Oxidation of cyclohexane—A significant impact of stainless steel reactor wall

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Abstract

The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone is an important chemical process and it has been paid more attentions recently. In the present work, the stainless steel reactor wall was found to influence the selective oxidation of cyclohexane very significantly, and a quasi-crystalline $Ti_{45}Zr_{35}Ni_{17}Cu_3$ alloy with the similar compositions as the reactor wall was used as a catalyst for the cyclohexane oxidation, as expected, a higher activity was obtained with it. The present results open up a new avenue for developing new catalyst for alkane oxidation.
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1. Introduction

The oxidation of cyclohexane to cyclohexanol and cyclohexanone is an important chemical process for the modern chemical industry, because the cyclohexanol and cyclohexanone are materials for producing adipic acid and caprolactam, which are intermediates of nylon-6 and nylon-66 polymers [1]. The increased environmental concerns call for benign oxidations including recoverable catalyst, solvent-free and clean oxidant like oxygen. Oxidation using molecular oxygen is more attractive because it is inexpensive, readily available and environmentally benign compared with other oxidants [2–4]. Cyclohexane oxidation is generally catalyzed by soluble metal salts or complexes industrially at temperature above 423 K, in which the total conversion of cyclohexane is lower than 4% and the selectivity of cyclohexanol and cyclohexanone reaches about 70–85% [5]. Recently, the oxidation of cyclohexane has been paid more attentions in developing new type of catalyst [6–10]. For example, the catalyst of Ce/AlPO-5 prepared by Zhao et al. [11] showed a high conversion of 13.5% and a high selectivity for

cyclohexanol and cyclohexanone of 92% at 413 K, 0.5 MPa O_2. Co_3O_4 nanocrystals synthesized by Zhou et al. [12] gave a result of 89.1% selectivity for cyclohexanol and cyclohexanone with 7.6% conversion of cyclohexane. Moreover, a mesoporous iron-titania catalyst [13], nanosize iron oxide deposited into the pores of mesoporous material (titania) with ultrasound radiation, was reported with a high conversion of 21.3% and selectivity of 80% for cyclohexane oxidation under high oxygen pressure (40 atm) at room temperature with using isobutyraldehyde and acetic acid as co-catalyst. Furthermore, metal-porphyrin as biomimetic catalyst had been developed by Guo et al. [14] for cyclohexane oxidation, which presented a conversion of 16.2% and selectivity of 82% to cyclohexanol and cyclohexanone. Most of the above studies were carried out in high-pressure stainless steel reactor [2,4,6,8,10–15], while in our present work, the oxidation of cyclohexane was found to be catalyzed by the stainless steel reactor wall accidentally with oxygen as oxidant and the results were beyond our expectation. So the effects of the stainless steel reactor wall in studies of cyclohexane oxidation could not be ignored. In this paper, we have shown the influence of stainless steel reactor wall on the reaction rate and product selectivity of cyclohexane oxidation. Several reaction parameters, such as temperature, pressure and reaction time have been discussed for the present reaction and the activity of a catalyst with sim-

ilar compositions as the stainless steel reactor wall has been checked. The present work suggests a new type of catalyst for cyclohexane oxidation.

2. Experimental

All the chemicals were used as received without any purification, and quasi-crystalline $Ti_xZr_yNi_zCu_3$ alloys prepared by mechanical alloying and subsequent annealing techniques and the alloys were characterized by XRD and TEM, and demonstrated as having an icosahedral quasi-crystalline structure [16]. Cyclohexane was purchased from Beijing chemical plant, and gas of O_2 (99.9%) was used as delivered. A certain amount of substrate was charged into the reactor at room temperature. The reactor was heated up to the desired temperature and then quantitative O_2 was introduced. The reaction runs were conducted while stirring with a magnetic stirrer. At the end of the reaction, the autoclave was cooled to room temperature, then depressurized carefully. The composition of reaction mixture was analyzed by a gas chromatograph (SHIMADZU GC-2010) using a flame ionization detector.

3. Results and discussion

The oxidation of cyclohexane can produce cyclohexanol (A), cyclohexanone (K) and intermediate cyclohexyl hydroperoxide (CHHP) companioning with several side products, such as acids, esters, alcohols and ketones as shown in Fig. 1. The influence of reactor wall has been checked in a stainless steel autoclave by varying the reaction parameters of temperature, pressure and reaction time in the absence of any catalyst and solvent. Furthermore, the catalytic efficiency of the reactor wall has been confirmed by using a Teflon liner reactor and with a new catalyst of $Ti_xZr_yNi_zCu_3$ alloy.

3.1. Influence of temperature

Fig. 2 shows the results of cyclohexane oxidation at different reaction temperature. With increasing of temperature, the conversion of cyclohexane increased, but the total selectivity for cyclohexanol (A), cyclohexanone (K) and cyclohexyl hydroperoxide (CHHP) decreased for the formation of other products. At 403 K, CHHP was produced with a selectivity of 32.06%, but CHHP is apt to decompose to cyclohexanol and cyclohexanone at higher temperature, so the selectivity of A and K increased obviously at 413 K. Subsequently, with increasing temperature, more cyclohexanone was oxidized to deep oxidation products and its selectivity decreased.
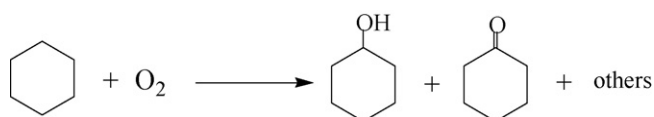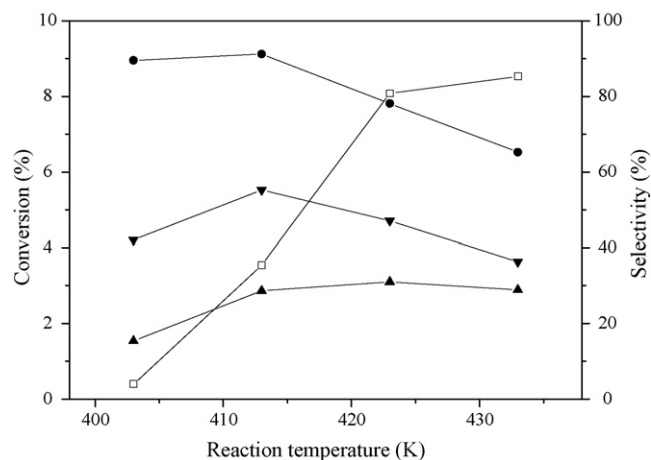

Fig. 2. Effect of reaction temperature on conversion and selectivity. Reaction conditions: cyclohexane 8 ml, oxygen 2 MPa, reaction time 6 h. (□) Conversion of cyclohexane; (▲) selectivity to A; (▼) selectivity to K; (●) selectivity to A + K + CHHP; (A) cyclohexanol, (K) cyclohexanone, (CHHP) cyclohexyl hydroperoxide.

3.2. Effect of reaction time

Fig. 3 illustrates the changes of conversion and selectivity with reaction time at temperature of 413 and 423 K, respectively. The conversion increased with reaction time and it reached a maximum value of 8.17% at 413 K after reaction for 12 h, and a maximum conversion of 8.7% came out at 423 K after reaction for 9 h. When the reaction proceeded for long reaction time, the peroxidation occurred leading to the selectivity of cyclohexanol and cyclohexanone to decrease. Therefore, both the selectivity of cyclohexanol and cyclohexanone presented a maximum value.

The maximal conversion of this reaction is about two times higher than that obtained from the present industrial process, and it is about a half of the conversion reported for cyclohexane oxidations in literature with some new catalyst [5,11–14]. However, the present work was carried out in the absence of any catalyst and solvent, so it is important and necessary to report this phenomenon from the viewpoint of scientific research and industrial application.

3.3. Influence of the concentration of oxygen

Fig. 4 depicts the effect of pressure of oxygen on conversion and selectivity at a certain mole ratio of cyclohexane/oxygen at reaction temperature of 413 and 423 K, respectively. As shown in the figure, the conversion increased initially with the increase in the pressure of oxygen and then it changed very slightly after the oxygen pressure reached a certain level under the reaction conditions. Higher oxygen pressure in the reaction system could accelerate the reaction rate and promote the formation of products. While, after a certain concentration of oxygen was reached, the reaction rate did not increase with its further increasing. The conversion of cyclohexane reached a flat value under the pressure of oxygen above 1 MPa at 413 K and above 1.5 MPa at 423 K, which suggested that the present oxidation was catalyzed by the reactor wall; otherwise, the reaction rate should increase with
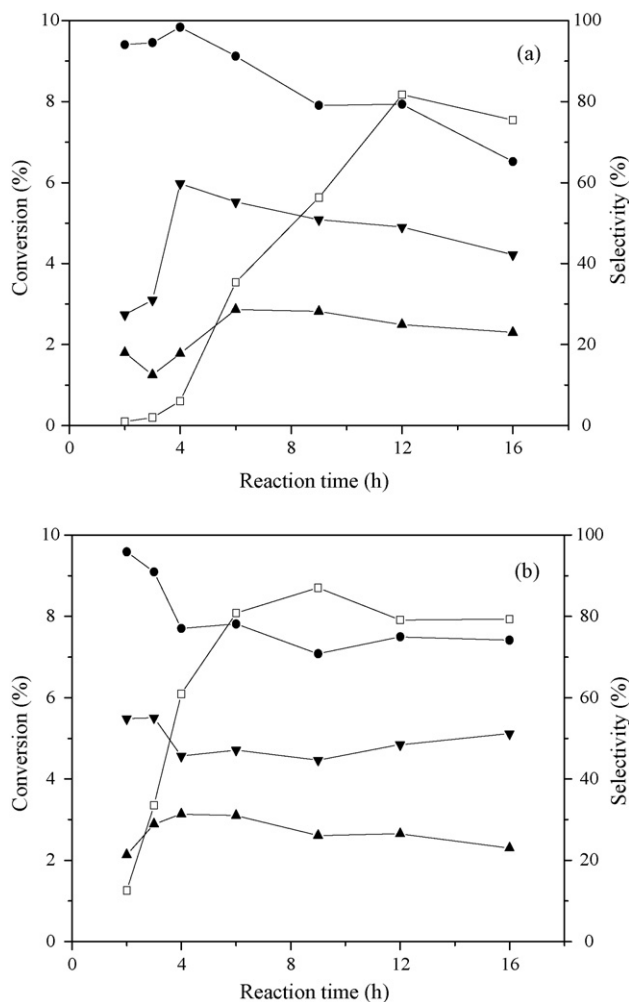

Fig. 1. Oxidation of cyclohexane.

Fig. 3. Effect of reaction time on conversion and selectivity at (a) 413 K and (b) 423 K. Reaction conditions: cyclohexane 8 ml, oxygen 2 MPa. (□) Conversion of cyclohexane; (▲) selectivity to A; (▼) selectivity to K; (●) selectivity to A + K + CHHP.
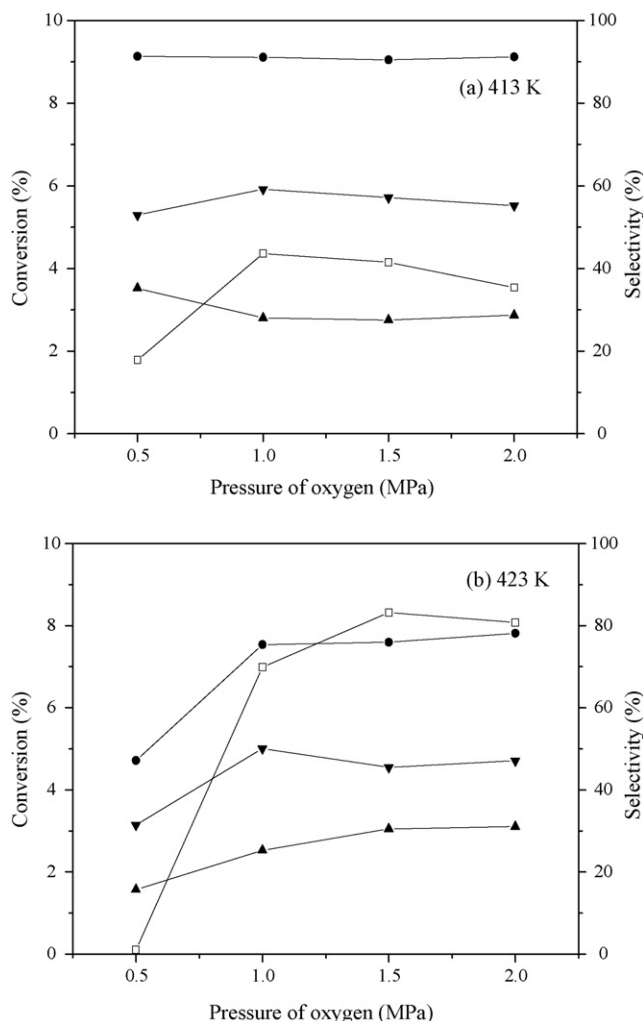

Fig. 4. Effect of pressure of oxygen on conversion and selectivity. Reaction conditions: mol ratio of cyclohexane/oxygen = 2.5 at 413 K; 2.6 at 423 K, reaction time 6 h. (□) Conversion of cyclohexane; (▲) selectivity to A; (▼) selectivity to K; (●) selectivity to A + K + CHHP.

the oxygen pressure linearly. The adsorption of oxygen on the reactor wall reached saturation at 1 MPa, 413 K and at 1.5 MPa, 423 K is in agreement with the gas phase equation. The selectivity of cyclohexanone had a maximum value at 1.0 MPa at both the temperatures and the total selectivity varied a little with the pressure, which is in coordinate with the result obtained by using chitosan-Schiff base Co(II) and Pd(II) complex catalysts [17].

3.4. Effect of stainless steel reactor wall

In order to confirm the role of the reactor wall acted in the present work, the oxidation was performed in an autoclave with a Teflon inner liner, the results were shown in Table 1. The conversion was lower in the presence of Teflon inner liner compared with the results in the bareness stainless reactor wall (entries 3 and 4). This testified that the stainless steel reactor wall could promote the present oxidation. Moreover, we checked the present results with several reactors such as new reactor from the company and old one used for a number of reactions, similar results were obtained. The reaction still showed some conver-

sion in the presence of the Teflon inner liner, which should be attributed to the auto-oxidation intrinsic nature of the reaction [3,18], except for that the reactants could not be isolated completely from the stainless steel wall for that some gases would come out into the gaps between the reactor and Teflon liner. More recently, Leitner and coworkers reported that the presence of the stainless steel reactor wall could initiate the formation of

Table 1
Oxidation of cyclohexane in the presence and absence of Teflon inner liner at different reaction time

Entry	Time (h)	Conversion (%)	Selectivity (%)		
			A	K	CHHP
1[a]	2	0.4	9.5	9.3	75.8
2[a]	4	2.4	19.3	9.7	67.4
3	2	1.3	21.4	54.8	19.7
4	4	6.1	31.4	45.6	11.4

Reaction conditions: cyclohexane 8 ml, oxygen 2 MPa, temperature 423 K.
[a] In presence of Teflon inner liner.

Table 2
Oxidation of cyclohexane in the presence of $Ti_xZr_yNi_zCu_3$ alloys powder

Entry	Catalyst	Conversion (%)	Selectivity (%)		
			A	K	CHHP
1	–	0.6	16.6	18.8	64.6
2[a]	–	4.0	28.7	57.6	2.6
3	$Ti_{45}Zr_{35}Ni_{17}Cu_3$	6.5	30.2	49.4	8.5
4	$Ti_{43}Zr_{33}Ni_{21}Cu_3$	4.9	37.1	44.3	9.7
5	$Ti_{41}Zr_{31}Ni_{25}Cu_3$	6.1	39.5	42.3	8.8
6	$Ti_{37}Zr_{27}Ni_{33}Cu_3$	5.2	37.6	45.5	6.5

Reaction conditions: the oxidations were carried out in autoclave with Teflon inner liner, cyclohexane 4 ml, catalyst 40 mg, oxygen 2 MPa, temperature 413 K, reaction time 6 h.

[a] In absence of Teflon inner liner.

acyl radicals for acetaldehyde oxidation, and they indicated that the stainless steel surface acts not only as the initiator for the radical chain, but can also function as a catalyst [15].

3.5. The catalytic activities of quasi-crystalline $Ti_xZr_yNi_zCu_3$ alloys

From the above discussion, we can draw a conclusion that the selective oxidation of cyclohexane could be catalyzed by stainless steel reactor wall largely with oxygen as oxidant in a solvent-free condition. These results present two important points for the oxidation of cyclohexane, one is that the effects of the reactor wall should be paid more attentions in the studies of the catalytic oxidation of cyclohexane, especially in the evaluation of the catalytic activity of new catalysts; the other is that it suggested an information for developing new type of catalyst for cyclohexane oxidation, which may be an alloy containing metals like Fe, Ti, Ni or Cr similar to the composition of the reactor wall in the present work. In literature, the Fe, Ti, Cr, Mn-containing molecular sieves were reported to be active for cyclohexane oxidation and their activities have been discussed at 403 K with oxygen as oxidant [19]. In addition, the metals containing ZSM-5 catalysts, such as Fe, Cu, Ni, Cr, Mn and Co-ZSM-5, had been also investigated for cyclohexane oxidation, and the catalytic activity of all the catalysts was in the sequence of Co-ZSM-5 > Fe-ZSM-5 > Cu-ZSM-5 > Mn-ZSM-5 > Cr-ZSM-5 > Ni-ZSM-5 [20]. In the present work, the catalytic activities of quasi-crystalline $Ti_xZr_yNi_zCu_3$ alloys powder have been checked, which is the first time for quasi-crystalline alloy used as a catalyst for oxidation reaction, the results are shown in Table 2. The oxidations were carried out at 413 K using the autoclave with a Teflon inner liner, fortunately, the presence of the quasi-crystalline alloys with different constituents could promote the oxidation efficiently, $Ti_{45}Zr_{35}Ni_{17}Cu_3$ alloy (entry 3) showed a higher conversion than that obtained with the bareness autoclave reactor wall (entry 2). More recently, a literature has reported that the quasi-crystalline alloy could catalyze the steam reforming of

methanol efficiently [21]. Therefore, it is a new challenge to develop a quasi-crystalline catalyst with high activity for cyclohexane oxidation. This part of work is going on in our research work.

4. Conclusion

In summary, the influence of the stainless steel reactor wall could not be ignored in the studies of the cyclohexane oxidation, because the reactor wall could catalyze the reaction. The present work presents a significant point that the quasi-crystalline alloy could act as a catalyst for cyclohexane oxidation with a higher activity. We expect, its development will contribute to the present and/or other oxidation reactions more efficiently in the near future.

Acknowledgements

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