



Magnetic CoFe_2O_4 nanocrystal: A novel and efficient heterogeneous catalyst for aerobic oxidation of cyclohexane

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ABSTRACT

Magnetic nanocrystalline spinel-type cobalt ferrite complex oxides were prepared by a simple sol-gel auto-combustion method at five different molar ratios of Co^{II} to Fe^{III} (1:4.0, 1:2.8, 1:2.0, 1:1.5, and 1:1.1) and characterized by X-ray diffractometry (XRD), Fourier transform infrared spectrophotometry (FT-IR) and transmission electron microscopy (TEM). Their catalytic performance was evaluated in the oxidation of cyclohexane with oxygen as oxidant in the presence of neither solvents nor reducing agents. It has been revealed that the catalysts had high catalytic activities for heterogeneous oxidation of cyclohexane. Especially, when pure CoFe_2O_4 was used as catalyst; excellent results with turnover number of 288 and 92.4% selectivity for cyclohexanone and cyclohexanol was obtained under 1.6 MPa of initial oxygen pressure at 418 K after 6.0 h of reaction. The influences of initial oxygen pressure, reaction temperature, reaction time, and free-radical initiator on the oxidation of cyclohexane over CoFe_2O_4 were investigated. The catalyst can be easily separated by an external magnet and no obvious loss of activity was observed when reused in five consecutive runs. CoFe_2O_4 was proved to be also efficient for oxidation of linear alkanes.

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1. Introduction

Although there have been major advances in the oxidation of hydrocarbons with molecular oxygen, the development of effective and selective methods for the catalytic functionalization of inactive carbon-hydrogen bonds in saturated hydrocarbons still remains a major challenge in oxidation chemistry [1,2]. Of particular importance is the oxidation of cyclohexane due to the large demand for cyclohexanone and cyclohexanol (K/A oil), which are important raw materials for the production of adipic acid and caprolactam finally used in the manufacture of nylon-6 and nylon-66 polymers [3,4]. However, the oxidation of cyclohexane turns out to be the least efficient of all major industrial processes [5]. The present industrial process for cyclohexane oxidation is carried out around 423 K and 1–2 MPa pressure employing metal cobalt salt or metal-boric acid as homogeneous catalyst worldwide. The drawback of this process is that the oxidation must be operated in 3–6% conversion of cyclohexane to maintain high selectivity (75–80%) for the K/A oil [6]. Great efforts have been devoted to the oxidation of cyclohexane in the past years [4,7–16]. However, owing to the

employment of large amounts of solvents and/or reducing agents as well as harsh reaction conditions, it is still difficult to apply these technologies to industrial processes [7–10,17,18]. So the great demand for these oxidation products and the high-energy intensity of the present process warrant a replacement with a more effective catalytic process. Oxidation of cyclohexane heterogeneously with molecular oxygen without any solvents or reducing agents is particularly desirable from both economical and environmental aspects.

Transition metal oxides are known for their redox properties and capacity to catalyze the oxidation of hydrocarbons [19–21]. In the last two decades, considerable applied as well as fundamental research efforts have been spent on the activation and the functionalization of hydrocarbons catalyzed by transition metal oxides [22–25]. In particular, nanosized materials have attracted great interests in recent years due to their well-known specific physical and chemical properties [12,21].

Nanoparticles of complex metal oxides such as spinel ferrites are thermally and chemically stable. The nanoparticles possess great potentials for application in catalysis, gas sensors, high quality ceramics and super paramagnetic materials [26–31]. The properties of these materials mainly depend on their shape, size, and structure, which are strongly determined by the synthetic processes. Among the many synthetic methods proposed, the sol-gel auto-combustion route, as a unique combination of the combustion and the chemical gelation process, is preferred in general because of its

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main advantages of inexpensive precursors, short preparation time, modest heating and relatively simple manipulations [30,32,33].

Cobalt ferrite, CoFe_2O_4 , as a well-known spinel ferrite and hard magnetic material, has attracted much attention on its very high cubic magnetocrystalline anisotropy, high coercivity, and moderate saturation magnetization in recent years [28–31,34]. However, only a few efforts have been devoted to its catalytic activity [35–37]. In this work, nanocrystalline cobalt ferrite samples were prepared by a modified sol–gel auto-combustion method at different Co:Fe ratios, and their catalytic abilities in the oxidation of cyclohexane with oxygen as oxidant in a solvent-free system without any additives were investigated. High conversion and selectivity were obtained.

2. Experimental

2.1. Materials and equipments

Cyclohexane and toluene were purified before use. Other reagents were of analytical grade and were used as received. FT-IR spectra were measured on a Nexus 870 FT-IR spectrophotometer. XRD patterns of the samples were collected using a PANalytical X'Pert Pro diffractometer with $\text{Cu K}\alpha$ radiation. TEM micrographs were obtained using a Hitachi H-600 microscope. The oxidation products were determined by an HP 6890/5973 GC/MS instrument and quantified by an Agilent 6820 gas chromatograph using toluene as internal standard.

2.2. Preparation of cobalt ferrite nanocrystals

The nanocrystalline cobalt ferrite complex oxides were prepared according to a modified procedure in the literature [30]. In a typical procedure, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid were completely dissolved in distilled water with a 1:1 ratio of metal ($\text{Co}^{\text{II}} + \text{Fe}^{\text{III}}$) to citric acid. The solution was allowed to evaporate in an oil bath under continuous stirring at 80–90 °C until a brown gel formed. After the reaction, the formed gel was dried at 110 °C for 1 h and a spumous xerogel was obtained. When the produced xerogel was ignited at 650 °C, a self-propagating combustion process occurred and a dark grey fluey product was obtained after it combusted completely. Five samples with different ratios of Co to Fe: 1:4.0, 1:2.8, 1:2.0, 1:1.5, and 1:1.1 were prepared as described above and designated as **cats. 1–5**, respectively.

The samples were ground finely and then used to catalyze the oxidation of cyclohexane with molecular oxygen.

2.3. Characterization of the catalysts

The XRD patterns of the samples is in agreement with the standard XRD pattern for cobalt ferrite (JCPDS NO. 22-1086), showing the presence of spinel ferrite phase (Fig. 1). It also shows clearly that pure spinel ferrite was obtained only when the stoichiometric molar ratio of Co to Fe was used (**cat. 3**), and a small amount of Fe_2O_3 or Co_2O_3 coexists with the spinel ferrite in other nonstoichiometric samples (**cats. 1, 2 and 4, 5**). The mean particle sizes of the samples calculated by applying the Sherrer equation to [3 1 1] reflections are 34, 29, 27, 25, and 21 nm for **cats. 1–5**, respectively.

Fig. 2 shows the FT-IR spectra of the five samples. A strong band associated with the Fe–O stretching vibration at 581, 574, 585, 583 and 577 cm^{-1} for **cats. 1–5** is presented. It confirms the presence of the cobalt ferrite phase [32]. No characteristic bands corresponding to citric acid or NO_3^- appeared, and this indicates that no citric acid or NO_3^- is residual in the samples.

The purpose of using nonstoichiometric molar ratios of Co to Fe is to prepare corresponding nonstoichiometric spinel ferrite. Unexpectedly, there is no shift in the spinel peak positions or IR; furthermore, the XRD peaks for the Fe_2O_3 or Co_2O_3 that form from

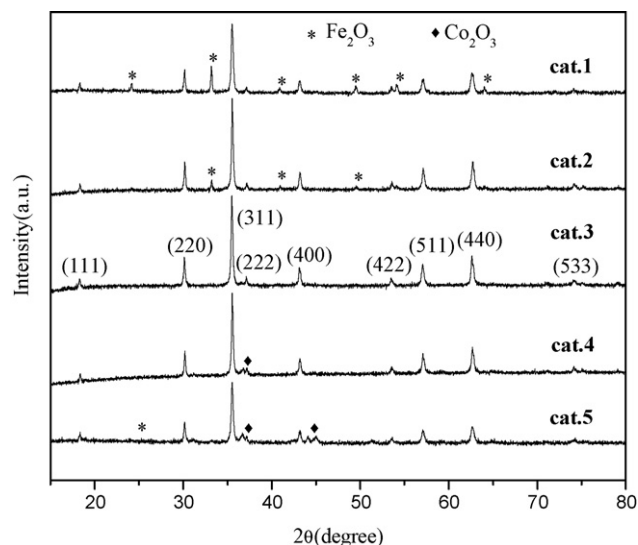


Fig. 1. The XRD patterns of the samples **cats. 1–5**.

a nonstoichiometric reaction mixture are on the same order of intensity as that for the spinel, so it seems likely that only the stoichiometric CoFe_2O_4 is formed, and any excess of either Co or Fe just goes to make the corresponding oxide.

The TEM micrographs of **cat. 3** and **cat. 1** are shown in Fig. 3 as representations. The samples of **cats. 3–5** are very similar (Fig. 3A): they show nanoparticles with an irregular morphology and a broad particle size distribution ranging from around 15–20 to 50–60 nm, with a high percentage of small particles (25–35 nm). More regular spherical shape and particle size (in the range of 35–40 nm) distribution were observed for the samples of **cats. 1 and 2** (Fig. 3B). It is clear that the samples have particle agglomeration forms.

2.4. Oxidation of cyclohexane

The oxidation of cyclohexane was performed in a 30 mL stainless steel autoclave equipped with a magnetic stirrer and an automatic temperature controller. In a typical reaction, 5.0 mg catalyst and 4.0 mL (37.3 mmol) cyclohexane were added to the autoclave. The autoclave was flushed three times with O_2 and pressurized to the

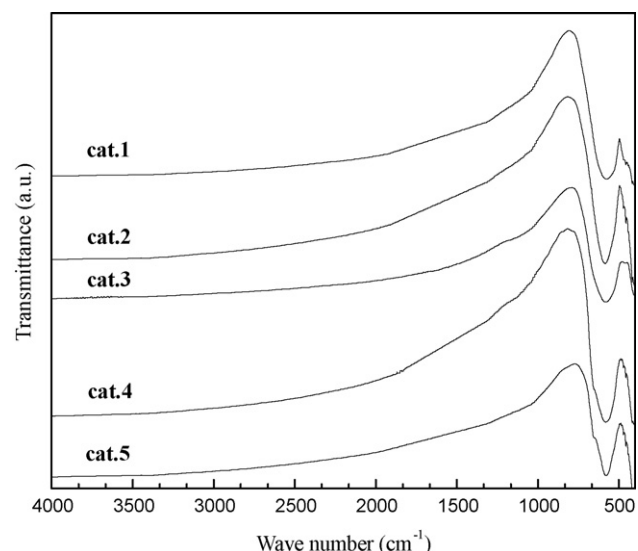


Fig. 2. The FT-IR spectra of **cats. 1–5**.

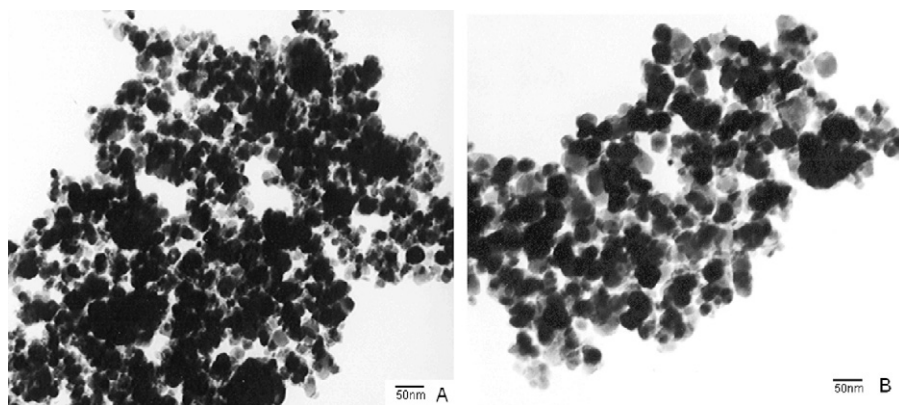


Fig. 3. The TEM morphology of **cat. 3** (A) and **cat. 1** (B).

desired pressure, and then heated to the desired temperature with stirring. After the reaction, the autoclave was cooled to room temperature and slowly depressurized. The samples were identified by GC–MS and quantified by GC using toluene as internal standard. The main by-products of the reaction are hexanedioic acid, hexanoic acid, dicyclohexyl adipate and cyclohexyl caproate (Scheme 1).

3. Results and discussion

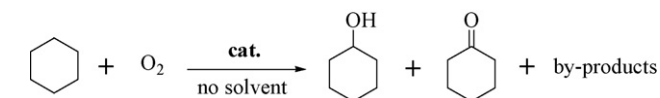
3.1. Catalysis tests

The results of cyclohexane oxidation over the as-prepared samples are listed in Table 1, and those over other catalysts are also listed for comparative purpose. As can be seen, the samples have high catalytic activities for oxidation of cyclohexane and high turnover numbers have been obtained. Obviously, the pure CoFe_2O_4 spinel (entry 3) shows better catalyst activity rather than other samples (entries 1, 2 and 4, 5), probably due to the presence of minor impurities in the latter. It also gave much higher conversion and turnover numbers than homogeneous cobalt acetate (entry 6), industrial cobalt salt and boric acid (entries 7 and 8), nanosized cobalt and iron oxides as well as their mechanical mixture (entries 9–14) while a comparable high selectivity for K/A oil was obtained. Cyclohexane can also be converted in the absence of catalyst under our experimental conditions; however, only a low conversion of 6.1% was obtained (entry 15).

In order to investigate the catalytic activity of the nanocrystalline CoFe_2O_4 spinels, a series of experiments was carried out by choosing pure CoFe_2O_4 (**cat. 3**) as catalyst with initial oxygen pressure, reaction temperature, reaction time and free-radical initiator changed.

3.2. Effect of initial oxygen pressure

Effect of initial oxygen pressure on the conversion as well as the products distribution of cyclohexane oxidation was investigated in the range of 1.2–2.0 MPa. The results are shown in Fig. 4. As can be seen, with an increase in the initial oxygen pressure, the conversion of cyclohexane increased expectedly. When the initial oxygen pressure was increased from 1.2 to 1.6 MPa, the selectivity for cyclohexanol decreased from 23.8 to 16.1%, and that for



Scheme 1. Oxidation of cyclohexane.

cyclohexanone increased from 70.5% to its maximum 77.3%. That is cyclohexanol is apt to be further oxidized to cyclohexanone at higher oxygen pressure. A possible reason for the decrease in selectivity for cyclohexanone when oxygen pressure is above 1.6 MPa is that cyclohexanone was oxidized deeply to acids and other by-products. The selectivity for K/A oil decreased all along with an increase in the initial oxygen pressure in the investigated range because of more deep oxidation products formed under higher oxygen pressure.

3.3. Effect of reaction temperature

Fig. 5 shows the results of cyclohexane oxidation at different temperatures. When the reaction temperature was raised from 140

Table 1
Oxidation of cyclohexane with different catalysts^a.

Entry	Catalyst	Conversion (%) ^b	TON ^c	Selectivity (%) ^b	
				-ol + -one ^d	-one ^d
1	cat. 1	9.7	169	89.9	71.1
2	cat. 2	9.8	171	90.3	75.8
3	cat. 3	16.2	288	92.4	73.9
4	cat. 4	10.3	181	92.9	74.0
5	cat. 5	12.5	220	89.9	71.5
6	$\text{Co}(\text{OAc})_2^e$	8.3	147	95.9	71.0
7	$(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Co}$	11.8	210	91.2	74.6
8	H_3BO_3^f	9.6	44	86.2	68.1
9	Co_2O_3^g	10.7	190	93.6	72.8
10	Co_3O_4^h	7.6	16	89.1	49.5
11	Fe_2O_3^i	8.4	149	84.3	53.8
12	Fe_3O_4^i	6.4	114	79.3	47.5
13	$\text{Co}_2\text{O}_3 + \text{Fe}_2\text{O}_3^j$	8.6	153	95.6	82.8
14	$\text{Co}_2\text{O}_3 + \text{Fe}_3\text{O}_4^j$	6.5	115	96.8	88.6
15	Blank	6.1	–	95.2	72.1

^a Reaction conditions: cyclohexane 4.0 mL (37.3 mmol); catalyst 0.021 mmol; initial oxygen pressure = 1.6 MPa; temperature = 418 K; reaction time = 6 h.

^b The amount of cyclohexane converted was calculated by subtracting that of unreacted cyclohexane quantified by GC using toluene as internal standard from that of starting cyclohexane. Conversion is defined as the percentage of cyclohexane converted. Selectivity is defined as molar ratio of one product to cyclohexane converted.

^c TON = moles of substrates converted per mol of catalyst.

^d -ol = cyclohexanol; -one = cyclohexanone.

^e $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ as catalyst.

^f Boric acid 5.0 mg; the reacted mixture was hydrolyzed with water, extracted with diethyl ether, after separation, the organic phase was analyzed by GC.

^g Average particle size = 15 nm.

^h Results from Ref. [39]. Reaction was carried out with the addition of TBHP (0.4 wt% of cyclohexane) at 393 K for 6 h.

ⁱ From Aldrich, product USA, MSDS available, <50 nm.

^j Co:Fe molar ratio is equal to the stoichiometric value in CoFe_2O_4 .

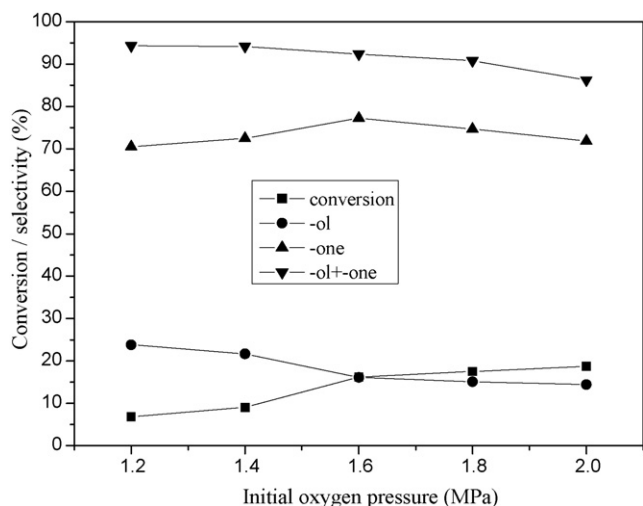


Fig. 4. Effect of initial oxygen pressure on cyclohexane oxidation. Reaction conditions: cyclohexane 4.0 mL (37.3 mmol); **cat. 3** 5.0 mg (0.021 mmol); temperature = 418 K; reaction time = 6.0 h.

to 145 °C, the conversion of cyclohexane increased sharply from 5.2 to 16.2%, but only a slight increase was shown above 145 °C. With increasing temperature, the selectivity for cyclohexanol decreased, and the molar ratio of K/A oil increased, probably due to cyclohexanol being further oxidized to cyclohexanone. As a result, in the range of 140–160 °C, the selectivity for cyclohexanol decreased from 37.3% to zero, but that for cyclohexanone increased from 62.7 to 90.6%. In addition, the selectivity for K/A oil decreased from 100 to 90.6% because of more by-products formed at higher temperature. It is also clear that, when the reaction temperature increased from 145 to 150 °C, the selectivity for cyclohexanol hardly changed, whereas that for K/A oil decreased by more than 4%. This is due to more cyclohexanone being converted to deep oxidation products; its selectivity also decreased from 77.3 to 72.9%.

3.4. Effect of reaction time

Fig. 6 presents the effect of reaction time on cyclohexane oxidation. Obviously, the reaction hardly occurred during the first 2 h, which might be the initiation period according to the generally accepted free radical mechanism [38]. After this period, the con-

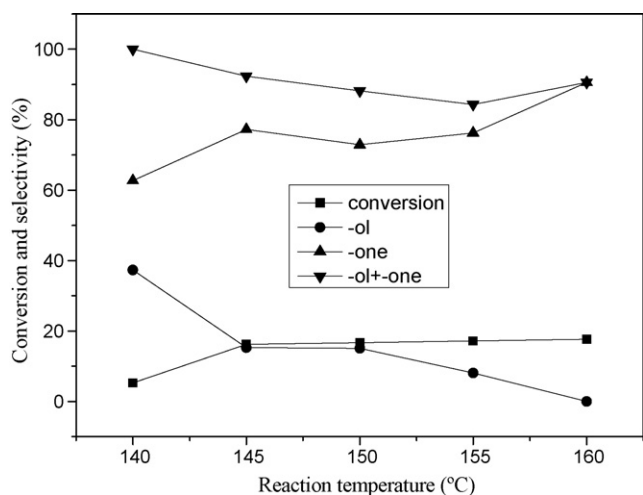


Fig. 5. Effect of reaction temperature on cyclohexane oxidation. Reaction conditions: cyclohexane 4.0 mL (37.3 mmol); **cat. 3** 5.0 mg (0.021 mmol); initial oxygen pressure = 1.6 MPa; reaction time = 6.0 h.

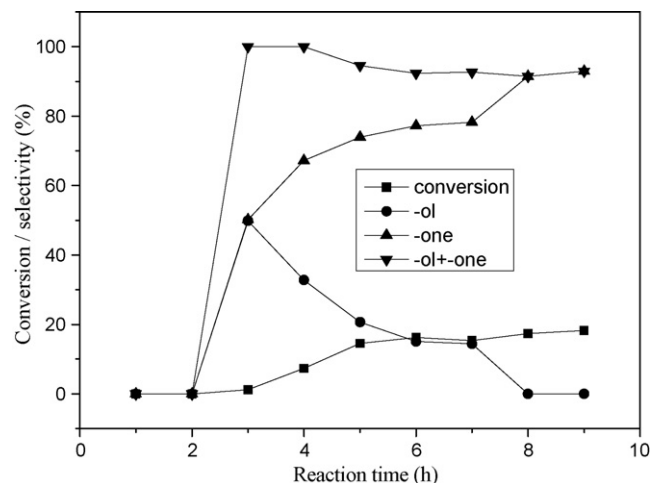


Fig. 6. Effect of reaction time on cyclohexane oxidation. Reaction conditions: cyclohexane 4.0 mL (37.3 mmol); **cat. 3** 5.0 mg (0.021 mmol); initial oxygen pressure = 1.6 MPa; temperature = 418 K.

version of cyclohexane exhibited an almost linear increase from 1.2 to 16.2% in an additional 3 h and reached 18.3% after 9 h of the reaction. When the reaction time was prolonged from 3 to 9 h, the selectivity for cyclohexanone increased rapidly from 50.1 to 93.0%, but that for cyclohexanol decreased sharply from 49.8% to zero because cyclohexanol is apt to be oxidized to cyclohexanone and other deep oxidation products. It is also clear that longer reaction time was unfavorable to the selective production of K/A oil because of more by-products formed. As can be seen in Fig. 6, the selectivity for K/A oil decreased from 100 to 93% when the reaction time was prolonged from 2 to 9 h.

3.5. Effect of *tert*-butyl hydroperoxide and acetone

Since the reaction had an induction period, the effect of *tert*-butyl hydroperoxide (TBHP) and acetone as free-radical initiators was investigated and the results are shown in Table 2. Obviously, the addition of TBHP greatly enhanced the rate of cyclohexane conversion while a high selectivity for the two desired products cyclohexanone and cyclohexanol was retained. After 2 h of reaction, the conversion of cyclohexane with the addition of TBHP reached the level of that with no initiator after 5 h of reaction. The reaction can also be initiated by acetone; 7.1% of cyclohexane conversion and 98.8% of selectivity for K/A oil were obtained with the addition of acetone after 2 h of reaction, while this was the initiation period for the system without additives (Fig. 6). These facts can afford the

Table 2
Effect of TBHP and acetone on cyclohexane oxidation^a.

Additive	Time (h)	Conversion (%)	TON	Selectivity (%)	
				-ol + -one	-one
TBHP ^b	0.5	11.0	192	96.8	64.9
	1.0	12.6	220	95.3	70.6
	1.5	13.8	241	95.6	70.9
	2.0	15.1	264	94.4	71.6
	3.0	17.6	308	92.6	75.6
Acetone ^b	1.0	–	–	–	–
	2.0	7.1	124	98.8	64.8
	3.0	10.7	187	94.2	66.6
	4.0	12.1	215	94.4	69.6

^a Reaction conditions: cyclohexane 4.0 mL (37.3 mmol); **cat. 3** 5.0 mg (0.021 mmol); initial oxygen pressure = 1.6 MPa; temperature = 418 K.

^b 3 wt% of cyclohexane.

Table 3
Oxidation of other substrates^a.

Substrate	Conversion (%)	TON	Selectivity (%) ^b	
Pentane	3.1	51	2-Pentanone (56.3)	3-Pentanone (43.7)
Hexane	4.9	70	2-Hexanone (28.5)	3-Hexanone (71.5)
Heptane	5.7	75	2-Heptanone (62.4)	4-Heptanone (37.6)
Octane	9.1	105	2-Octanone (23.8)	3-Octanone (70.0) 4-Octanone (6.2)

^a Reaction conditions: substrate 4.0 mL; **cat. 3** 5.0 mg (0.021 mmol); initial oxygen pressure = 1.6 MPa; temperature = 418 K; reaction time = 6 h.

^b Trace of other products were ignored.

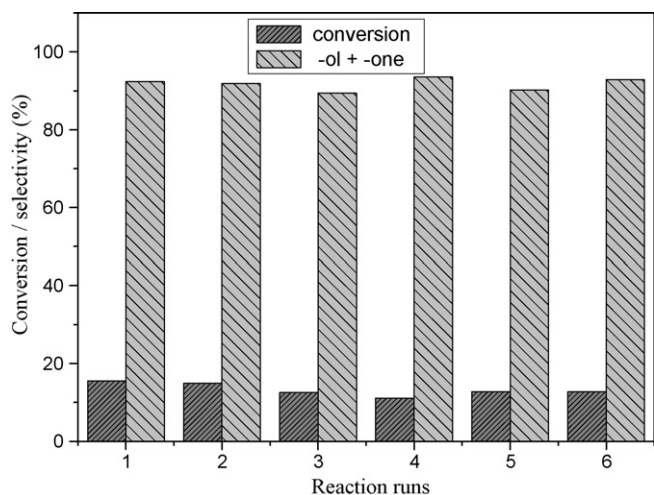


Fig. 7. Reuse of the catalyst. Reaction conditions: cyclohexane 4.0 mL (37.3 mmol); **cat. 3** 5.0 mg (0.021 mmol); initial oxygen pressure = 1.6 MPa; temperature = 418 K; reaction time = 6 h.

evidence that the oxidation of cyclohexane proceeds by a free-radical mechanism.

3.6. Reuse of the catalyst

After the reaction, the mixture was poured into a flask and the catalyst can be seen being adsorbed on a magnet. The catalyst together with the magnet can be easily separated by simple decantation after applying a magnetic field on the surface of the flask, and then subjected to the second run under the same conditions. The data obtained are listed in Fig. 7. The total selectivity changed only slightly after six runs, but the conversion of cyclohexane dropped from 15.5 to 12.7%. The decrease in the activity could be mainly attributed to unavoidable loss of the catalyst during the process of collection. The results confirm that the nanocrystalline CoFe_2O_4 spinel has good stability and recyclable applicability for the oxidation of cyclohexane with O_2 in a solvent-free system.

4. Extension to other substrates

The optimal reaction conditions were applied to the oxidation of linear alkanes. The results are listed in Table 3. Unfortunately, the as-prepared nanocrystalline CoFe_2O_4 spinel is less effective for the oxidation of linear alkanes under the same conditions. The conversions and selectivities listed in Table 3 are based on the area normalization method, and hence there are probably substantial amounts of by-products not accounted for in the analysis (CO_2 very probably is one of the more important ones). So the apparent conversions are possibly artificially low and the selectivities are probably high.

5. Conclusions

Spinel cobalt ferrite nanocrystals were prepared by a modified sol-gel auto-combustion route without calcination. The precursor is cheap, and the method is simple and effective. The samples prove to be highly active and easily reusable catalysts for cyclohexane oxidation in a green catalytic system; high turnover numbers and selectivity can be obtained. The pure stoichiometric CoFe_2O_4 nanocrystal showed optimum catalytic activity; 16.2% of cyclohexane conversion and 92.4% of selectivity for cyclohexanone and cyclohexanol were obtained after 6 h of reaction. The catalyst exhibited excellent reusability; when it was reused five times, only a slight loss of the activity was observed and the selectivity was practically unchanged.

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