



## Short Communication

## Solvent-free oxidation of cyclohexene over catalysts Au/OMS-2 and Au/La-OMS-2 with molecular oxygen

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## ABSTRACT

Supported gold catalysts Au/OMS-2 and Au/La-OMS-2 were prepared and used for liquid phase oxidation of cyclohexene with oxygen as an oxidant. These catalysts were characterized by XRD, SEM, TEM and EDX. The reactions were carried out in an autoclave at 80 °C without any solvent. Effects of Au content and La content on catalytic performance were studied. Au/La-OMS-2 (0.24) was found to be an efficient catalyst for the oxidation of cyclohexene with a high conversion (48.0%). More than 86% selectivity for  $\Sigma C_6$  (including cyclohexene oxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one) was obtained.

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## 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]. Traditionally, these catalytic procedures produced a great deal of environmentally undesirable wastes [2–4]. It is highly desirable to replace the traditional process by a green procedure [5,6]. There are many easily available oxidants including molecular oxygen and  $H_2O_2$ . Although the use of  $H_2O_2$  is atom efficient and the only by-product is water, compared with molecular oxygen, the relatively high cost of  $H_2O_2$  severely hinders its wide application in catalytic oxidation [7,8]. Therefore, many effective and recyclable heterogeneous catalytic systems for olefin oxidation using oxygen in the liquid phase have been studied. Unfortunately, most of these catalysts are prepared by immobilization of biomimetic catalysts [9–11], preparation processes of which are troublesome and expensive. Some of these catalytic systems are generally performed in volatile and toxic organic solvents [12,13], which involve a difficult process for product separation. In view of above, oxidation of alkenes with oxygen under a solvent-free condition would be valuable.

Nowadays, the research of gold has made great development [14–16]. It was discovered that gold has remarkable catalytic properties for selective oxidation of cyclohexene [8]. Extensive studies on 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 [17]. Cyclohexene oxidation over the Au/C catalyst with oxygen gave a good conversion (approximately

50.2%) along with many notable products [8]. The properties of molecular sieves have made them highly desirable as support materials for gold [18,19]. Some manganese compounds are good catalysts for cyclohexene oxidation [20]. Manganese oxide octahedral molecular sieve (K-OMS-2 or OMS-2) has been reported as an effective catalyst in many oxidation reactions [21,22]. Ce-incorporated OMS-2 material displays a good combination of high activity, stability patterns and capacity for reactive phenol adsorption [23]. Therefore, we chose La (III), which lies in the same group with Ce (III), to modify K-OMS-2. In this work we report the application of Au/OMS-2 and Au/La-OMS-2 to improve efficiency of the catalyst for cyclohexene oxidation using oxygen as oxidant, and explore the effect of composition of catalysts on oxidation of cyclohexene.

## 2. Experimental

## 2.1. Catalyst preparation

K-OMS-2 was prepared according to procedures described in the literature [24]. Potassium permanganate solution in deionized water ( $0.4 \text{ mol L}^{-1}$ , 225 mL) was added to a mixture of manganese sulfate hydrate solution ( $1.75 \text{ mol L}^{-1}$ , 67.5 mL) and concentrated nitric acid (6.8 mL) in a 500 mL flask fitted with a reflux condenser. The slurry was refluxed for 24 h, then filtered and washed with deionized water several times. The catalyst was dried at 120 °C overnight before use.

$K^+$  ions were then exchanged with  $La^{3+}$  ions by ion-exchanging K-OMS-2 with  $La(NO_3)_3 \cdot 6H_2O$  to obtain La-OMS-2. 2.0 g K-OMS-2 was added to 15 mL  $La(NO_3)_3 \cdot 6H_2O$  methanol solution. The slurry was stirred vigorously at room temperature for 8 h. After filtration, the solid was washed with deionized water several times. The product

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was dried at 120 °C overnight and then calcined in air at 300 °C for 3 h. The final material was named La-OMS-2 (0.12) with the number in brackets indicating the molar concentration ( $\text{mol L}^{-1}$ ) of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  methanol solution.

Au/OMS-2 and Au/La-OMS-2 catalysts with varied gold loadings were prepared by the DP procedure. 2.0 g K-OMS-2 or La-OMS-2 was stirred in  $0.5 \text{ mmol L}^{-1}$   $\text{HAuCl}_4$  aqueous solution for 1 h at 60 °C. The pH of the slurry was kept at 10 adjusted with  $1.0 \text{ mol L}^{-1}$  NaOH solution. After filtration, the resulting solid was first washed with 15 mL ammonia liquor ( $4.0 \text{ mol L}^{-1}$ ) and then washed twice using 20 mL deionized water to remove  $\text{Cl}^-$  ions. Finally, the resulting solid was dried at 120 °C overnight and calcined at 300 °C for 3 h, Au/OMS-2 or Au/La-OMS-2 was obtained.

## 2.2. Catalyst characterization

Scanning electron micrographs were taken on a Zeiss ULTRA 55 Gemini field emission scanning microscope with a Schottky Emitter at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained on a JEM-200CX at 80 kV. The structure of these materials was studied by X-ray diffraction experiments. A D/max-RA instrument with  $\text{CuK}\alpha$  radiation with a beam voltage of 40 kV and a beam current of 40 mA was used to collect the X-ray data. The chemical compositions of the synthesized catalysts were determined by an energy dispersive X-ray analysis (EDX) on a Philips Oxford 7426 EDX spectrometer. This analysis provides a measure of the amount of  $\text{La}^{3+}$  in the tunnel of K-OMS-2 which was exchanged with  $\text{K}^+$  cations.

## 2.3. Catalytic testing

The catalytic experiments for cyclohexene oxidation were carried out in a PTFE-lined autoclave (Capacity = 30 mL, pressure maximum

6 MPa). In a typical oxidation reaction, 20 mL cyclohexene and 0.20 g catalyst were placed into the autoclave. The reactor was then heated to the desired reaction temperature in oil bath under oxygen pressure with a magnetic stirrer. After reaction, the reactor was cooled to room temperature and the liquid phase was separated from the reaction slurry. The solid catalyst was washed by acetone and dried at 120 °C for 5 h. The liquid samples were analyzed by gas chromatography (GC) with an SE-54 capillary column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.5 \mu\text{m}$ ) and a flame ionization detector (FID). N-heptane was used as the internal standard for product analysis.

## 3. Results and discussion

### 3.1. Catalyst properties

The scanning electron micrographs show a fibrous needle-like morphology of K-OMS-2 and La-OMS-2 in Fig. 1. The morphology of K-OMS-2 is similar to that of La-OMS-2. The result shows that the tunnel cation substitution has no effect on the morphology. TEM images in Fig. 2 show that the gold particle sizes of Au/OMS-2 and Au/La-OMS-2 are around 10–20 nm.

The X-ray diffraction patterns (Fig. 3) of K-OMS-2, Au/La-OMS-2 and regenerated Au/La-OMS-2 show that the catalysts are pure phases and comparable to standard OMS-2 materials (JCPDS file #29-1020). No typical signal of gold at  $38.19^\circ$  and  $44.42^\circ$  is observed in Au/La-OMS-2 in Fig. 3. This is due to the low loadings (0.75 %) and high dispersions of gold, which are out of detection limit for the diffractometer. The XRD patterns show that the catalyst retains its structure after ion-exchange with  $\text{La}^{3+}$ , loading with Au, and regeneration of Au/La-OMS-2.

From the EDX analysis data the amount of  $\text{K}^+$  cation in OMS-2 and Au/La-OMS-2 materials was obtained as shown in Table 1. The

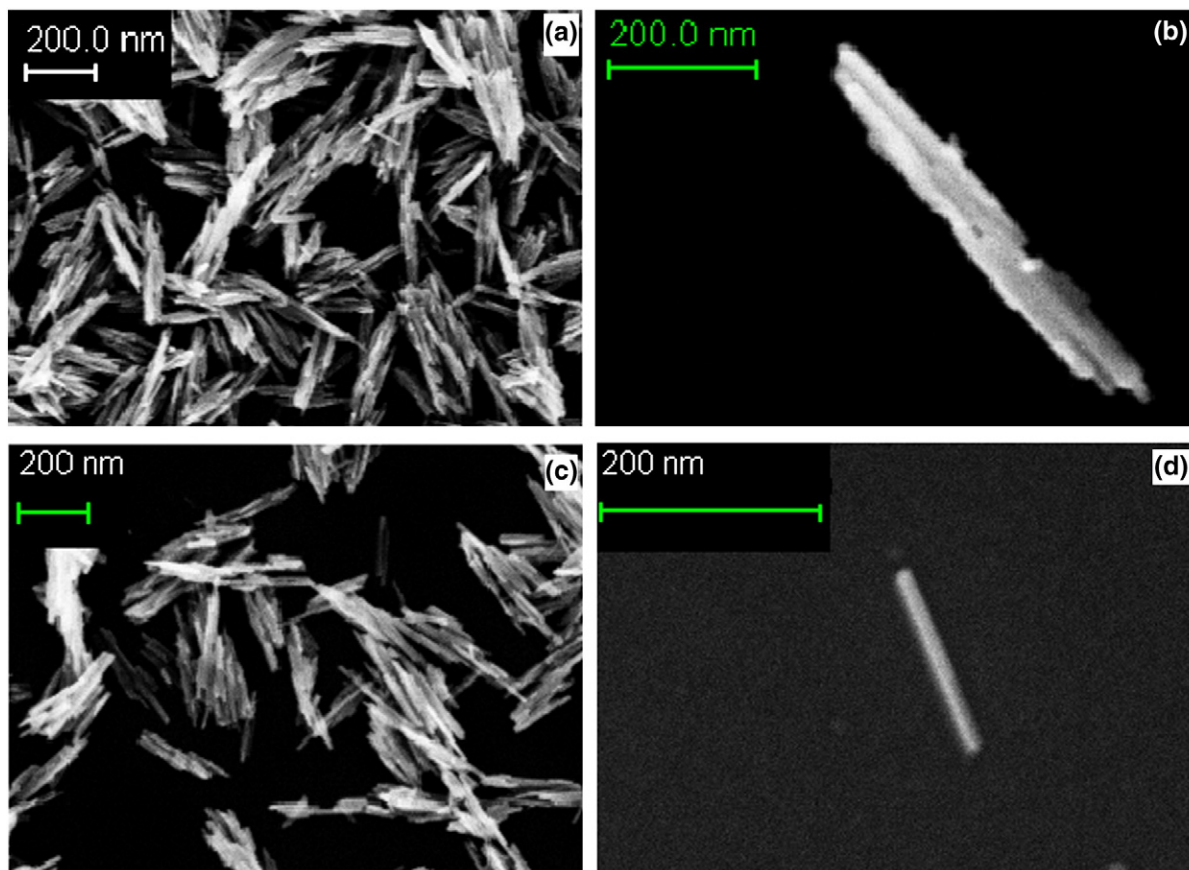


Fig. 1. SEM micrograph of K-OMS-2 (a), (b) and La-OMS-2 (c), (d).

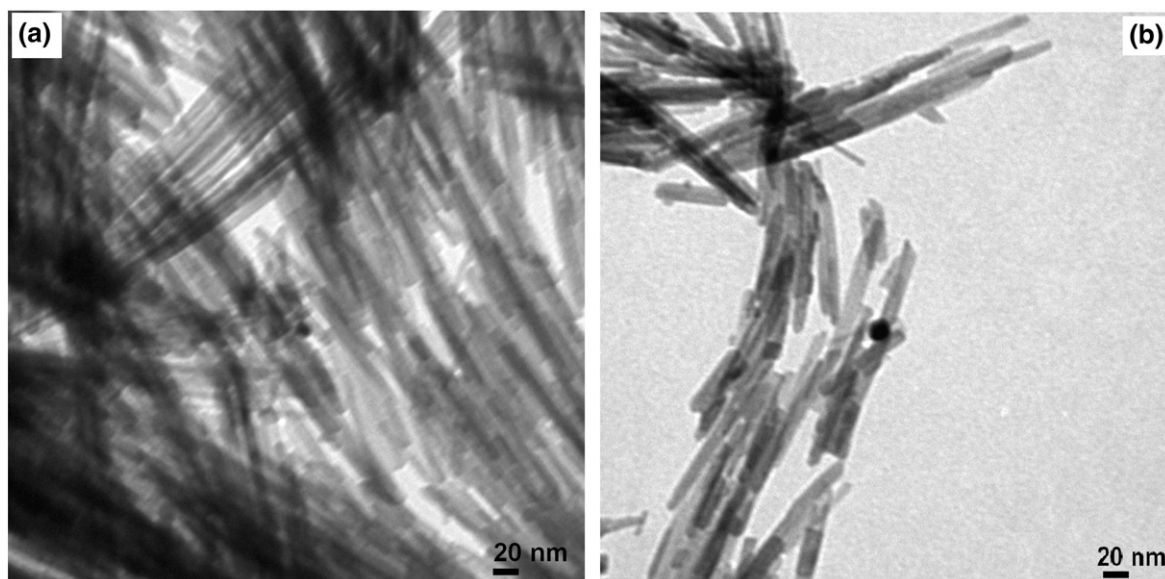


Fig. 2. Typical TEM images of Au/OMS-2 (0.75% Au) (a) and Au/La-OMS-2 (0.24) (b).

percentage of  $K^+$  exchanged with  $La^{3+}$  was calculated based on the mass fraction % of K and La assuming that the mass fraction % of Mn does not decrease in the ion-exchange process. The error of La content and K content is  $< \pm 0.5\%$ . The content of gold was also obtained from the EDX analysis; we could confirm that the DP method was effective to prepare Au/OMS-2 and Au/La-OMS-2 catalysts. But the loadings of gold were too low to get the accurate quantities, which resulted in invalidity of the content of gold in quantitative analysis (Table 2).

### 3.2. Catalytic performance

In preliminary experiments, K-OMS-2 and various Au/OMS-2 were tested for their catalytic activity for cyclohexene oxidation, the products obtained were cyclohexene oxide, 2-cyclohexene-1-ol, and 2-cyclohexene-1-one, and they are collectively called  $\sum C_6$ . Table 3 shows the conversion of cyclohexene and selectivity of products. Compared with the uncatalyzed oxidation reaction (Table 3, Entry 1 and 7), both K-OMS-2 and Au/OMS-2 exhibit a good catalytic performance. The conversion was only 19.5% with K-OMS-2 as the catalyst while the reaction time was 12 h (Table 3, Entry 2), and the Au/OMS-2 catalyst afforded much better conversion with higher selectivity of  $\sum C_6$  at the same reaction condition (Table 3, Entry 3 to Entry 6). Although the effect of the Au content is not obvious under the reaction condition while the Au content varies from 0.5% to 1.25%,

the results show that such a small quantity of gold loading can significantly enhance the catalytic performance. In the synthesis of the Au/OMS-2 catalyst, loading gold on the support proceeds by a direct deposition of  $[Au(OH)_x]^{-(x-3)}$  ( $x \geq 3$ ) making gold disperse on a molecular scale. Moreover, the subsequent activation of the catalyst precursor at a low temperature might suppress the conglomeration of gold nanoparticles. These lead to a high dispersion as well as a fine size control of gold on the support, thus resulting in a high activity for cyclohexene oxidation in spite of a relatively low gold loading of the catalyst. Furthermore, a surprisingly high conversion up to 39.9% was obtained over Au/OMS-2 (Au, 0.75%) as the reaction time was extended to 24 h, and the selectivity of  $\sum C_6$  remains 89.9%.

To study the effect of La content of Au/La-OMS-2 on catalytic performance in cyclohexene oxidation, reactions were done at 80 °C and 0.4 MPa for 24 h (Table 4). The conversion of cyclohexene rises with the increase of the La content of Au/La-OMS-2. Compared to K-

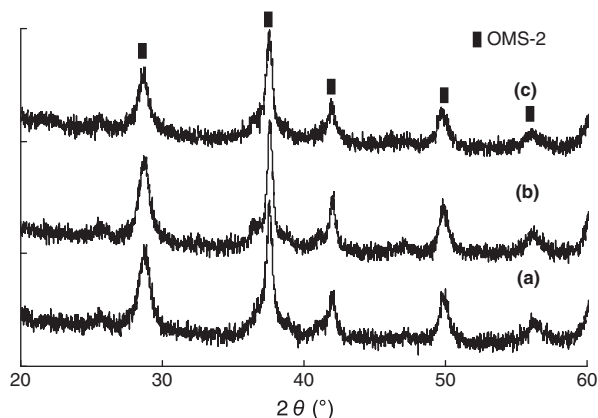


Fig. 3. XRD patterns of K-OMS-2 (a), Au/La-OMS-2 (b) and regenerated Au/La-OMS-2 (c).

Table 1  
Amount of  $La^{3+}$  exchange in the synthesized catalysts.

Catalyst (mol L <sup>-1</sup> La <sup>3+</sup> ) <sup>a</sup>	La content (wt.%)	K content (wt.%)	La <sup>3+</sup> /K <sup>+</sup> (mol:mol)
K-OMS-2	0	4.6	0
Au/La-OMS-2 (0.06)	4.5	4.9	0.26
Au/La-OMS-2 (0.12)	5.1	4.4	0.33
Au/La-OMS-2 (0.18)	6.6	4.5	0.41
Au/La-OMS-2 (0.24)	9.2	5.5	0.47
Au/La-OMS-2 (0.24) <sup>b</sup>	6.2	4.6	0.38

<sup>a</sup> The number in brackets indicate the molar concentration (mol L<sup>-1</sup>) of La (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O methanol solution.

<sup>b</sup> The catalyst was regenerated after used for 4 times.

Table 2  
Content of gold in the synthesized catalysts.

Catalyst (wt.% Au)	Au content (wt.%)		Error (±%)
	Theoretical	Actual	
Au/OMS-2 (0.5)	0.50	0.11	0.69
Au/OMS-2 (0.75)	0.75	0.93	0.54
Au/OMS-2 (1.0)	1.00	0.96	0.47
Au/OMS-2 (1.25)	1.25	1.26	0.68

**Table 3**  
Effects of Au contents and preparation methods of catalysts on catalytic performance in cyclohexene oxidation<sup>a</sup>.

Entry	Catalyst (Au (wt.%)	Time (h)	Conversion (%)	Selectivity (%)			
				Cy-oxide	Cy-nol	Cy-one	$\sum C_6$
1	No	12	12.1	8.1	15.4	21.7	45.2
2	K-OMS-2	12	19.5	4.1	41.4	42.3	87.7
3	Au-OMS-2 (0.5)	12	27.1	4.1	40.0	46.1	90.4
4	Au-OMS-2 (0.75)	12	28.6	4.4	37.7	48.1	90.2
5	Au-OMS-2 (1.0)	12	26.2	4.4	36.5	49.1	89.9
6	Au-OMS-2 (1.25)	12	25.8	4.9	37.9	46.7	89.4
7	No	24	21.9	7.1	26.8	35.0	68.9
8	K-OMS-2	24	28.9	3.2	42.7	42.6	88.5
9	Au-OMS-2 (0.75)	24	39.9	2.5	35.5	51.9	89.9

<sup>a</sup> All reactions were done with 0.20 g of catalyst, 20 mL cyclohexene, at 80 °C, and the pressure of oxygen 0.4 MPa.

OMS-2 (Table 3, Entry 8) and La-OMS-2 (Table 4, Entry 1), Au/La-OMS-2 presented a much better catalytic activity (Table 4, Entry 2 to 5). When the reaction was done with K-OMS-2 (Table 3, Entry 8), 28.9% conversion was obtained, which increased to 38.7% with La-OMS-2 (0.24) (Table 4, Entry 1) as the catalyst, and the conversion was up to 48.0% on Au/La-OMS-2 (0.24) (Table 4, Entry 5).

The stability of a catalyst is an important consideration for the industrial application. As Au/La-OMS-2 (0.24) possesses the highest La doping among the doped K-OMS-2 supported catalysts and has a good catalytic performance, Au/La-OMS-2 (0.24) was used for the recycling test to evaluate the stability of the catalyst. The catalyst was recovered by filtration after the reaction and regenerated by a simple regeneration procedure. By washing with acetone and drying at 120 °C for 5 h, Au/La-OMS-2 (0.24) restored the original activity. As shown in Table 5, there is only a slight decrease of conversion as well as selectivity of 2-cyclohexene-1-ol and 2-cyclohexene-1-one after the first run. Moreover, the activity and the selectivity of the catalyst were well retained after subsequent three runs. This is because leaching was minimal in the oxygen and solvent-free system comparing to the reaction carried out in an organic solvent with other oxidant. A similar trend has been observed using CrMCM-41 in a solvent-free/dioxygen condition [6]. The result of La<sup>3+</sup>/K<sup>+</sup> (Table 1) shows that the composition of Au/La-OMS-2 changed only a little after four runs of the reaction. This suggests that the supported gold catalyst Au/La-OMS-2 is quite stable under the reaction conditions.

In order to explain how the oxidation occurred, and how the major products were formed, we also speculated the oxidation mechanism. According to the literature [20,25,26] and the analysis of the relevant factors of the oxidation, the oxidation of cyclohexene with molecular

**Table 4**  
Effect of La contents of catalysts on catalytic performance in cyclohexene oxidation<sup>a</sup>.

Entry	Catalyst (mol L <sup>-1</sup> La <sup>3+</sup> ) <sup>b</sup>	Time (h)	Conversion (%)	Selectivity (%)			
				Cy-oxide	Cy-nol	Cy-one	$\sum C_6$
1	La-OMS-2 (0.24)	24	38.7	2.8	40.0	47.0	89.7
2	Au/La-OMS-2 (0.06)	24	41.2	2.7	40.9	47.4	91.0
3	Au/La-OMS-2 (0.12)	24	43.8	3.2	42.7	41.9	87.8
4	Au/La-OMS-2 (0.18)	24	46.7	2.1	40.0	45.0	87.1
5	Au/La-OMS-2 (0.24)	24	48.0	2.5	40.3	44.0	86.2

<sup>a</sup> All reactions were done with 0.20 g of catalyst, 20 mL cyclohexene, at 80 °C, and the pressure of oxygen is 0.4 MPa.

<sup>b</sup> Au content of the catalysts was kept constant, Au (wt.%) = 0.75.

**Table 5**  
Catalytic performance of fresh and regenerated Au/La-OMS-2 catalyst<sup>a</sup>.

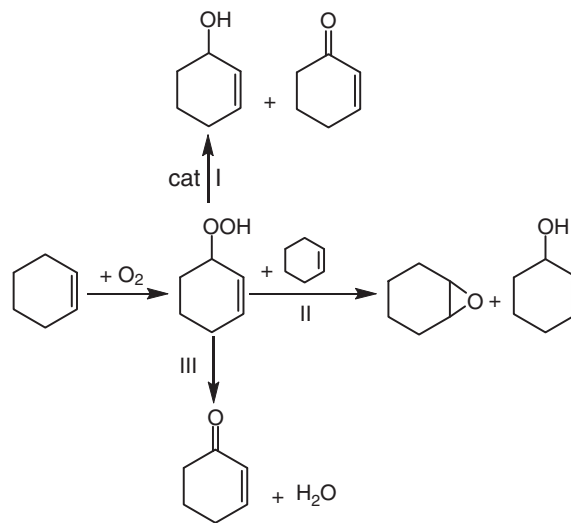
Cycles	Catalyst <sup>b</sup>	Time (h)	Conversion (%)	Selectivity (%)			
				Cy-oxide	Cy-nol	Cy-one	$\sum C_6$
1	Au/La-OMS-2	24	48.0	2.5	40.3	44.0	86.2
2	Au/La-OMS-2	24	47.1	2.8	40.3	42.0	85.1
3	Au/La-OMS-2	24	46.0	2.3	36.7	47.7	86.7
4	Au/La-OMS-2	24	44.0	2.5	34.6	49.0	86.1
1[6]	CrMCM-41 <sup>c</sup>	24	52.2	3.1	14.0	71.2	88.3
4[6]	CrMCM-41 <sup>c</sup>	24	41.5	3.7	11.2	74.2	89.1

<sup>a</sup> Reactions were done with 0.20 g of catalyst, 20 mL cyclohexene, at 80 °C, and the pressure of oxygen 0.4 MPa.

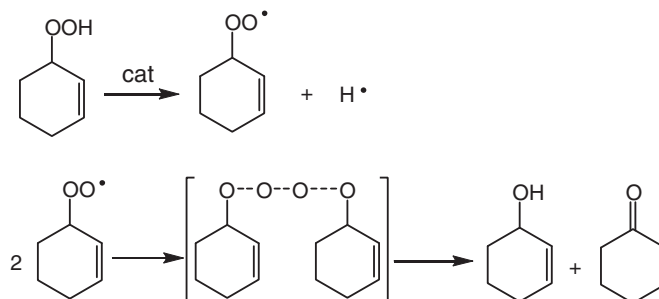
<sup>b</sup> Au content of the catalyst is 0.75 wt. % theoretically, and the molar concentration (mol L<sup>-1</sup>) of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O methanol solution is 0.24.

<sup>c</sup> Reaction conditions: cyclohexene, 1 g; catalyst, 20 mg; O<sub>2</sub> pressure, 1 atm; time, 24 h; temperature, 343 K.

oxygen initially formed 2-cyclohexene-1-hydroperoxide as shown in Scheme 1. 2-Cyclohexene-1-hydroperoxide was unstable and easily formed other products. There were three main paths. As the selectivity of cyclohexene oxide was 2.0%–4.0%, we could infer that step II played a minor role in the reaction. Comparing the selectivity of 2-cyclohexene-1-one with that of 2-cyclohexene-1-ol, it is inferred that there was 5%–15% of 2-cyclohexene-1-hydroperoxide dehydration through step III. Most of 2-cyclohexene-1-one and 2-cyclohexene-1-ol were obtained from step I. The radical-chain sequence mechanism of step I was proposed as follows (Scheme 2).



**Scheme 1.** Mechanism of cyclohexene oxidation.



**Scheme 2.** Radical-chain sequence mechanism of step I.

#### 4. Conclusion

In summary, the OMS-2 supported gold catalyst with low gold loading and La doping has shown high efficiency for cyclohexene oxidation to 2-cyclohexene-1-ol and 2-cyclohexene-1-one using molecular oxygen in the solvent-free system under mild conditions. The good activity and stability of the catalyst Au/La-OMS-2 are ascribed to both the effect of gold and the structure and composition of the La-OMS-2 molecular sieve. Au/La-OMS-2 may be useful in the selective oxidation of certain important compounds in the modern industrial world.

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