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Article

Solvent-free selective oxidation of cyclohexane with molecular oxygen over manganese oxides: Effect of the calcination temperature

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ABSTRACT

The effects of calcination temperature on the physicochemical properties of manganese oxide catalysts prepared by a precipitation method were assessed by X-ray diffraction, N₂ adsorption-desorption, X-ray photoelectron spectroscopy, H₂ temperature-programmed reduction, O₂ temperature-programmed desorption, and thermogravimetry-differential analysis. The catalytic performance of each of these materials during the selective oxidation of cyclohexane with oxygen in a solvent-free system was subsequently examined. It was found that the MnO_x-500 catalyst, calcined at 500 °C, consisted of a Mn₂O₃ phase in addition to Mn₅O₈ and Mn₃O₄ phases and possessed a low surface area. Unlike MnO_x-500, the MnO_x-400 catalyst prepared at 400 °C was composed solely of Mn₃O₄ and Mn₅O₈ and had a higher surface area. The pronounced catalytic activity of this latter material for the oxidation of cyclohexene was determined to result from numerous factors, including a higher concentration of surface adsorbed oxygen, greater quantities of the surface Mn⁴⁺ ions that promote oxygen mobility and the extent of O₂ adsorption and reducibility on the catalyst. The effects of various reaction conditions on the activity of the MnO_x-400 during the oxidation of cyclohexane were also evaluated, such as the reaction temperature, reaction time, and initial oxygen pressure. Following a 4 h reaction at an initial O₂ pressure of 0.5 MPa and 140 °C, an 8.0% cyclohexane conversion and 5.0% yield of cyclohexanol and cyclohexanone were achieved over the MnO_x-400 catalyst. In contrast, employing MnO_x-500 resulted in a 6.1% conversion of cyclohexane and 75% selectivity for cyclohexanol and cyclohexanone. After being recycled through 10 replicate uses, the catalytic activity of the MnO_x-400 catalyst was unchanged, demonstrating its good stability.

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1. Introduction

The selective liquid phase oxidation of cyclic hydrocarbons is one of the most widely used industrial processes producing

oxygenates [1]. Because of the importance of cyclohexanol (A) and cyclohexanone (K) in the production of adipic acid and caprolactam, compounds that in turn are used in the manufacture of nylon-6 and nylon-6,6 polymers, the selective oxidation

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of cyclohexane has become a very important reaction [2,3]. In general, there is the trade-off between selectivity and high conversion in hydrocarbon liquid phase oxidation reactions. Thus, conditions generating low conversions (less than 5%) are generally preferable as a means of preventing over-oxidation to form undesired by-products [4–6]. The greatest challenge associated with conventional industrial processes for cyclohexane oxidation is therefore the inherent difficulty in controlling the selectivity for the target products while obtaining a high conversion [7].

To date, a large number of catalysts have been reported for the oxidation of cyclohexane, such as metalloporphyrins [8,9], metal oxides [10–12], molecular sieves [13–16], carbon nanotubes [17,18], metal-organic frameworks materials [19,20], and small organic molecules [21]. Recently, polyoxometalate-based organic-inorganic hybrids demonstrated superior catalytic activity, producing a 29.4% yield of KA oil using H_2O_2 as the oxidant with acetonitrile as the solvent [22]. This same work also investigated changing the structure of the ionic liquid (IL) cation and obtained homogeneous catalysts having the structure $[\text{MimC}_4]_5\text{PMoV}_2$ IL-cation. Using this catalyst, a 28.5% yield of KA oil was obtained from the cyclohexane oxidation. However, a homogeneous catalyst such as this cannot be separated from the reaction mixture and recycled. Therefore, significant research work has been devoted to the development of heterogeneous catalysts for the selective oxidation of cyclohexane as substitutes for conventional homogeneous catalysts.

Iglesia et al. [23] reported that Mn species in MnAPO materials can serve as active sites during cyclohexane oxidation when using O_2 as the oxidant. Xu et al. [24] also studied the catalytic activity of MnAPO materials with regard to cyclohexane oxidation, and reported 3.7% conversion of cyclohexane and 64.5% selectivity for KA oil. However, the complicated process required to synthesize these catalysts and the uneconomical raw materials limit the potential industrial applications of these materials. Various hetero-mixed oxide catalysts have also been studied for the oxidation of cyclohexane, and $\text{WO}_3/\text{V}_2\text{O}_5$ has exhibited high catalytic activity with H_2O_2 as the oxidant [11]. Unfortunately, this approach suffers from the toxicity of the vanadium-based catalyst, and so effective, environmentally friendly, inexpensive and safe catalysts for the oxidation of cyclohexane are still required.

The catalytic oxidation of cyclohexane with oxygen as the oxidant has also been widely studied because of the inherently environmentally friendly nature of this process, although the resulting cyclohexane conversion is generally lower compared with that obtained with H_2O_2 or *tert*-butyl hydroperoxide (TBHP). Yang et al. [18] proposed that cyclohexane oxidation proceeds through a radical mechanism with O_2 as the oxidant. Hence, in some cases, the use of a radical initiator such as H_2O_2 or TBHP in the reaction mixture decreases the induction period and increases the conversion of cyclohexane. Chen et al. [25] also added TBHP to a cyclohexane reaction mixture as a free radical initiator to increase both the reaction rate and the conversion of cyclohexane. Recently, hollow sulfated V-doped TS-1 photocatalysts were evaluated for the selective photooxidation of cyclohexane with molecular oxygen and exhibited high effi-

ciency (TOF = 2.37 h^{-1} , based on the molar amount of V sites) and chemoselectivity (cyclohexanone/cyclohexanol molar ratio = 3.46) [26].

Compared with molecular sieves and metal-organic frameworks materials, transition metal oxides are much easier to prepare and to apply in industrial processes. In the present work, we selected a transition metal oxide (manganese oxide) as the catalyst for the solvent-free oxidation of cyclohexane with molecular oxygen because this oxide is inexpensive, readily available, and environmentally friendly. This study investigated the effect of the calcination temperature on the physicochemical properties of manganese oxide catalysts prepared by a precipitation method. Based on the relationship between the calcination temperature and the resulting physicochemical properties and catalytic performance of the manganese oxide catalysts, we attempted to synthesize a highly effective and stable oxide catalyst for the solvent-free oxidation of cyclohexane with molecular oxygen.

2. Experimental

2.1. Synthesis of catalysts

Manganese oxide catalysts were prepared by a precipitation method using an aqueous $\text{Mn}(\text{NO}_3)_2$ solution as the source of Mn. In a typical procedure, a quantity of a 50 wt% $\text{Mn}(\text{NO}_3)_2$ solution was added to a 250-mL three-neck flask followed by the dropwise addition of an aqueous NaOH solution (1 mol/L) at 60°C with stirring until the mixture reached a pH of 8. The solution was subsequently held at 60°C for 4 h with stirring during which time its pH was maintained at 8 by adding the NaOH solution as required. The solid product was collected by filtration, washed several times with de-ionized water, dried at 120°C overnight, and finally calcined in air at either 350, 400, 450, or 500°C for 4 h. The corresponding samples are designated as $\text{MnO}_x\text{-350}$, $\text{MnO}_x\text{-400}$, $\text{MnO}_x\text{-450}$, and $\text{MnO}_x\text{-500}$, respectively.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus X-ray diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at a scanning rate of $6^\circ/\text{min}$. N_2 adsorption-desorption isotherms were acquired on an ASAP 2010 analyzer (Micromeritics) at -196°C . Prior to these measurements, all samples were degassed at 300°C for 6 h under vacuum to remove moisture and any volatile impurities. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of samples. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250 spectrometer with a monochromatized $\text{Al } K_\alpha$ X-ray source (1486.6 eV), employing the C 1s (binding energy 284.6 eV) peak of adventitious carbon as a reference. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out using a PerkinElmer Pyris Diamond instrument together with a WCT-2 thermal analyzer at a rate of $10^\circ\text{C}/\text{min}$ in air.

H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) profiles

were collected with a PX200 apparatus (Tianjin Pengxiang Technology Co., Ltd., China) equipped with a thermal conductivity detector (TCD). The samples were heated from room temperature to 800 °C at a rate of 10 °C/min under 5 vol% H₂ in N₂ (40 mL/min). The hydrogen consumption during this process was measured quantitatively by the TCD. O₂ temperature-programmed desorption (O₂-TPD) was performed using a conventional flow system equipped with a quadrupole mass spectrometer (MS, INFICON IPC400). In these trials, a 200-mg sample was pretreated in Ar at its original calcination temperature for 1 h. After cooling to 50 °C, the sample was again pretreated in 3 vol% O₂ in He (30 mL/min) for 1 h, after which the system was flushed with Ar for 30 min to sweep residual oxygen from the sample surface. Finally, the sample was heated from 50 to 800 °C at a heating rate of 10 °C/min, and the gas released was analyzed online using the MS.

2.3. Catalytic activity analysis

The catalytic performance of the catalysts during cyclohexane oxidation was assessed in a 50-mL Teflon-lined stainless steel autoclave while stirring. Molecular oxygen was used as the oxidant without any solvent. In a typical reaction, 8 mL cyclohexane and 20 mg catalyst were introduced into the reactor. Subsequently, O₂ was introduced until the desired initial pressure was obtained at room temperature, after which the reactor was heated to 140 °C with stirring and these conditions were maintained for 4 h. The post-reaction mixture was analyzed using a PerkinElmer Clarus 500 gas chromatograph equipped with a PE-2 capillary column (25 m × 0.32 mm × 1.0 μm) and a flame ionization detector (FID). Methylbenzene was used as the internal standard. The main by-products of the reaction were found to be hexanedioic acid, hexanoic acid, di-

cyclohexyl adipate, and cyclohexyl caproate (Scheme 1). The concentration of acids in the reaction solution was determined by titration with 0.1 mol/L NaOH.

2.4. Recycling of the catalyst

Recycling trials were carried out using solely the MnO_x-400 catalyst. Following completion of each reaction trial, the catalyst was separated by filtration from the reaction solution, washed with ethanol three times in a glass beaker with stirring, dried at 100 °C for 6 h, and calcined in air at 400 °C for 2 h, thus producing the regenerated catalyst. The catalytic performance of the regenerated catalyst together with a supplement of fresh catalyst was then examined using the same reaction procedures applied with the fresh catalyst.

3. Results and discussion

3.1. XRD

The powder XRD patterns of MnO_x samples calcined at different temperatures are shown in Fig. 1. The diffraction peaks of the MnO_x-350 sample are consistent with those of hausmannite Mn₃O₄ (JCPDS 24-0734) and Mn₅O₈ (JCPDS 39-1218). The Mn₃O₄ can be considered to have a spinel structure composed of Mn²⁺(Mn³⁺)₂O₄, in which Mn²⁺ and Mn³⁺ occupy the tetrahedral and octahedral sites of the structure, respectively [27]. During the calcination process, the octahedral Mn³⁺ ions in Mn₃O₄ are oxidized to Mn⁴⁺ preferentially over Mn²⁺, leading to the formation of (Mn²⁺)₂(Mn⁴⁺)₃O₈ [28]. In the case of the MnO_x-400 and MnO_x-450 samples, the intensities of the Mn₃O₄ and Mn₅O₈ diffraction peaks are markedly strengthened. When the calcination temperature is further increased to 500 °C, Mn₂O₃ peaks appear in the pattern of the MnO_x-500 sample, and this evidently becomes the main MnO_x phase.

3.2. N₂ adsorption-desorption isotherms

The N₂ adsorption-desorption isotherms and the pore size distributions of samples are shown in Fig. 2. All isotherms ex-

Fig. 1. XRD patterns of MnO_x-350 (1), MnO_x-400 (2), MnO_x-450 (3), and MnO_x-500 (4) samples.

Fig. 2. N₂ adsorption-desorption isotherms and pore size distributions (inset) of MnO_x-350 (1), MnO_x-400 (2), and MnO_x-500 (3) samples.

Table 1Textural properties of MnO_x-350, MnO_x-400, and MnO_x-500 samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Aaverage pore diameter (nm)
MnO _x -350	31.4	0.13	16.3
MnO _x -400	24.0	0.13	16.0
MnO _x -500	20.5	0.12	17.0

hibit typical V-type shapes as defined by IUPAC. The BET surface areas, average pore diameters, and pore volumes of samples are listed in Table 1. The BET surface areas of the MnO_x samples are seen to have decreased with increases in the calcination temperature, such that the BET surface areas of the MnO_x-350 and MnO_x-500 were 31.4 and 20.5 m²/g, respectively. The pores in these samples are secondary particle-piled pores composed of MnO_x, and both the pore volume and pore diameter show only a very slight variation with increasing calcination temperature.

3.3. XPS results

The XPS Mn 2p and O 1s spectra of the MnO_x-400 and MnO_x-500 samples are shown in Fig. 3. The Mn and O atom surface concentrations are summarized in Table 2. It can be seen that the surface concentrations of Mn and O on the MnO_x-400 sample are close to those on the MnO_x-500.

The Mn 2p peaks can be deconvoluted to three peaks, and the peaks at binding energy (BE) values of 640.8 and 641.9 eV are assigned to Mn³⁺ and Mn⁴⁺, respectively, while the peak at 643.6 eV is a satellite peak of manganese [29,30]. The Mn⁴⁺/(Mn⁴⁺+Mn³⁺) atomic ratios were calculated from these XPS spectra using XPSPEAK 4.1 and are presented in Table 2. It is evident that the Mn⁴⁺/(Mn⁴⁺+Mn³⁺) ratio of the MnO_x-400 sample is higher than that of the MnO_x-500, as result of the appearance of a Mn₂O₃ phase in the MnO_x-500 (Fig. 1). This phase is responsible for the greater oxidation ability of the MnO_x-400 sample compared with the MnO_x-500.

The XPS O 1s spectra of the MnO_x-400 and MnO_x-500 samples are also provided in Fig. 3, and here two peaks can be distinguished at 530 and 531 eV. The peak at 530 eV is assigned to lattice oxygen (O²⁻, O_{lat}), while the peak at 531 eV is attributed

Table 2Surface atom concentrations on MnO_x-400 and MnO_x-500 samples as determined by XPS.

Sample	Surface atom concentration (%)			Mn ⁴⁺ /(Mn ⁴⁺ +Mn ³⁺)	O _{ads} /(O _{ads} +O _{lat})
	O	Mn	Mn/O		
MnO _x -400	49.9	30.6	0.61	0.25	0.30
MnO _x -500	50.9	31.2	0.61	0.22	0.27

to surface oxygen (O_{ads}). These species include surface-adsorbed oxygen and weakly bonded oxygen, such as O₂²⁻ or O⁻, belonging to defect-oxide or hydroxyl-like surface groups [31,32]. The O_{ads}/(O_{ads}+O_{lat}) ratios of both MnO_x samples were calculated and are given in Table 2. It is interesting to observe that the O_{ads}/(O_{ads}+O_{lat}) ratio for the MnO_x-400 sample is slightly higher than that for the MnO_x-500 sample, indicating that the MnO_x-400 has more surface oxygen. This suggests greater oxidation ability for this material compared with the MnO_x-500, which in turn favors the selective oxidation of cyclohexane when using O₂ as the oxidant.

3.4. H₂-TPR results

The H₂-TPR profiles of the MnO_x-400 and MnO_x-500 samples are shown in Fig. 4. There are two reduction peaks in the MnO_x-400 sample, at 315 and 450 °C, attributed to the reductions Mn₅O₈ → Mn₃O₄ and Mn₃O₄ → MnO, respectively [33]. With regard to the MnO_x-500 sample, four reduction peaks are seen at 161, 348, 376, and 500 °C. The small reduction peak at 161 °C can be attributed to the reduction of Mn(III) in tetrahedral sites [34,35], while the two overlapped peaks at 348 and 376 °C are assigned to Mn₅O₈ → Mn₃O₄ and Mn₂O₃ → Mn₃O₄ respectively, and the peak at 500 °C is assigned to Mn₃O₄ → MnO [28,36,37]. Compared with the MnO_x-400 sample, the main reduction peaks of the MnO_x-500 sample are obviously shifted to higher temperatures, showing the lower reducibility of the MnO_x-500 sample.

3.5. O₂-TPD results

Figure 5 presents the O₂-TPD profiles of the MnO_x-400 and MnO_x-500 samples. The MnO_x-400 sample exhibits three de-

Fig. 3. XPS Mn 2p (a) and O 1s (b) spectra of MnO_x-400 (1) and MnO_x-500 (2) samples.

Fig. 4. H_2 -TPR profiles of MnO_x -400 (1) and MnO_x -500 (2) samples.

sorption peaks at 487, 613, and 772 °C. The peaks at 487 and 613 °C are attributed to the desorption of adsorbed and lattice oxygen from Mn_5O_8 to Mn_2O_3 , while the peak at 772 °C is assigned to the desorption of lattice oxygen from Mn_2O_3 to Mn_3O_4 [35]. The MnO_x -500 sample only generates a weak peak at 540 °C and a strong peak at 844 °C, assigned to the desorptions of adsorbed and lattice oxygen from Mn_2O_3 to Mn_3O_4 [35,38]. It can be seen that the MnO_x -400 sample has a greater capacity for O_2 adsorption compared with the MnO_x -500, which could account for the higher reactivity of the MnO_x -400 sample for the selective oxidation of cyclohexane by O_2 .

3.6. TG-DTA results

Figure 6 shows the TG-DTA curves obtained from the MnO_x -400 sample before and after the selective oxidation of cyclohexane. Following the reaction, the MnO_x -400 sample was collected by filtration, washed several times with deionized water, and dried overnight at 120 °C. The resulting sample was assessed by TG-DTA analysis with the results presented in Fig. 6. It can be seen that the mass of the unreacted MnO_x -400 sample exhibits a very slow decrease on heating due to the loss of adsorbed water, and does not generate an obvious exothermic peak in its DTA curve. This result indicates that the MnO_x -400 sample is stable when heated to 800 °C. After being used in the reaction, the MnO_x -400 sample undergoes a mass loss of 83% as the temperature is raised to 400 °C, accompanied by a strong

Fig. 5. O_2 -TPD profiles of MnO_x -400 (1) and MnO_x -500 (2) samples.

Fig. 6. TG-DTA curves of the MnO_x -400 sample before (1) and after (2) the reaction.

exothermic peak at approximately 400 °C, which is due to the combustion of carbon deposited on the MnO_x -400 sample during the reaction [39,40].

3.7. Catalytic performance of MnO_x catalysts

Table 3 summarizes the catalytic performance of the MnO_x catalysts for the selective oxidation of cyclohexane with O_2 as the oxidant. These results show that a 1.2% conversion of cyclohexane with 92% total selectivity for KA oil was achieved in the blank test. Using MnO_x as the catalyst, the conversion of cyclohexane was greatly increased while the selectivity for KA markedly decreased. The calcination temperature evidently had a significant effect on the catalytic activity of the MnO_x . As the calcination temperature applied to the MnO_x catalysts was increased, the conversion of cyclohexane first increased and then decreased, although the total selectivity for KA exhibited a continual gradual increase. As shown in Table 3, when employing the MnO_x -400 catalyst, an 8.0% conversion of cyclohexane was achieved with 62% total selectivity for KA oil, such that the yield of KA oil was 5.0%. When using the MnO_x catalyst calcined at 500 °C, the conversion of cyclohexane decreased to 6.1%, but the selectivity for KA oil increased to 75%. Compared with the MnO_x -400 catalyst, the MnO_x -500 catalyst exhibited a lower surface area and lower concentrations of surface Mn^{4+} and surface oxygen (O_{ads}), which account for its reduced ability for O_2 adsorption and activation and the lower conversion of cyclohexane that it provides. In contrast, the MnO_x -500 catalyst's lower ability for O_2 adsorption and activation also limited the over-oxidation of cyclohexanol and cyclohexanone, leading to the increase in its selectivity for KA oil. The reported performance of other catalysts intended for the selective oxidation of cyclohexane is also listed in Table 3. When using O_2 as the oxidant, the MnO_x -400 catalyst showed higher activity for the selective oxidation of cyclohexane than has been reported for Co-TUD-1, Au/MgO, and Mn_3O_4 in the literature [41–43]. However, the yield of KA oil over the MnO_x -400 catalyst was much lower than that obtained from a Mn-TUD-1 catalyst when employing TBHP as the oxidant [44].

Table 3Catalytic performance of the MnO_x catalysts for the selective oxidation of cyclohexane with O₂.

Catalyst	Time (h)	Atmosphere (MPa)	Conversion (%)	Selectivity (%)				Yield of KA oil (%)
				Cyclohexanol (A)	Cyclohexanone (K)	KA oil ^a	Acids ^b	
Blank test	5	O ₂ /0.5	1.2	43	49	92	4	1.1
MnO _x -400	4	N ₂ /0.5	—	—	—	—	—	—
MnO _x -350	4	O ₂ /0.5	7.5	30	29	59	8	4.4
MnO _x -400	4	O ₂ /0.5	8.0	32	30	62	6	5.0
MnO _x -450	4	O ₂ /0.5	6.6	34	33	67	7	4.4
MnO _x -500	4	O ₂ /0.5	6.1	38	37	75	8	4.6
Co-TUD-1 ^c [41]	24	8% O ₂ /N ₂ /1.5	3.8	56	31	87	—	3.3
Au/MgO ^d [42]	17	O ₂ /0.3	5.0	50	29	79	19	4.0
Mn ₃ O ₄ ^e [43]	6	O ₂ /1.0	5.2	36	27	63	35	3.3
Mn-TUD-1 ^f [44]	24	TBHP	13.5	24	60	84	—	11.3

Reaction conditions: cyclohexane 4 mL, catalyst 20 mg, 140 °C.

^a Cyclohexanol (A) and cyclohexanone (K).^b Adipic acid, glutaric acid, and succinic acid.^c Reaction conditions: cyclohexane 175 mmol, cyclohexyl hydroperoxide (radical initiator) 0.05 mmol, active metal species 0.1 mmol, 120 °C.^d Reaction conditions: cyclohexane 10 mL, *tert*-butylhydroperoxy (radical initiator) 0.05 mmol, catalyst amount 6 mg, 140 °C.^e Reaction conditions: cyclohexane 10 g, catalyst amount 0.1 g, 140 °C.^f Reaction conditions: cyclohexane 9.8 g, *tert*-butylhydroperoxy 4.4 g, Mn catalyst 0.1 mmol, 70 °C.

3.8. Effect of reaction conditions on the activity of the MnO_x-400 catalyst

The effects of the reaction temperature, reaction time, and the initial oxygen pressure on the catalytic activity of the MnO_x-400 catalyst for the cyclohexane oxidation were evaluated. As shown in Fig. 7(a), with increases in the reaction temperature from 120 to 160 °C, the conversion of cyclohexane gradually increased, while the selectivity for cyclohexanol and cyclohexanone markedly decreased at first, then plateaued. This occurs because the higher reaction temperature enhances the activation of cyclohexane but also promotes the over-oxidation of cyclohexanol and cyclohexanone to esters, which can be detected by GC-MS. Considering both the conversion of cyclohexane and the selectivity for KA oil, it can be seen that the most appropriate reaction temperature is 140 °C.

The effect of the reaction time on the activity of the MnO_x-400 catalyst for cyclohexane oxidation is summarized in Fig. 7(b). Increasing the reaction time evidently results in a slight enhancement of the cyclohexane conversion, while the selectivity for cyclohexanol and cyclohexanone decreases

gradually because of the over-oxidation of cyclohexanol and cyclohexanone [45,46]. The generation of acidic by-products changed only minimally with variations in the reaction time, although esters resulting from over-oxidation of cyclohexanol and cyclohexanone were detected by GC-MS. From these data, the optimal reaction time appears to be 4 h.

Figure 7(c) shows the effect of the initial O₂ pressure on the cyclohexane oxidation over the MnO_x-400 catalyst. The results demonstrate that raising the initial oxygen pressure can enhance both the conversion of cyclohexane and the selectivity for acids, and thus reduce the selectivity for cyclohexanol and cyclohexanone. This phenomenon may be caused by the over-oxidation of cyclohexanol and cyclohexanone under high pressure O₂. Taking into account both the conversion of cyclohexane and the selectivity for KA oil, the optimal initial O₂ pressure is evidently 0.5 MPa.

3.9. Repeated use of the MnO_x-400 catalyst

After the reaction finished, the catalyst was separated by filtration from the reaction solution, washed with ethanol three

Fig. 7. Effect of the reaction temperature (a), reaction time (b), and initial oxygen pressure (c) on the catalytic activity of MnO_x-400 for cyclohexane oxidation. Reaction conditions: cyclohexane 4 mL, catalyst 20 mg; (a) O₂ 0.5 MPa, 4 h; (b) O₂ 0.5 MPa, 140 °C; (c) 140 °C, 4 h.

Fig. 8. Effect of recycling on the catalytic activity of MnO_x-400 for cyclohexane oxidation.

times, dried at 100 °C for 6 h, then calcined in air at 400 °C for 2 h. The catalytic activity of this regenerated MnO_x-400 catalyst was subsequently assessed, and the results obtained from 10 such recycling trials are shown in Fig. 8. It can be seen that the conversion of cyclohexane and the selectivity for KA oil are barely changed by the repeated usage. These results indicate that the MnO_x-400 catalyst exhibits good stability for the selective oxidation of cyclohexane by O₂ in a solvent-free system.

4. Conclusions

The effect of calcination temperature on the physicochemical and catalytic properties of MnO_x catalysts prepared by the precipitation method was investigated. These MnO_x catalysts exhibited high catalytic performance during the selective oxidation of cyclohexane with O₂ in a solvent-free system. The calcination temperature markedly affected the catalytic activity, such that the catalyst calcined at 400 °C exhibited the highest activity, giving an 8.0% cyclohexane conversion and a 5.0% yield of cyclohexanol and cyclohexanone at 0.5 MPa initial O₂ pressure and 140 °C over 4 h. After 10 reaction cycles, the catalytic activity of the MnO_x-400 catalyst was unchanged,

demonstrating that this material is highly stable during the selective oxidation of cyclohexane by O₂ in a solvent-free system. Compared with the MnO_x-500 catalyst, the MnO_x-400 catalyst, consisting of both Mn₃O₄ and Mn₅O₈, possessed a higher surface area and elevated concentrations of surface adsorbed oxygen and surface Mn⁴⁺ ions. These species can promote oxygen mobility, O₂ adsorption, and the reducibility of the catalyst, leading to the observed superior catalytic activity of the MnO_x-400 catalyst for the selective oxidation of cyclohexane in a solvent-free system.

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Graphical Abstract

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Solvent-free selective oxidation of cyclohexane with molecular oxygen over manganese oxides: Effect of the calcination temperature

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MnO_x exhibited high catalytic activity and excellent stability during cyclohexane oxidation with molecular oxygen. The MnO_x phase state, as determined by the calcination temperature, had a crucial effect on its catalytic activity.

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氧化锰催化剂在环己烷无溶剂选择性氧化反应中的活性：焙烧温度的影响

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摘要: 环己醇和环己酮俗称KA油, 是用于制备尼龙材料的己二酸和己内酰胺的重要中间体。工业上制取环己醇和环己酮的方法主要为苯酚加氢法、环己烯水合法和环己烷氧化法, 其中环己烷氧化法的应用最为普遍, 包括硼酸氧化法、过氧化物氧化法和钴盐催化氧化法三种路线。为获得适宜的环己醇和环己酮选择性, 工业上环己烷氧化单程转化率通常控制在5.0%以下, 从而使得产物选择性在80%以上。因此, 现有环己烷氧化法生产KA油的最大挑战是如何同时获得高环己烷转化率和KA油选择性。迄今, 已有多种催化剂被尝试用于环己烷氧化反应, 包括金属卟啉、金属氧化物、分子筛、碳纳米管和金属-有机骨架材料等。由于均相催化剂无法从环己烷氧化反应体系中分离出来, 导致催化剂不能重复利用, 因此多相催化剂的研究更受青睐。另外, 由于采用氧气为氧化剂时具有环境友好和更高的原子经济性, 因此氧气选择性氧化环己烷反应已逐渐成为环己烷氧化法制KA油中最具挑战性的研究。目前, 氧气为氧化剂时的环己烷转化率通常低于过氧化氢和叔丁基过氧化氢等为氧化剂时的转化率, 其关键在于适用于固(催化剂)液(环己烷)气(氧化剂)反应体系的高性能催化剂。本课题组前期研究了系列金属掺杂分子筛(Ce/AlPO-5, Ce-MCM-41/48和Mg-Cu/SBA-15等)对氧气催化氧化环己烷的反应性能, 发现无论是稀土还是过渡金属掺杂, 通过影响环己烷氧化反应的自由基产生和反应历程, 可显著提高环己烷转化率或者KA油的选择性。基于此, 本文选择原料易得、成本较低和氧化能力强的氧化锰(MnO_x)作为具有强氧化能力的过渡金属氧化物的代表, 深入研究了 MnO_x 的焙烧温度对其结构和选择性氧化环己烷反应性能的影响, 同时研究了反应条件对催化剂性能的影响。

结果表明, 400 °C焙烧制得的催化剂(MnO_x -400)比350, 450和500 °C焙烧制得的催化剂具有更高的活性。在最佳反应条件(140 °C, O_2 起始压力0.5 MPa, 反应4 h)下, 使用20 mg MnO_x -400可使环己烷转化率达8.0%, KA油得率为5.0%。过高的反应温度、过长的反应时间和过高的反应压力都会导致产物被过度氧化, KA油选择性降低。另外, 该催化剂重复使用10次, 其活性没有明显下降, 显示出了很好的稳定性。表征测试结果表明, MnO_x 催化剂在不同温度焙烧后形成了不同的结晶形态: 焙烧温度小于500 °C时, 催化剂主要组成为 Mn_3O_4 和 Mn_5O_8 , 500 °C时主要为 Mn_3O_4 , Mn_5O_8 和 Mn_2O_3 。而且随着焙烧温度升高, MnO_x 催化剂的比表面积逐渐降低。相比于350 °C焙烧制得的催化剂, MnO_x -400催化剂具有更好的结晶形态, 这可能是造成其活性较好的原因。而相比于 MnO_x -400, 500 °C焙烧制得的催化剂表面 Mn^{4+} 含量和表面吸附氧含量较低, 使其吸附和

活化氧能力降低,从而导致催化剂活性低于 MnO_x -400;但是吸附和活化氧能力的降低有利于减缓反应产物的深度氧化,因而KA油的选择性增加.

关键词: 氧化锰; 环己烷选择氧化; 氧气; 焙烧温度; 无溶剂反应

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