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Highly efficient oxidation of cyclopentene catalyzed by magnetically recoverable Ca-Co ferrite spinels with high solvent selectivity

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Abstract

The calcium doped CoFe₂O₄ spinels Ca_xCo_{1-x}Fe₂O₄ (x = 0, 0.1, 0.3, 0.5 and 0.7) were prepared by simple sol-gel auto-combustion method. The samples were characterized by X-ray diffractometry, Raman spectrometry, scanning and transmission electron microscopy, N₂-physisorption and inductive coupled plasma– atomic emission spectroscopy. The samples have shown prominent activities in oxidation of cyclopentene using 30 % hydrogen peroxide as oxidant. When compared to the pristine CoFe₂O₄, the Ca-doped were more efficient having a conversion ranging from 72.1 to 100 % and a H₂O₂ utilization efficiency range of 80.0 to 84.7 %. When the calcium content was 0.3 and above, the cyclopentene was quantitatively converted to cyclopentenone at 60 °C for 8 hours reaction. More interestingly, the catalyst has shown great solvent selectivity with respect to the product distribution.

Finally, the catalyst can be easily separated magnetically for reuse and no obvious loss of activity was observed after five consecutive runs.

Keywords: Sol-gel auto-combustion; Magnetic nanocrystals; Ca-Co composite ferrites; Cyclopentene oxidation; Solvent selectivity

1. Introduction

The increased industrial pyrolysis processes raise the problem of comprehensive use of their products, in particular, cyclopentene[1]. The ineluctable amount of cyclopentene has been obtained as a main by-product of the C_5 fraction in the petrochemical or coking industry[2, 3]. Thus, various researches have been introduced to be able to convert cyclopentene to more useful functionalized products, in which mostly employed the selective oxidation process to produce cyclopentene oxide, cyclopentanone, glutaraldehyde and cyclopentenone. These products are widely utilized in the production of macromolecular compounds, plasticizers, fragrances, pharmaceuticals, bactericides, and agricultural chemicals[1, 4]. In past decade, most of the efforts were on the oxidation of cyclopentene to glutaraldehyde. So far, majority of the reported catalysts are tungsten based, such as supported WO_{3 [3, 5, 6]}, tungsten-substituted molybdophosphoric acids[4], phosphotungstic quaternary ammonium salt[7], tungsten-containing mesoporous material[8] and others. To our best knowledge, little attention has been paid in the allylic oxidation of cyclopentene. From the "green chemistry" point of view, it is critical to develop a highly active, selective and recyclable catalysts for heterogeneous processes to replace those homogeneous reactions which introduces serious environmental problems[9]. One example is the use of magnetically-recyclable catalysts that was able to combine the advantages of high activity and easy recycling in heterogeneous catalytic processes[10]. Among the magnetically-recyclable catalysts, the magnetic spinel ferrites have attracted more attention due to their controllable structure, magnetism

and catalytic properties[11-14]. These ferrite composite oxides have been widely used in oxidation reactions, such as oxidative conversion of methane[15], oxidation of alcohols[16], toluene[17], cyclohexane[18], styrene[19], and monoterpenic alkenes[20] among others.

It is well known that the properties of the ferrites strongly depend on its compositions[21-23] which can be easily manipulated, in which the development of new ferrites is focused on the doping with various metals[24-29] that is commonly prepared using sol–gel auto-combustion method which combines the advantages of chemical sol–gel and combustion processes through a thermally induced anionic redox reaction. The process takes the advantages of inexpensive precursors, simple process, and produces highly reactive nanosized powder[30-32].

In our previous work[18, 19], Cobalt and Mg–Cu ferrite oxides nanocrystals were synthesized through sol–gel auto-combustion method and the samples were proven to be the most active and easily recoverable catalysts in the oxidation of cyclohexane and styrene. As part of our interest in hydrocarbon oxidation catalyzed by spinel ferrites, we are reporting here alkaline earth metal Ca-doped cobalt ferrites that can efficiently catalyze the oxidation of cyclopentene. Interestingly, the catalysts showed high solvent selectivity, wherein the product distribution can be tuned by simply using different solvents.

2. Experimental

2.1. Materials and equipments

All reagents are of analytical grade and were used as received. Visible Raman spectra were recorded on a Jobin–Yvon U1000 scanning double monochromator with a spectral resolution of 4 cm⁻¹. The line at 532 nm from a DPSS 532 Model 200 532 nm single-frequency laser was used as the excitation source. X-ray powder diffraction (XRD) patterns of the samples were collected using a PANalytical X Pert Pro diffractometer with Cu K α radiation. Scanning (SEM) and transmission (TEM) electron microscopy images were obtained using a JSM-5600LV and Hitachi H-600

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microscope, respectively. The Brunauer–Emmett–Teller (BET) surface area measurements were performed on a Micromeritics ASAP 2010 instrument at liquid nitrogen temperature. The metal content was determined by inductive coupled plasma –atomic emission spectrometer (ICP-AES) on a PerkinElmer ICP/6500. The oxidation products were determined by an HP 6890/5973 GC/MS instrument and quantified by a Shimadzu GC-2010 gas chromatograph using toluene as internal standard.

2.2. Preparation of the catalysts

The alkaline earth metal Ca doped cobalt ferrite samples $Ca_xCo_{1-x}Fe_2O_4$ (x = 0, 0.1, 0.3, 0.5, 0.7 and 1.0) were prepared by sol-gel auto-combustion route under optimized conditions reported in our previous work[18] and were designated as CFO-Ca_{0.1}, CFO-Ca_{0.3}, CFO-Ca_{0.5}, CFO-Ca_{0.7} and CaFe₂O₄, respectively.

2.3. Oxidation of cyclopentene

The selective oxidation of cyclopentene was carried out in a 25 mL Schlenk tube. In a typical procedure, 0.06 mmol of catalyst, 2.0 mL (22.6 mmol) of cyclopentene, 10 mL of solvent and 3.5 mL of 30 % hydrogen peroxide, molar ratio of cyclopentene/ $H_2O_2 = 2.3$, were added successively into the flask. The flask was then immersed in an oil bath at desired temperature for desired reaction time under stirring. The products were identified by gas chromatrography-mass spectrometry (GC-MS) and quantified by GC using toluene as internal standard. Four products of cyclopentene oxide (CPEO), cyclopentanone (CPTA), cyclopentenone (CPTE) and glutaraldehyde (GTA) was detected.

3. Results and discussion

3.1. Characterization of the catalysts

Figure 1 shows the XRD patterns of the samples, wherein only the spinel phase was found in low Ca-content samples such as CFO-Ca_{0.1} and CFO-Ca_{0.3}. This indicates that Ca was doped in the lattices of CoFe₂O₄ spinel. The diffraction peak around 20 value of 18.2°, 30.3°, 35.4°, 37.3°, 43.2°, 53.4°, 57.2°, 62.1° and 74.2° can be ascribed to the diffractions of (111), (220), (311), (222), (400), (422), (511), (440) and

(533) of the spinel CoFe₂O₄ (International Centre for Diffraction Data (ICDD) Number 221086). However, in the samples of CFO-Ca_{0.5} and CFO-Ca_{0.7} having high Ca-content, CaFe₂O₄ phase (ICDD No. 72-1199) was also found aside from the spinel phase, which suggests that at this high calcium concentration resulted to the replacement of some cobalt with calcium in the spinel phase. The mean particle sizes of the samples based on the Scherrer equation are 27, 30, 28, 26 and 29 nm for the sample CoFe₂O₄, CFO-Ca_{0.1}, CFO-Ca_{0.3}, CFO-Ca_{0.5} and CFO-Ca_{0.7}, respectively.



Figure 1. The XRD patterns of the as-prepared samples.

The Raman spectra of as-prepared samples along with those of $CoFe_2O_4$ are displayed in Figure 2. $CoFe_2O_4$ crystallizes in cubic spinel structures which yield 6 Raman active modes $(A_{1g} (A_{1g^*}) + E_g + 3T_{1g})$, wherein the highest frequency was split into two modes due to cation inversion. The six modes are clearly seen in Figure 2 consistent with the literature[33, 34]. These Raman active modes are divided into two configuration sites, the tetrahedral (> 600 cm⁻¹) and the octahedral (< 600 cm⁻¹) metal-oxygen bonding sites[35]. When calcium was added to the spinel structure,

three main Raman active modes at 304 cm⁻¹ (E_g), 464 cm⁻¹ (T_{1g}), and 688 cm⁻¹ (A_{1g}) can still be seen on the as-prepared samples. As the concentration of Ca increases, the A_{1g} is broaden and its position shifts to a lower frequency. The frequency red shift of A_{1g} peak implies that there was an elongation of Fe-O bond, which was induced by doping of Ca. The peak broadening is due to the decrease in the grain size caused by the doping. This is consistent with the XRD results which is also reflected in Zn²⁺ doped spinel ferrites (Zn_xCo_{1-x}Fe₂O₄), wherein the octahedral sites were enlarged when Co²⁺ were replaced by Fe²⁺ ions, due to the exchange reaction of Co²⁺ + Fe³⁺ \Leftrightarrow Co³⁺ + Fe²⁺, while Zn is located at the tetrahedral sites[36]. Thus, it is reasonable to assume in the present work that Co²⁺ and Fe²⁺ are distributed at the octahedral sites, and Ca²⁺ and Fe³⁺ are distributed at the tetrahedral sites.



Figure 2. The Raman spectra of the as-prepared samples and CoF₂O₄ nanoparticles.



Figure 3. The SEM and TEM images of the sample CFO-Ca_{0.3}.

The SEM and TEM images of the sample CFO-Ca_{0.3} are shown in Figure 3. The sample CFO-Ca_{0.3} features nanoparticles with an irregular morphology and a broad particle size distribution ranging from 10-20 to 40-60 nm, with a high percentage of small particles (30-40 nm). Other samples showed similar morphologies to the sample CFO-Ca_{0.3}, although their particle sizes are different based on the calculation with the Scherrer equation using the XRD patterns.

N₂-physisorption measurements were also performed for the as-prepared samples and the N₂ adsorption-desorption isotherm of CFO-Ca_{0.3} was shown in Figure 4 as representative. As can be seen, the sample exhibited type III isotherm with H3 hysteresis loop, which indicates existence of piled macropores and slips in the sample. The BET surface area of the sample CFO-Ca_{0.1}, CFO-Ca_{0.3}, CFO-Ca_{0.5}, CFO-Ca_{0.7} and CaFe₂O₄ is 36.1, 35.3, 34.8, 37.2 and 38.1 m²/g respectively. For comparison purpose, the pristine CoF₂O₄ was also prepared under the same conditions and the sample exhibited BET surface area of 35.8 m²/g. The metal content of the samples determined by ICP-AES are listed in Table 1. As can be seen, the determined metal contents are consistent with the given formula.

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Figure 4. The N_2 adsorption-desorption isotherm of CFO-Ca_{0.3}.

Catalyst	Ca content (wt %)	Co content (wt %)	Fe content (wt %)
CoFe ₂ O ₄	-	25.16	47.63
CFO-Ca _{0.1}	1.68	22.72	47.93
CFO-Ca _{0.3}	5.30	18.06	48.70
CFO-Ca _{0.5}	8.87	13.01	49.50
CFO-Ca _{0.7}	12.71	8.02	50.36
CaFe ₂ O ₄	18.55	_	51.80

Table 1. Metal content of the samples

3.2. Catalysis tests

The results of cyclopentene oxidation over the as-prepared samples are listed in Table 2. As shown in the table, all six samples can efficiently catalyze the oxidation of cyclopentene and CPTE was found to be the major product in all the Ca contained samples. It was observed that increasing the Ca content favors the production of CPTE and the selectivity of CPTE reached 100% when the calcium content is above

0.3. As for cyclopentene conversion, it increased firstly but then decreased with increase of Ca content, and the 100% conversion was obtained with CFO-Ca_{0.3}. The selectivity of both CPEO and CPTA decreased with the further increase in Ca content and no CPTA was detected for any Ca contained samples. With respect of GTA selectivity, only very low GTA has been detected with CFO-Ca_{0.1} and CFO-Ca_{0.3} samples. It was hypothesized that the activity of spinels depends on the ability of the metallic ions to migrate between the sublattices without altering the crystal structure[22]. We hypothesized that the migration of iron ions was made easier as the cobalt ions were partially substituted by larger Ca ions. Considering both cyclopentene conversion and the selectivity for CPTE, the sample CFO-Ca_{0.3} was chosen as catalyst to optimize the reaction conditions and investigate the recyclable performance of the catalyst. As can be seen, the sample CFO-Ca_{0.3} also obtained the highest H_2O_2 utilization efficiency and turnover number (TON) of 84.7% and 377 respectively.

		Contraction	H ₂ O ₂ utilization		Selectivity (%) ^c			
Entry	Catalyst		Efficiency	TON ^b	CDEO	CDTA	ODTE	CT A
		(%)	(%)		CPEO	CPIA	CPIE	GIA
1	CoF ₂ O ₄	58.1	76.3	219	15.6	5.7	78.7	_
2	CFO-Ca _{0.1}	88.2	83.1	332	12.9	_	85.9	1.2
3	CFO-Ca _{0.3}	100	84.7	377	_	_	99.5	0.5
4	CFO-Ca _{0.5}	85.2	82.6	321	_	-	100	_
5	CFO-Ca _{0.7}	72.1	80.0	272	_	-	100	_
6	CaF ₂ O ₄	65.3	78.4	246	_	_	100	_

Table 2. Oxidation of cyclopentene over the as-prepared samples^a

^a Reaction conditions: cyclopentene 2.0 mL (22.6 mmol); catalyst 0.06 mmol; DMF 10 mL; 30 % hydrogen peroxide 3.5 mL (molar ratio of cyclopentene/ $H_2O_2 = 2:3$); 60 ^oC, 8h; ^bTON = molar of substrate converted per mol catalyst; ^c CPEO = cyclopentene epoxide, CPTA = cyclopentanone, CPTE = cyclopentenone, GTA = glutaraldehyde.

3.3. Effect of the solvent

Table 3 shows the effects of different solvents on cyclopentene conversion and products distribution over the sample CFO-Ca_{0.3}. It is clear that the solvent has great influence on cyclopentene conversion and the products distribution. The highest cyclopentene conversion and TON of 100% and 377 was achieved in dimethylformamide (DMF) respectively. Interestingly, the selectivity of products exhibited strong dependence on the solvents. As shown in Table 3, as high as 99.5% of selectivity for CPTE was obtained when DMF was used as solvent. Up to 86.7% of selectivity for CPEO in 1,4-dioxane and 100% of selectivity for CPTA in toluene were observed. Such high selectivity for CPTE, CPEO and CPTA when using different solvents has rarely been observed especially with this high conversion rate. However when acetonitrile (CH₃CN) and *tert*-butanol were used as solvents, the conversion decreased to below 50% and the selectivity of each product was below 45%.

	~		H_2O_2		Selectiv	vity (%) ^c		
		Conversio	utilizatio	TON				
Entry	Solvent	n	n	b	CPE	CPT	CPT	GT
		(%)	efficiency		0	А	Е	А
0			(%)					
1	_	16.2	30.1	61	78.5	3.3	_	8.2
2	DMF	100	84.7	377	_	_	99.5	0.5
3	CH ₃ CN	48.5	72.9	183	28.8	15.8	44.1	11.3
4	Toluene	87.6	83.0	330	_	100	_	_
F	1,4-dioxan		91.0	290	967	5.0	0.1	
5	e	/0./	81.0	289	80.7	5.2	8.1	—
6	<i>tert</i> -butanol	35.8	66.5	135	25.3	15.3	42.2	17.2

T-11. 7 Eff. (4) $f = 1 + 4$ (4) $f = -1 + 4$		
LODIO A HITOOT OT COLUMNT ON OVOLODODIONO OV1001	inn	a
Table 5. Effect of solvent on cyclopentelle oxidat.	юп	

^a Reaction conditions: cyclopentene 2.0 mL (22.6 mmol); catalyst 0.06 mmol; solvent 10 mL; 30 % hydrogen peroxide 3.5 mL (molar ratio of cyclopentene/ $H_2O_2 = 2:3$); 60 ^oC, 8h; ^b TON = molar of substrate converted per mol catalyst; ^c CPEO = cyclopentene epoxide, CPTA = cyclopentanone, CPTE = cyclopentenone, GTA = glutaraldehyde.



Scheme 1. Proposed pathways for the catalytic oxidation of cyclopentene.

The solvent effect observed here is rather interesting. The oxidation of cyclopentene by H₂O₂ generally undergoes in two distinctive pathways (Scheme 1). It can occur either on the carbon-carbon double bond to form epoxide or on the allylic C-H bond resulting in 3-hydroperoxycyclopent-1-ene[37-39]. As presented in Table 3, although with a very low conversion (16.2%), the dominant product for the solvent-free reaction is an epoxide which is shown as pathway I in Scheme 1.

It is apparent that in toluene and 1, 4-dioxane, the oxidation is also via carbon-carbon double bond. The epoxide can be further converted to ketone in the presence of the catalyst. The cobalt catalyst was proposed to form a cationic intermediate with epoxide[40] and nonpolar solvent like toluene accelerate the conversion from the cationic intermediate to ketone product[41]. The source of the hydrogen needed to convert the epoxide to a ketone might be coming from the toluene

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via the Yamase/Hill mechanism that will result in the formation of a dimer[42]. However, no trace of toluene dimer was observed under the present condition. For the case of oxidation of cyclopentene in DMF, it would probably follow pathway II (Scheme 1). DMF would likely form a strong complex with the catalyst as observed in synthesis of cobalt oxide/N-doped grapheme nanohybrids (CNG) in DMF wherein it forms very strong coordination complexes[43]. The oxidation reduction reaction onset potential of CNG-DMF was 0.919 V, close to that of Pt/C (1.005V). The oxidation of cyclopentene in DMF is likely through the allylic C-H bond interacting with the H₂O₂ to form cyclopentene hydroperoxide and further oxidation to cyclopentenone[37].

Before convincing evidences are obtained, as for the increasing Ca ions doping causing higher selectivity to cyclopentenone in DMF solvent, a possible explanation is that DMF has tendency to coordinate with cobalt ions in the catalyst through its C=O group at the reaction temperature to form Co-DMF complex [43]. The coordination lead to introduction of nitrogen in the Co-DMF complex and therefore offering active centers where 3-hydroperoxycyclopent-1-ene can be adsorbed by Co-DMF complex to form an intermediate. On the other hand, partially substitution of Co ions in the spinel by larger Ca ions will make Co ions more accessible to DMF molecule and therefore supply more active centers for 3-hydroperoxycyclopent-1-ene absorption to form more intermediates. Adsorbed by Co-DMF complex may also facilitate rearrangement of 3-hydroperoxycyclopent-1-ene in the intermediates to form cyclopentenone [44-45]. The above possible reasons can account for increasing cyclopentenone selectivity with increase in Ca doping. We are trying our best investigating the reaction mechanism and more useful results will be reported in our future works.

Based on Scheme 1, the cyclopentene hydroperoxide has also a tendency to form an epoxide but was not observed in our results. This is probably due to the full conversion of the epoxide to the glutaraldehyde. In order to confirm this hypothesis,

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we are currently undertaking a computational study to be published as a separate paper. Based on the above facts, DMF was selected as the proper solvent for following investigations in pursuit of high cyclopentene conversion and CPTE selectivity. The highest H_2O_2 utilization efficiency of 84.7% was also obtained in the case of DMF.

3.4. Effect of reaction temperature

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The temperature dependence of the cyclopentene oxidation was tested in the range of 50 to 90 °C for 8 h reaction and the results are listed in Table 4. The conversion increases with the increasing temperature and reaches 100% at 60 °C. However, the H_2O_2 utilization efficiency decreases with the temperature. The selectivity for CPTE reaches the highest at 60 °C and decreases at higher temperature. Although the selectivity for GTA is highest at 90 °C, the utilization efficiency and the selectivity for CPTE are both lowest at this temperature. In order to obtain high selectivity of CPTE, 60 °C is considered as proper reaction temperature.

Reaction	Conversion	H_2O_2	Selectiv	vity (%)	b	
temperature		utilization efficiency	CDEO	CDTA	ODTE	СТА
(°C)	(%)	(%)	CPEO	CPIA	CPIE	GIA
50	95.3	85.8	12.2	_	87.8	
60	100	84.7	_	_	99.5	0.5
70	100	78.7	_	1.9	95.4	2.7
80	100	76.0	-	6.2	88.3	5.5
90	100	72.7	-	14.7	76.6	8.7

Table 4. Effect of reaction temperature on cyclopentene oxidation^a

^a Reaction conditions: cyclopentene 2.0 mL (22.6 mmol); catalyst 0.06 mmol; DMF 10 mL; 30% hydrogen peroxide 3.5 mL (molar ratio of cyclopentene/ $H_2O_2 = 2:3$); 8h; ^b CPEO = cyclopentene epoxide, CPTA = cyclopentanone, CPTE = cyclopentenone, GTA = glutaraldehyde.

3.5. Effect of cyclopentene $/H_2O_2$ molar ratio

The effects of molar ratio cyclopentene/ H_2O_2 were investigated and the results are shown in Table 5. The increase in the amount of H_2O_2 is in favor of conversion of cyclopentene and selectivity of GTA. As the molar ratio of cyclopentene/ H_2O_2 increased from 2:1 to 2:3, the conversion of cyclopentene increased 64.4 %. Although the selectivity of GTA increased as the molar fraction of H_2O_2 increases, the selectivity of CPTE is highest at the molar ratio cyclopentene/ H_2O_2 of 2:3, and the utilization efficiency of H_2O_2 reaches maximum at the molar ratio cyclopentene/ H_2O_2 of 1:1. Finally, to ensure a high conversion and high selectivity for CPTE, but not to sacrifice the H_2O_2 utilization efficiency, the molar ratio cyclopentene/ H_2O_2 of 2:3 was selected as the optimum molar ratio of cyclopentene to H_2O_2 .

Cyclopentene/	Conversion	H_2O_2	Selectiv	vity (%)	b	
H_2O_2	Conversion	utilization efficiency	CDEO	CDTA	ODTE	CTA
(mol/mol)	(%)	(%)	CPEO	CPIA	CPIE	GIA
2:1	35.6	87.6	13.8	7.8	78.4	K
1:1	87.1	88.0	8.7	4.6	86.7	-
2:3	100	84.7	_	-	99.5	0.5
1:2	100	76.9	-	-	94.0	6.0
2:5	100	69.0	-		84.1	15.9

Table 5. Effect of H₂O₂ amount on cyclopentene oxidation ^a

^a Reaction conditions: cyclopentene 2.0 mL (22.6 mmol); catalyst 0.06 mmol; DMF 10 mL; 60 °C, 8h; ^b CPEO = cyclopentene epoxide, CPTA = cyclopentanone, CPTE = cyclopentenone, GTA = glutaraldehyde.

3.6. Effect of reaction time

The effect of reaction time on cyclopentene oxidation was investigated at 60 °C in the range of 2-10 hours at the cyclopentene/ H_2O_2 molar ratio of 2:3. As shown in Table 6, the conversion of cyclopentene increases with the increase in the reaction time. The utilization efficiency of H_2O_2 does not exhibit strong reaction time dependence. The selectivity of CPTE is highest at the reaction time of 8 hours. Within the short reaction time (2 hours), there is significant amount of CPEO (16.5%) and CPTA (15.1%) other than CPTE (68.4%). As the reaction time prolongs, the selectivity of CPTE increases and reaches the highest at the reaction time of 8 hours. Further extending the reaction time from 8 hours leads to the conversion from CPTE to GTA. Therefore, 8 hours was selected as optimum reaction time.

Desetion	G	H_2O_2	Selectiv	vity (%)	b	
Keaction		utilization efficiency	CDEO	CDTA	ODTE	ОТА
time (n)	(%)	(%)	CPEO	CPIA	CPTE	GIA
2	56.2	80.4	16.5	15.1	68.4	K
4	71.8	81.7	13.7	10.6	75.7	
6	87.1	82.9	6.7	4.9	88.4	_
8	100	84.7	-	-	99.5	0.5
10	100	81.6	-		93.5	6.5

Table 6. Effect of reaction time on cyclopentene oxidation ^a

^a Reaction conditions: cyclopentene 2.0 mL (22.6 mmol); catalyst 0.06 mmol; DMF 10 mL; 30 % hydrogen peroxide 3.5 mL (molar ratio of cyclopentene/ $H_2O_2 = 2:3$); 60 ^oC; ^b CPEO = cyclopentene epoxide, CPTA = cyclopentanone, CPTE = cyclopentenone, GTA = glutaraldehyde.

3.7. Reuse of the catalyst

After the reaction, the catalyst can be adsorbed on the magnet. The catalyst attached to the magnet can be easily separated using simple decantation by applying a magnetic field on the surface of the tube, and then subjected to the second run under the same conditions. The results of these experiments are shown in Figure 5. Both the selectivity of CPEO and the conversion of cyclopentene barely changed after five runs. The slight decrease in cyclopentene conversion can be mainly attributed to unavoidable loss of the catalyst during the process of collection. The average value of cyclopentene conversion and CPTE selectivity was 99.4 % and 99.7 %, respectively. The results confirm that the sample CFO-Ca_{0.3} possesses good stability and recyclable applicability for the oxidation of cyclopentene under our present laboratory conditions.



Figure 5 Reuse of the catalyst CFO-Ca_{0.3}.

Reaction conditions: cyclopentene 2.0 mL (22.6 mmol); catalyst 0.06 mmol; DMF 10 mL; 30 % hydrogen peroxide 3.5 mL (molar ratio of cyclopentene/ $H_2O_2 = 2:3$); 60 °C, 8h;

4. Conclusions

Nanosized Ca-Co ferrite oxides were prepared through a simple and effective route of sol-gel auto-combustion using less expensive precursors. The ferrite catalysts are more active and easily reusable catalysts for cyclopentene oxidation using hydroperoxide as green oxidant. The catalytic performances of the samples are highly related to their components. The Ca contained samples have shown much higher cyclopentene conversion and cyclopentenone selectivity, and the cyclopentenone selectivity increased with increasing Ca content. Interestingly, the products distribution showed strong dependence on the solvents, that is, special product can be obtained by selecting special solvent. The highest cyclopentene conversion of 100% and cyclopentenone selectivity of 99.5% was achieved with the catalyst sample Ca_{0.3}Co_{0.7}Fe₂O₄ in DMF solvent. The catalyst has shown prominent recyclability and no drop in activity was observed in five consecutive runs. This work, along with other

published ones, indicates that ferrite complex oxides have a considerable potential for becoming a kind of tunable catalysts with respect of catalytic performances and components. Based on this purpose, more efforts have been and will be focused on investigating structure-activity relationships of the ferrite complex oxides in catalytic oxidation reactions in our present and future work.

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Supporting information

¹H NMR data of the reaction products were shown in supporting information.

References

[1] L.V. Mel'nik, A.E. Meshechkina, G.V. Rybina, S.S. Srednev, Y.A. Moskvichev,
O.S. Kozlova, Synthesis of 1,2-epoxycyclopentane and/or 1,2-cyclopentanediol by
oxidation of cyclopentene with aqueous solution of hydrogen peroxide, Pet. Chem.,
52 (2012) 313-317.

[2] Z. Zhu, W. Bian, Characterization of tungsten-based catalyst used for selective oxidation of cyclopentene to glutaraldehyde, Chinese Journal of Chemical Engineering, 16 (2008) 895-900.

[3] Z. Zhu, W. Bian, L. Liu, Z. Lü, Catalytic oxidation of cyclopentene to glutaraldehyde over WO₃/Ti–HMS catalyst, Catal. Lett., 117 (2007) 79-84.

[4] J. Xue, H. Yin, H. Li, D. Zhang, T. Jiang, L. Yu, Y. Shen, Oxidation of cyclopentene catalyzed by tungsten-substituted molybdophosphoric acids, Korean J. Chem. Eng., 26 (2009) 654-659.

[5] Y. Lu, H. Yin, H. Wu, H. Liu, T. Jiang, Y. Wada, Structural effect of tungsten oxides on selective oxidation of cyclopentene to glutaraldehyde, Catalysis Communications, 7 (2006) 832-838.

[6] G. Lu, X. Li, Z. Qu, Y. Wang, G. Chen, Selective oxidation of cyclopentene to glutaraldehyde over the $WO_{3/}SiO_2$ catalyst, Applied Surface Science, 255 (2008) 3117-3120.

[7] J. Xue, A. Wang, H. Yin, J. Wang, D. Zhang, W. Chen, L. Yu, T. Jiang, Oxidation of cyclopentene catalyzed by phosphotungstic quaternary ammonium salt catalysts, Journal of Industrial and Engineering Chemistry, 16 (2010) 288-292.

[8] X. L. Yang, W.-L. Dai, H. Chen, J. H. Xu, Y. Cao, H. Li, K. Fan, Novel tungsten-containing mesoporous HMS material: its synthesis, characterization and catalytic application in the selective oxidation of cyclopentene to glutaraldehyde by aqueous H_2O_2 , Appl. Catal., A, 283 (2005) 1-8.

[9] P. Wu, D. Nuntasri, Y. Liu, H. Wu, Y. Jiang, W. Fan, M. He, T. Tatsumi, Selective liquid-phase oxidation of cyclopentene over MWW type titanosilicate, Catal. Today, 117 (2006) 199-205.

[10] D. H. Zhang, H. B. Li, G. D. Li, J. S. Chen, Magnetically recyclable Ag-ferrite catalysts: general synthesis and support effects in the epoxidation of styrene, Dalton Trans., (2009) 10527-10533.

[11] N. Bahlawane, P.H.T. Ngamou, V. Vannier, T. Kottke, J. Heberle, K.Kohse-Hoinghaus, Tailoring the properties and the reactivity of the spinel cobalt oxide, Phys. Chem. Chem. Phys., 11 (2009) 9224-9232.

[12] A. I. Borhan, V. Hulea, A. R. Iordan, M. N. Palamaru, Cr³⁺ and Al³⁺
co-substituted zinc ferrite: structural analysis, magnetic and electrical properties,
Polyhedron, 70 (2014)110-118.

[13] G. Baldi, D. Bonacchi, M.C. Franchini, D. Gentili, G. Lorenzi, A. Ricci, C.Ravagli, Synthesis and Coating of Cobalt Ferrite Nanoparticles: A first step toward the obtainment of new magnetic nanocarriers, Langmuir, 23 (2007) 4026-4028.

[14] T. Bala, C.R. Sankar, M. Baidakova, V. Osipov, T. Enoki, P.A. Joy, B.L.V.Prasad, M. Sastry, Cobalt and magnesium ferrite nanoparticles: preparation using liquid foams as templates and their magnetic characteristics, Langmuir, 21 (2005) 10638-10643.

[15] F. Papa, L. Patron, O. Carp, C. Paraschiv, B. Ioan, Catalytic activity of neodymium substituted zinc ferrites for oxidative conversion of methane, J. Mol. Catal. A: Chem., 299 (2009) 93-97.

[16] R. Klimkiewicz, J. Wolska, A. Przepiera, K. Przepiera, M. Jabłoński, S. Lenart, The zinc ferrite obtained by oxidative precipitation method as a catalyst in n-butanol conversion, Mater. Res. Bull., 44 (2009) 15-20.

[17] M. Florea, M. Alifanti, V.I. Parvulescu, D. Mihaila-Tarabasanu, L.Diamandescu, M. Feder, C. Negrila, L. Frunza, Total oxidation of toluene on ferrite-type catalysts, Catalysis Today, 141 (2009) 361-366.

[18] J. Tong, L. Bo, Z. Li, Z. Lei, C. Xia, Magnetic $CoFe_2O_4$ nanocrystal: A novel and efficient heterogeneous catalyst for aerobic oxidation of cyclohexane, J. Mol. Catal. A: Chem., 307 (2009) 58-63.

[19] J. Tong, X. Cai, H. Wang, Q. Zhang, Improvement of catalytic activity in selective oxidation of styrene with H₂O₂ over spinel Mg–Cu ferrite hollow spheres in water, Mater. Res. Bull., 55 (2014) 205-211.

[20] L. Menini, M.C. Pereira, L.A. Parreira, J.D. Fabris, E.V. Gusevskaya, Cobaltand manganese-substituted ferrites as efficient single-site heterogeneous catalysts for aerobic oxidation of monoterpenic alkenes under solvent-free conditions, J. Catal., 254 (2008) 355-364.

[21] G. Evans, I.V. Kozhevnikov, E.F. Kozhevnikova, J.B. Claridge, R. Vaidhyanathan, C. Dickinson, C.D. Wood, A.I. Cooper, M.J. Rosseinsky, Particle size-activity relationship for $CoFe_2O_4$ nanoparticle CO oxidation catalysts, J. Mater. Chem., 18 (2008) 5518-5523.

[22] B. T. V. Srinivas, V. S. Rawat, K. Konda, B. Sreedhar, magnetically separable copper ferrite nanoparticles-catalyzed synthesis of diaryl, alkyl/aryl sulfones from arylsulfinic acid salts and organohalides/boronic acids [J]. Adv. Syn & Catal., 2014, 356(4): 805-817.

[23] N. Ma, Y. Yue, W. Hua, Z. Gao, Selective oxidation of styrene over nanosized spinel-type Mg_xFe_{3-x}O₄ complex oxide catalysts, Appl. Catal., A, 251 (2003) 39-47.
[24] X. Zhao, W. Wang, Y. Zhang, S. Wu, F. Li, J.P. Liu, Synthesis and characterization of gadolinium doped cobalt ferrite nanoparticles with enhanced adsorption capability for Congo Red, Chemical Engineering Journal, 250 (2014) 164-174.

[25] Y.J. Yang, M.M. Yang, Z.L. Luo, C.S. Hu, J. Bao, H.L. Huang, S. Zhang, J.W. Wang, P.S. Li, Y. Liu, Y.G. Zhao, X.C. Chen, G.Q. Pan, T. Jiang, Y.K. Liu, X.G. Li, C. Gao, Anomalous thickness-dependent strain states and strain-tunable magnetization in Zn-doped ferrite epitaxial films, J. Appl. Phys., 115 (2014) 173505.
[26] B. Xiao, S.-Q. Liu, Enhancing the photocatalytic activity of nickel ferrite doped with graphene, Asian Journal of Chemistry, 26 (2014) 1391-1393.

[27] M. Srivastava, S. Layek, J. Singh, A.K. Das, H. Verma, A.K. Ojha, N.H. Kim, J.H. Lee, Synthesis, magnetic and Mössbauer spectroscopic studies of Cr doped lithium ferrite nanoparticles, J. Alloys Compd., 591 (2014) 174-180.

[28] I. Sabikoglu, L. Parali, FT-IR and VSM properties of samarium-doped nickel ferrite, Functional Materials Letters, 7, 1450046 (2014)1450041-1450045.

[29] P. Samoila, T. Slatineanu, P. Postolache, A. Iordan, M. Palamaru, The effect of chelating/combustion agent on catalytic activity and magnetic properties of Dy doped Ni–Zn ferrite, Mater. Chem. Phys., 136 (2012) 241-246.

[30] A. Raut, R. Barkule, D. Shengule, K. Jadhav, Synthesis, structural investigation and magnetic properties of Zn^{2+} substituted cobalt ferrite nanoparticles prepared by the sol–gel auto-combustion technique, J. Magn. Magn. Mater., 358 (2014) 87-92.

[31] C. Cannas, A. Musinu, D. Peddis, G. Piccaluga, New synthesis of ferrite–silica nanocomposites by a sol–gel auto-combustion, J. Nanopart. Res., 6 (2004) 223-232. [32] C. Cannas, A. Falqui, A. Musinu, D. Peddis, G. Piccaluga, $CoFe_2O_4$ nanocrystalline powders prepared by citrate-gel methods: synthesis, structure and magnetic properties, J. Nanopart. Res., 8 (2006) 255-267.

[33] M. A. Woo, T.W. Kim, M. J. Paek, H. W. Ha, J. H. Choy, S. J. Hwang,
Phosphate-intercalated Ca–Fe-layered double hydroxides: Crystal structure, bonding character, and release kinetics of phosphate, J. Solid State Chem., 184 (2011)
171-176.

[34] M. Laguna-Bercero, M. Sanjuan, R. Merino, Raman spectroscopic study of cation disorder in poly and single crystals of the nickel aluminate spinel, J. Phys.: Condens. Matter, 19 (2007) 186217.

[35] R. Nongjai, S. Khan, K. Asokan, H. Ahmed, I. Khan, Magnetic and electrical properties of in doped cobalt ferrite nanoparticles, J. Appl. Phys., 112 (2012) 084321. [36] D.S. Nikam, S.V. Jadhav, V.M. Khot, R.A. Bohara, C.K. Hong, S.S. Mali, S.H. Pawar, Cation distribution, structural, morphological and magnetic properties of $Co_{1-x}Zn_xFe_2O_4$ (x = 0-1) nanoparticles, RSC Adv., 5 (2015) 2338-2345.

[37] A. Kumar, D. Srinivas, P. Ratnasamy, Synthesis of framework Ti-substituted,
3-D hexagonal, mesoporous Ti-SBA-12 for selective catalytic oxidation, Chem.
Commun., 42(2009) 6484-6486.

[38] T. Tatsumi, Y. Watanabe, Y. Hirasawa, J. Tsuchiya, Probable mechanism for alkane oxidation with H₂O₂ over VS₂, Res. Chem. Intermed., 24 (1998) 529-540.

[39] D. Srinivas, P. Manikandan, S. Laha, R. Kumar, P. Ratnasamy, Reactive oxo-titanium species in titanosilicate molecular sieves: EPR investigations and structure–activity correlations, J. Catal., 217 (2003) 160-171.

[40] J. Prandi, J. Namy, G. Menoret, H. Kagan, Selective catalyzed-rearrangement of terminal epoxides to methyl ketones, J. Organomet. Chem., 285 (1985) 449-460.

[41] D.G. Lee, K.C. Brown, H. Karaman, Oxidation of hydrocarbons. 17. Solvent and substituent effects on the oxidation of styrene derivatives by quaternary ammonium permanganates, Can. J. Chem., 64 (1986) 1054-1059.

[42] J.G. West, D. Huang, E.J. Sorensen, Acceptorless dehydrogenation of small molecules through cooperative base metal catalysis, Nat. Commun, 6 (2015)1-7
[43] W. Y. Kao, W. Q. Chen, Y.-H. Chiu, Y. H. Ho, C. H. Chen, General solvent-dependent strategy toward enhanced oxygen reduction reaction in graphene/metal oxide nanohybrids: effects of nitrogen-containing solvent, Sci. Rep., 6 (2016)37174.

[44] G. Krow, The Baeyer-villiger oxidation of ketones and aldehydes, Org. Reac., 43 (1993) 251–798.

[45] M. Renz, B. Meunier, 100 Years of Baeyer–Villiger oxidations, Eur. J. Org. Chem., (1999) 737-750.

Graphical abstract



(100%, In toluene)

In this work, Ca-doped spinel Co ferrites were prepared by a facile, mild and environment-friendly route. The samples exhibit remarkably high activities in the oxidation of cyclopentene using H_2O_2 as green oxidant. The Ca-doped samples have shown greatly enhanced performances than the pristine CoFe₂O₄. More interestingly,

the products distribution showed strong dependence on the solvents, that is, special product can be obtained by selecting special solvent. The highest cyclopentene with conversion of 100% and cyclopentenone selectivity of 99.5% was achieved with the