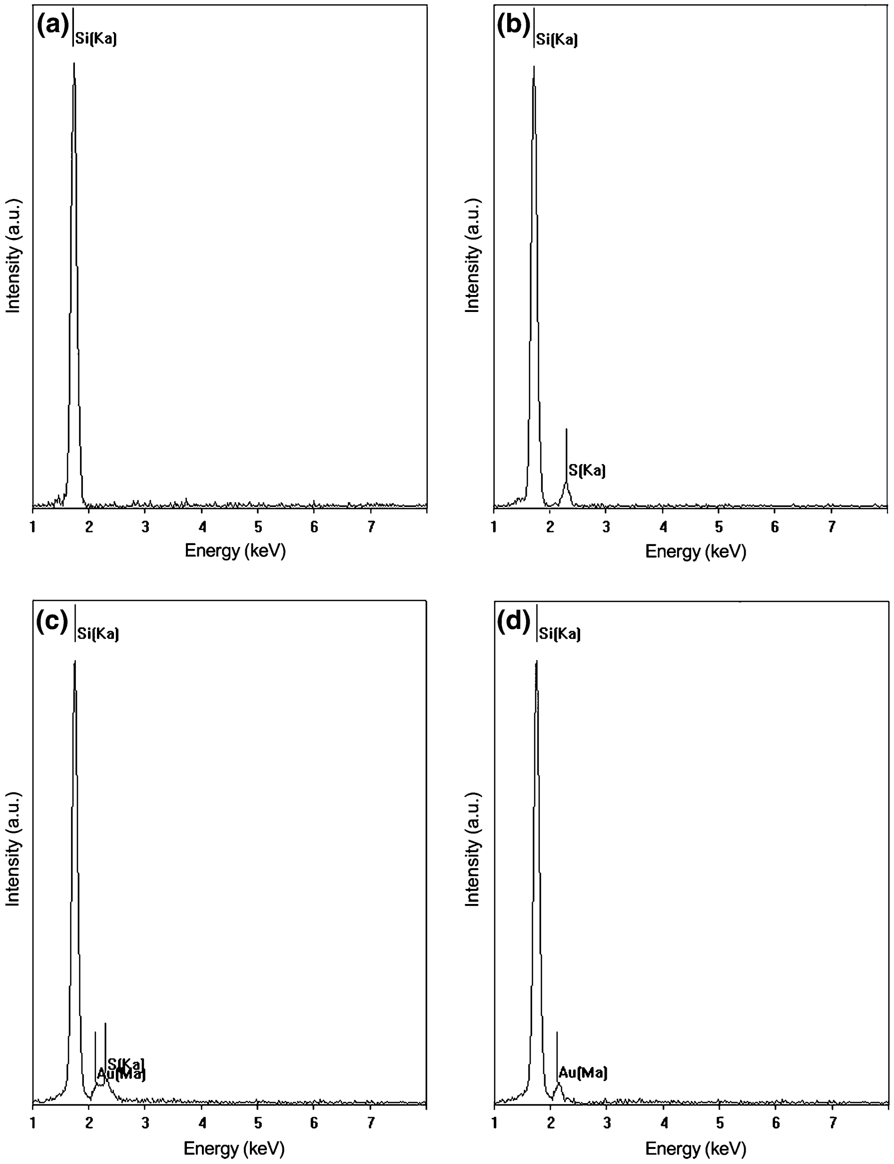


Fig. 1 EDS spectrums of **a** SiO$_2$; **b** MPTMS/SiO$_2$; **c** 5% Au-MPTMS/SiO$_2$; **d** 5% Au/SiO$_2$

AAS analysis

Au loading (wt%) determined by AAS and calculated Au loading rate are listed in Table 1. As observed in Table 1, using the self-assembly preparation method can make Au nanoparicles support on the SiO$_2$ supports effectively, obtaining a high Au loading rate.

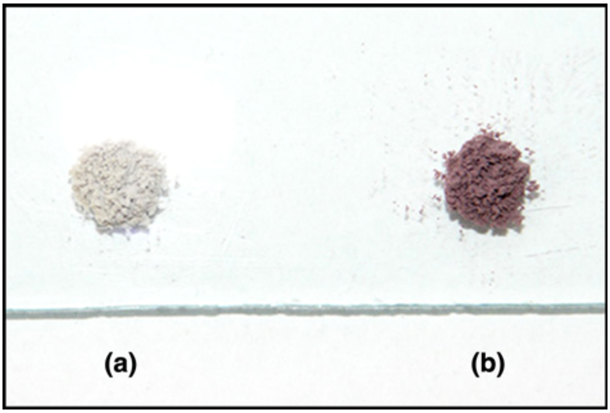
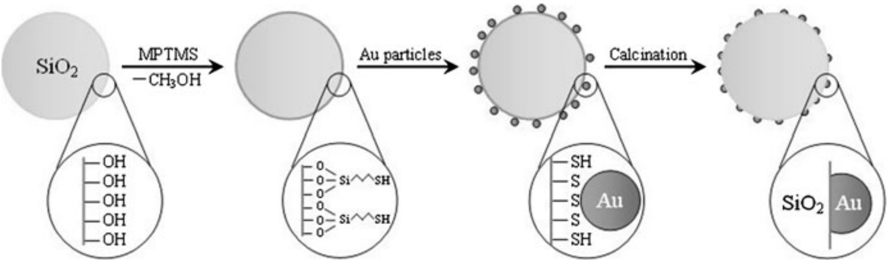


Fig. 2 Digital photograph of different samples. **a** MPTMS/SiO_2; **b** 5% Au-MPTMS/SiO_2



Scheme 1 Schematic representation for the formation of Au/SiO_2 catalyst by self-assembly technique

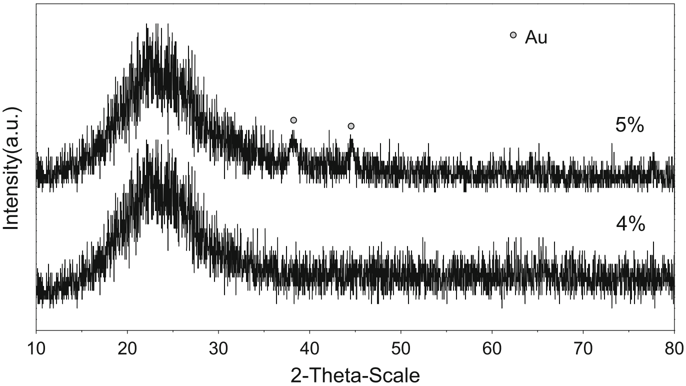


Fig. 3 XRD patterns of the Au/SiO_2 catalysts prepared with different Au loadings

Textural properties

Fig. 5 depicts the N_2 adsorption/desorption isotherms and the corresponding pore size distributions of SiO_2 and 5% Au/SiO_2. As shown, pure SiO_2 and 5% Au/SiO_2

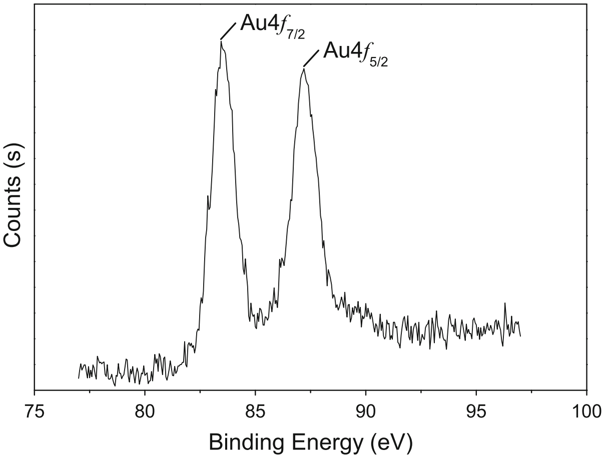


Fig. 4 XPS spectra at Au 4*f* regions of 5% Au/SiO$_2$ catalyst

Table 1 Au loading (wt%) determined by AAS and calculated Au loading rate

Sample	wt%		Loading rate (%)
	Theoretical value	Measured value	
1% Au/SiO$_2$	1.0	1.00	100
3% Au/SiO$_2$	3.0	2.98	99.3
5% Au/SiO$_2$	5.0	4.95	99.0

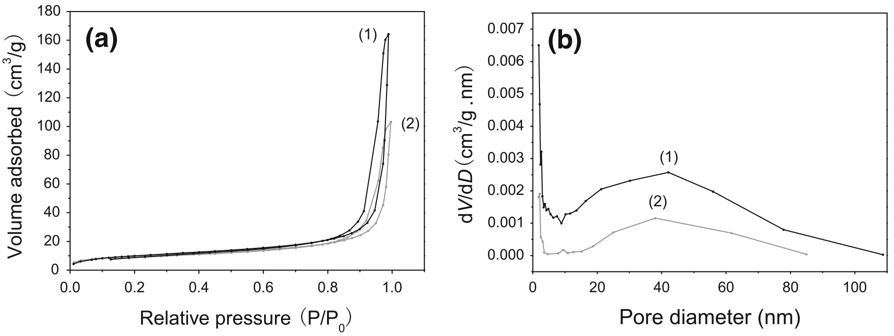


Fig. 5 **a** N$_2$ adsorption/desorption isotherms and **b** pore size distribution of the samples. (*1*) SiO$_2$; (*2*) 5% Au/SiO$_2$

exhibit similar N$_2$ adsorption/desorption isotherms of type H1 following the IUPAC classification [40]. The narrow hysteresis loops and almost parallel adsorption–desorption branches indicate that pores of the samples are both cylinder-shaped. After gold nanoparticles were loaded, the pore diameter peak value of SiO$_2$ reduces from 42.13 nm to 38.04 nm; the pore volume also decreases from the original 0.070 cm^3 g^{-1} to 0.023 cm^3 g^{-1}; the specific surface area drops sharply to

23.58 m^2 g^{-1} from 36.04 m^2 g^{-1}. That is to say, loading gold in this way resulted in dramatic decrease of specific surface area and pore volume. The decrease of pore diameter can be accounted for by the dispersion of gold nanoparticles within the channels of SiO_2 [13].

Catalytic cyclohexane oxidation over Au/SiO_2

Blank tests were performed in the absence of catalyst and presence of pure SiO_2 supports, under the conditions of reaction temperature 150 °C, 3.0 MPa air and reaction time 4 h. However, almost no cyclohexane conversion can be monitored after these reactions, which are similar to the experimental results reported by Lü et al. and Reddy et al. [10, 41].

Effect of Au loading

We used the Au/SiO_2 catalysts with different gold content to study the effect of Au loading on the aerobic oxidation of cyclohexane. The experimental results are presented in Fig. 6. With increasing Au loading, the conversion of cyclohexane increased, while the total selectivity of cyclohexanone and cyclohexanol slightly decreased. The reason may be that when the Au loading is lower, there are fewer active sites on the Au/SiO_2 catalyst, but enhancing the gold content can cause much more active sites disperse evenly on the SiO_2 supports. Finally, 1% Au/SiO_2 was chosen to test other catalytic properties of Au/SiO_2 catalysts, owing to the biggest ratio of cyclohexanone to cyclohexanol (4.27) at this moment.

Effect of reaction temperature

Fig. 7 shows the influence of reaction temperature. When the reaction temperature increased from 130 to 190 °C, the conversion of cyclohexane sharply increased. In

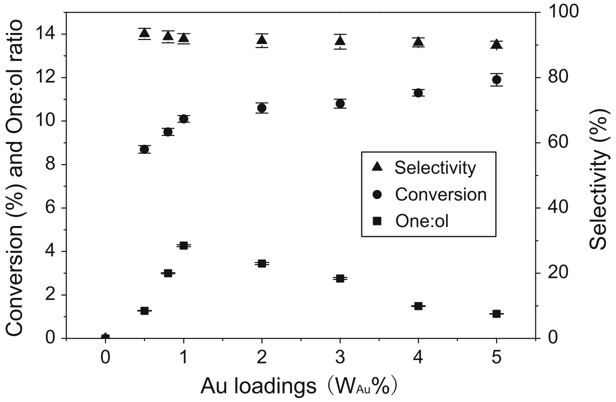


Fig. 6 Influence of Au loading on cyclohexane oxidation. (Standard *error bars* are indicated) Reaction conditions: 3.0 MPa; 150 °C; 4 h

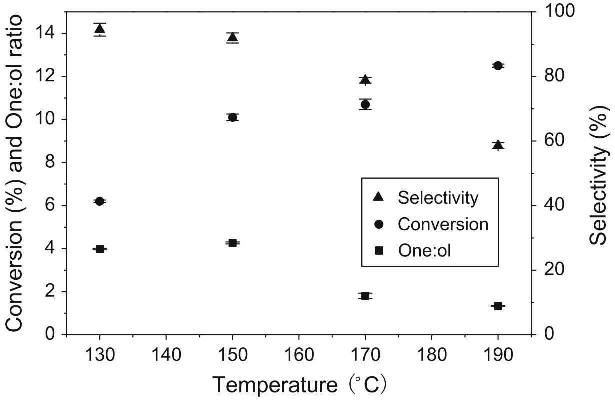


Fig. 7 Influence of reaction temperature on cyclohexane oxidation. (Standard *error bars* are indicated) Reaction conditions: 3.0 MPa; 4 h

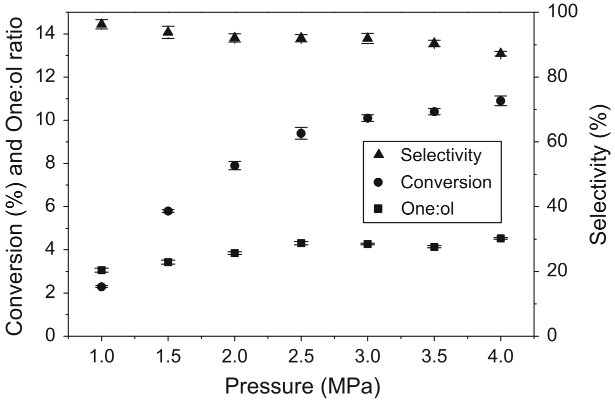


Fig. 8 Influence of reaction pressure on cyclohexane oxidation. (Standard *error bars* are indicated) Reaction conditions: 150 °C; 4 h

contrast, the total selectivity of cyclohexanone and cyclohexanol and the ratio of cyclohexanone to cyclohexanol decreased with reaction temperature. 12.5% of cyclohexane conversion and 60.0% of cyclohexanone and cyclohexanol selectivity were obtained at 190 °C. It is evident that the higher reaction temperature is unbeneficial to get the target products of catalytic cyclohexane oxidation, due to the decomposition and deep oxidation of cyclohexane at higher temperature. Considering all factors synthetically, 150 °C was chosen as the best reaction temperature.

Effect of reaction pressure

At the optimum temperature, the effect of reaction pressure on cyclohexane oxidation was explored. As shown in Fig. 8, with an increase in the air pressure, the conversion of cyclohexane increased, while the total selectivity of cyclohexanone

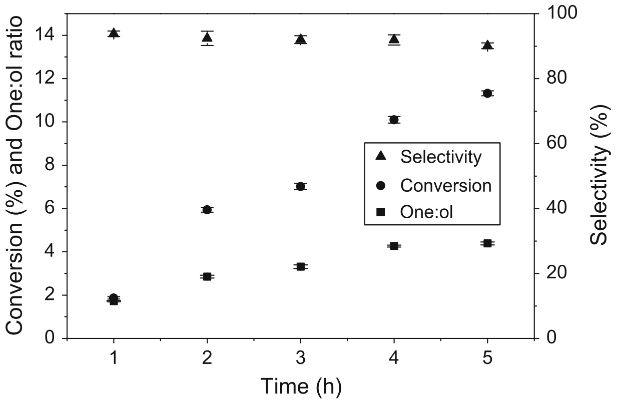


Fig. 9 Influence of reaction time on cyclohexane oxidation. (Standard *error bars* are indicated) Reaction conditions: 3.0 MPa; 150 °C

and cyclohexanol decreased. Only the ratio of cyclohexanone to cyclohexanol had little change. This is because the oxygen concentration is promoted by high pressure, which is advantageous for forward reaction. Based on the data, 3.0 MPa was defined as the optimum pressure of the reaction when all other factors were fixed.

Effect of reaction time

Fig. 9 illustrates the effect of reaction time over Au/SiO_2. It can be seen that the conversion of cyclohexane and the ratio of cyclohexanone to cyclohexanol smoothly increased with time, while the total selectivity of cyclohexanone and cyclohexanol was downtrend. Obviously, the longer reaction time is unfavorable for the selective production of cyclohexanone and cyclohexanol because of more by-products. At the optimum reaction time (4 h), the Au/SiO_2 catalyst showed 10.1% cyclohexane conversion, and 91.9% selectivity for cyclohexanone and cyclohexanol.

Recycling studies

Recycling tests with repeated use of 1% Au/SiO_2 in four consecutive reactions were carried out under the typical reaction conditions. It can be seen from Fig. 10 that with every run, the total selectivity and the ratio of cyclohexanone to cyclohexanol changed slightly, but the conversion of cyclohexane gradually dropped from 10.1 to 7.53%. The decrease in activity probably related to the unavoidable loss of Au active component and surface carbon depositions on the catalyst. The change of Au content in four consecutive reactions (Table 2) partially confirms our conjecture. As can be seen, the loss of Au was relatively great after Au/SiO_2 was used for the first time, whereas Au content was still above 0.9% even after repeated use for 4 times.

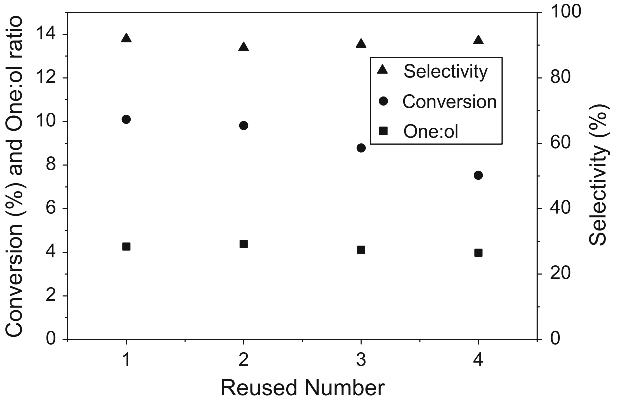


Fig. 10 Repeated use of the 1% Au/SiO$_2$ catalyst. Reaction conditions: 3.0 MPa; 150 °C; 4 h

Table 2 Au content in 1% Au/SiO$_2$ catalyst in four consecutive reactions

Reused number	Au content (wt%)	Au loss index (%)
1	0.947	5.3
2	0.928	2.0
3	0.915	1.4
4	0.906	0.98

Conclusions

Gold nanoparticles supported on nanosilica were prepared by a novel self-assembly technique. Experimental results indicate that this catalyst is effective for the oxidation of cyclohexane with air. 1% Au/SiO$_2$ yielded a maximum of 10.1% of cyclohexane conversion, 91.9% of selectivity for cyclohexanone and cyclohexanol under the suitable conditions of reaction temperature 150 °C, 3.0 MPa air, reaction time 4 h.

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