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Liquid oxidation of cyclohexane to cyclohexanol over cerium-doped MCM-41

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Abstract

Liquid phase oxidation of cyclohexane was carried out under mild reaction conditions over mesoporous Ce-MCM-41 catalysts using aqueous hydrogen peroxide (30%) as oxidant and acetic acid as solvent without adding any initiator. The catalysts exhibited high substrate conversion and good product (cyclohexanol) selectivity and it can be reused once with almost the same activity. The catalyst was characterized by a combination of various physicochemical techniques, such as N_2 physisorption, diffuse reflectance UV–vis, X-ray diffraction and FT-IR.
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Keywords: Ce-MCM-41; Selective oxidation of the cyclohexane; Cyclohexanol

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1. Introduction

Cyclohexane oxidation is an important commercial reaction to produce cyclohexanol and cyclohexanone, which mainly used in the production of nylon-6 and nylon-66. However, cyclohexane oxidation is considered to be the least efficient in all major industrial chemical processes [1,2]. In general, there are three commercial routes to produce cyclohexanol. A method still being used to a small extent is the hydrogenation of phenol [3], but this process suffers from the high hydrogen consumption in the hydrogenation step. The second method currently being used by Asahi Chemical Co. is the hydration of cyclohexene using a strongly hydrophilic zeolite catalyst, which avoids the formation of significant amount of by-products [4], but the activity is not high. The most important catalytic system currently in use for industrial cyclohexane oxidation employs homogeneous cobalt salts, molecular oxygen and temperature above 423 K, with conversion around 4% and selectivity of 85% to cyclohexanone and cyclohexanol [5]. However, this process is still expensive, polluting and risky. By contrast, heterogeneous catalysts with significant advantages for recovery and stabilities were studied intensively. Most of the catalysts are molecular sieves incorporated with divalent (Co, Zn), trivalent (B, Al, Ga, Cr, Fe) and tetravalent (Ti, V, Mn, Sn, Zr, etc.) transition and non-transition metal ions [6]. Particularly, V-MCM-41 [3] and Cr-MCM-41 [7] have been used as efficient catalysts for the oxidation of cyclohexane to cyclohexanol by using methyl ethyl ketone (MEK) as an initiator. Recently, the incorporation of Ce into the framework of MCM-41 (Ce-MCM-41) was synthesized and found that Ce incorporated in MCM-41 can impart dual catalytic activity in heterogeneous acid as well as redox catalysis [8]. Furthermore, Ce-MCM-41 exhibited good activity and selectivity for catalytic acylation of alcohols, thiols, phenols and amines [9]. But so far there is no report on using mesoporous Ce-MCM-41 for the oxidation of cyclohexane as we know. In this investigation, Ce-doped MCM-41 material was synthesized and used for the oxidation of cyclohexane under mild condition without adding any initiator.

2. Experimental

2.1. Synthesis of Ce-MCM-41

Normally, Ce-MCM-41 was synthesized using fumed silica [8,9]. In our investigation group, tetraethyl orthosilicate (TEOS)

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was used as silicon source [10] and a brief description of the procedure is as follows: 5.0 g CTAB was added to 66 ml solution containing 1.0 g sodium hydroxide and 20 ml TEOS was added slowly until the solution became a clear gel. Subsequently, the cerium precursor ($Ce(NO_3)_3 \cdot 6H_2O$) was introduced dropwise with Si/Ce (molar) ratio of 50. The final mixture was stirred for 24 h and then transferred into a Teflon bottle and treated under autogenous pressure without stirring at 363 K for 7 days, filtered, washed, dried and calcined at 823 K in air for 24 h.

2.2. *Characterization*

Pore size distributions, BET surface areas and pore volumes were measured by nitrogen adsorption/desorption using a NOVA 2000e gas sorption analyzer (Quantachrome Corp.). Prior to the analysis, the samples were outgased at 150 °C for ∼1 h.

X-ray powder diffraction (XRD) experiments were conducted on a D/max-3B spectrometer with Cu Kα radiation, scans were made in the 2θ range 0.5–7° with a scan rate of 0.5°/min (low angle diffraction), and in the 2θ range 7–100° with a scan rate of 10°/min (wide angle diffraction).

UV–vis diffuse reflectance spectra were measured at room temperature in air on a SHIMADZU UV-2401PC photometer over the range from 200 to 900 nm.

FT-IR measurements were performed on a Thermo Nicolet AVATAR FT-IR 360 instrument. Potassium bromide pellets containing 0.5% of the catalysts were used in FT-IR experiments and 125 scans were accumulated for each spectrum in transmission, at a spectral resolution of 4 cm^{-1}. The spectrum of dry KBr was taken for background subtraction.

2.3. *Oxidation of cyclohexane*

The oxidation reactions were carried out at the atmospheric pressure as follows: The catalyst (400 mg), cyclohexane (AR, 2 g) and 20 ml of solvent (acetic acid, acetonitrile, acetone, methanol, dichloromethane) were used as received without further purification and added successively into a temperature-controlled, round bottom, three-necked-flask having a reflux condenser. The aqueous H_2O_2 (30%, approximate 4 ml, with cyclohexane/H_2O_2 molar ratio of 0.77) was added dropwise after the reaction mixture heated to the set temperature. Reaction mixture was filtered under reduced pressure after the set time. The residue was extracted with diethyl ether. Anhydrous $MgSO_4$ (AR) was used to remove more water from the extracted organic phase. Then the mixture was filtered under reduced pressure and washed again by diethyl ether. The obtained products were analyzed by GC–MS (Fínnigan GC800 TP/MS Voyager) using DB-5MS capillary column. Reference substances were used for the identification of the products.

3. Results and discussion

Using above preparing process, Ce-MCM-41 was pale yellow in color with BET surface area of 991 m^2/g, pore volume of 0.73 ml/g and pore diameter of 29.6 Å. Fig. 1 shows the N_2 adsorption/desorption isotherm of the Ce-MCM-41. The sample showed typical isotherm of type IV having inflection around $P/P_0 = 0.15–0.35$, a characteristic of MCM-41 type ordered mesoporous materials.

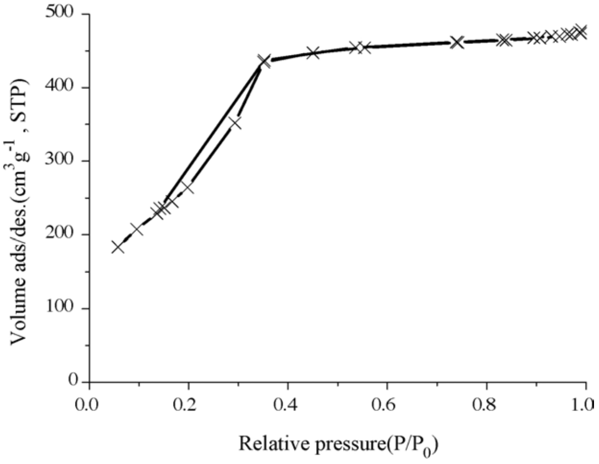

Fig. 1. Nitrogen adsorption/desorption isotherm of Ce-MCM-41.

The low angle X-ray diffractogram patterns of Ce-MCM-41 are shown in Fig. 2. The presence of four Bragg angles can be distinguished in hexagonal lattice symmetry, characteristic of MCM-41 structure [6]. A prominent peak of *h k l* = 1 0 0 as well as weaker peaks of *h k l* = 1 1 0, 2 0 0, 2 1 0 were observed in the Ce-MCM-41, which all indicated that the obtained mesoporous sample has a highly ordered pore system with a high porosity [6]. This is supported by the high BET surface areas (991 m^2/g). It is worth noting that the sample is amorphous and no peaks corresponding to cerium oxides were observed in the wide-angle diffractograms (Fig. 2, inset). This indicates that our cerium oxides were well incorporated into the MCM-41 framework.

The FT-IR spectra of Ce-MCM-41 was recorded between 400 and 4000 cm^{-1} in transmission mode using pressed KBr pellets, and shown in Fig. 3. It has been reported that vibration band at ca. 1090 cm^{-1} was assigned to the symmetric stretching of Si–O–Si vibration of the MCM-41 [8]. However, after the incorporation of Ce into the framework of MCM-41, the shift of the band from 1090 to 1079 cm^{-1} was observed, which generally is considered

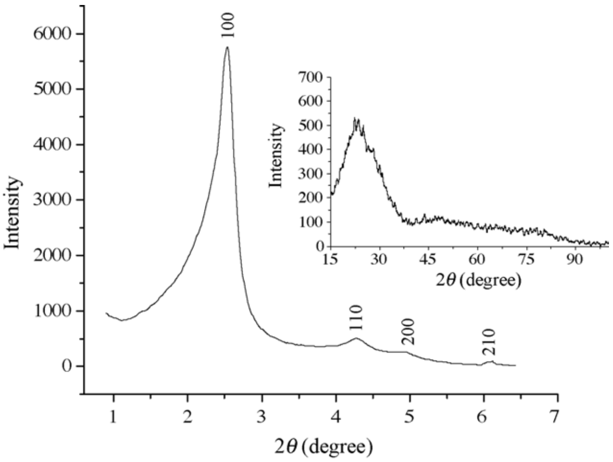

Fig. 2. XRD of Ce-MCM-41.

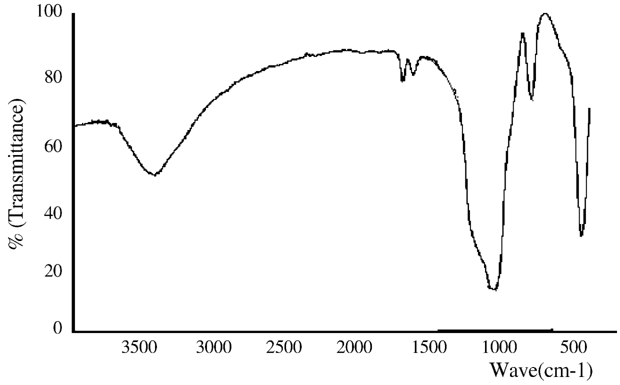

Fig. 3. FT-IR spectrum of Ce-MCM-41.

an indication of the incorporation of Ce into the framework of MCM-41. In the hydroxyl region (3000–4000 cm^{-1}), the broad band is observed at ca. 3420 cm^{-1} for Ce-MCM-41. The band shift from 3444 to 3420 cm^{-1} for Ce-MCM-41 compared with MCM-41 is probably attributed to the presence of more defect sites (SiOH group). This band was assigned to silanol group vibrations situated inside the channels of MCM-41, resulting from silanol groups interacting via hydrogen bonding. These observations are in good agreement with Ref. [8].

The diffuse reflectance UV–vis spectroscopy was known to be a very sensitive probe for the identification and characterization of metal ion coordination and its existence in the framework and/or in the extra-framework position of metal containing zeolites [8]. The diffuse reflectance UV–vis spectrum of Ce-MCM-41 given in Fig. 4 shows a single peak with a maximum at ca. 274 nm. This peak position is a little different from that reported in Ref. [8], where the single peak with a maximum at ca. 300 nm. The reason is probably due to the different preparation condition. The position of ligand to metal charge transfer ($O^{2-} \rightarrow Ce^{4+}$) spectra depends on the ligand field symmetry surrounding the Ce center, and the electronic transitions from oxygen to cerium require higher energy for a tetra-coordinated Ce^{4+} than for a hexa-coordinated one [9]. Therefore, it may be inferred that the presence of a strong absorption around 300 nm and the absence of any absorption band at 400 nm for Ce-MCM-41 sample was due to the presence of one type of well-dispersed Ce^{4+} species (presumably in a tetra-coordinate environment) [8].

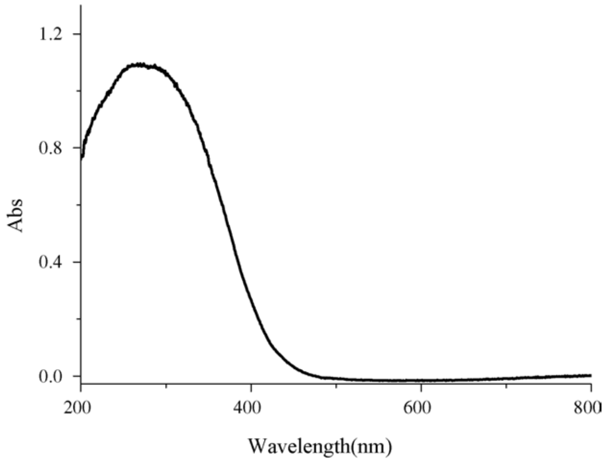

Fig. 4. UV–vis spectra of Ce-MCM-41.

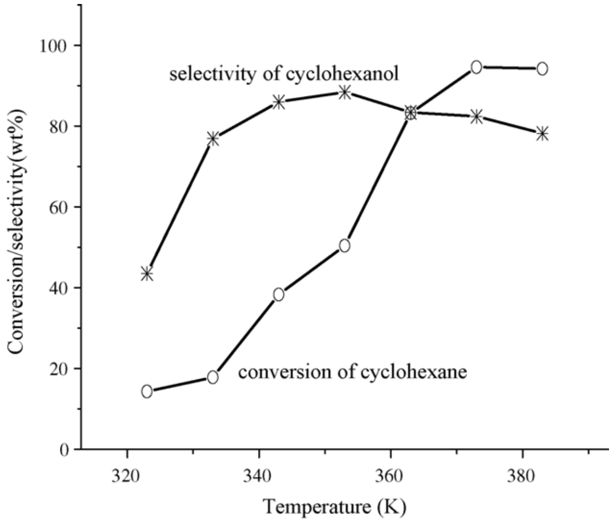

Fig. 5. Effect of reaction temperature on the conversion and selectivity over Ce-MCM-41. *Reaction conditions*: substrate/oxidant, 0.77; reaction time, 12 h; catalyst, 400 mg; solvent, acetic acid.

Using Ce-MCM-41 as a catalyst, it was found that cyclohexanol was the major product, and only small amounts of other products, viz., cyclohexanone, cyclohexyl acetate, were observed for the oxidation of cyclohexane. Cyclohexyl acetate was possibly produced due to the termination reaction between unreacted cyclohexyl and acetoxy radicals and/or by a possible reaction of cyclohexanol with excess acetic acid in the presence of Ce-MCM-41 [3]. Interestingly, at 323 K more cyclohaxnone was produced than cyclohexanol. This would imply that the catalyst may be also a potential good catalyst for production of cyclohanone if suitable condition and modification are used. The effect of reaction temperature on cyclohexane reaction over Ce-MCM-41 is shown in Fig. 5. It is clear that the conversion of cyclohexane was found to increase with increase in reaction temperature and passed through a maximum at 373 K. But the highest selectivity was obtained at 353 K. A further increase in the reaction temperature resulted in slight decrease in the conversion but significant decrease in the selectivity of cyclohexanol, probably owing to a quicker decomposition of H_2O_2 at higher temperature and the formation of cyclohexyl acetate by interaction of cyclohexyl and acetoxy radicals and/or due to the reaction between cyclohexanol with excess acetic acid. Considering the effect of temperature on both conversion of cyclohexane and selectivity of cyclohexanol, 373 K was chosen as the suitable temperature for the oxidation of cyclohexane.

The effect of reaction time on cyclohexane reaction over Ce-MCM-41 was also investigated and depicted in Fig. 6. It is seen that the conversion of the cyclohexane increased with time up to 12 h while the selectivity of cyclohexanol was fluctuated between 78% and 88%. Similar to the selectivity of cyclohexanol, selectivity of cyclohexanone and cyclohexyl acetate changed a little. Therefore, the optimum conversion and selectivity could be achieved at about 12 h.

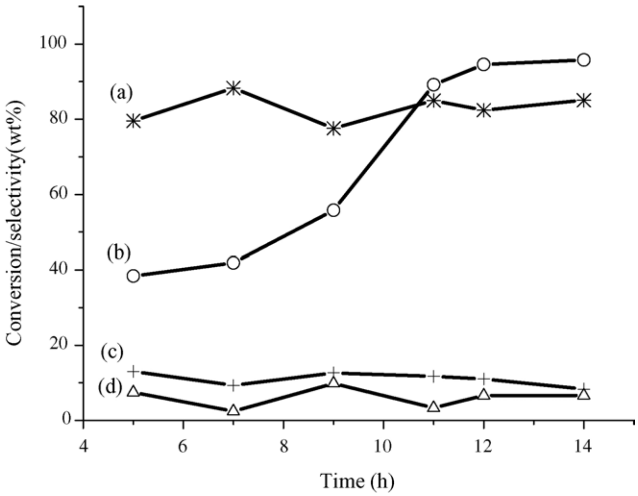

Fig. 6. Effect of reaction time on the conversion and selectivities over Ce-MCM-41. *Reaction conditions*: substrate/oxidant, 0.77; reaction temperature, 373 K; catalyst, 400 mg; solvent, acetic acid. (a) Selectivity of cyclohexanol; (b) conversion of cyclohexane; (c) selectivity of cyclohexanone; (d) selectivity of cyclohexyl acetate.

Fig. 7 presents the effect of catalyst concentration on cyclohexane reaction over Ce-MCM-41 at 12 h by using acetic acid as solvent. An initial steep increase in the conversion of cyclohexane and a slightly increase in selectivity of cyclohexanol were observed when the amount of the catalyst was increased up to 300 mg. Beyond this amount, the conversion of cyclohexane and selectivity of cyclohexanol only increased a little. Therefore, 400 mg was selected as the suitable amount of the catalyst for the selectively producing cyclohexanol. These results indicate that in the system catalyzed by Ce-MCM-41 only small amount of catalyst is active in the oxidation of cyclohexane at higher amount of catalyst. This could be also attributed to the competent interaction of metal oxo-species in Ce-MCM-41 sample with alkylperoxy species and cyclohexane [3,11].

The nature of solvents was known to have a major influence on reaction kinetics and product selectivity in the oxidation of cyclohexane. The effects of various solvents on the reaction are summarized in Table 1. It shows that a significantly lower conversion was obtained in the case of methanol, acetone, acetonitrile and dichloromethane. This is due to possible partial decomposition of hydrogen peroxide because it was reported that the decomposition of hydrogen peroxide are faster in these solvents than in acetic acid [12]. The higher catalytic activities of Ce-MCM-41 are because of those cerium ions which are incorporated in the framework positions of MCM-41 during synthesis [9]. Moreover, it has been reported that acetic acid does not only act as a solvent, but also serves as a good oxidizing agent because of the formation of the framework titanium–peracetic acid complex when it reacts with hydrogen peroxide in the presence of titanium-containing zeolites (TS-1) [12–14]. Similarly, if in our system a complex with peroxy acetic acid was possibly formed in the pores of Ce-MCM-41 then it would be relatively more hydrophobic and stable, as compared to hydrogen peroxide. The high activity at even 373 K inferred that the possible complex can still serve as the oxidizing agent at high temperature. Therefore, a better interaction of this complex with cyclohexane can be expected. In consequence, these species would be readily active for the oxidation of cyclohexane. In general, it is considered that acetic acid does not only facilitate homogeneity of the liquid phase, but also be responsible for the increase in overall oxidation activity.

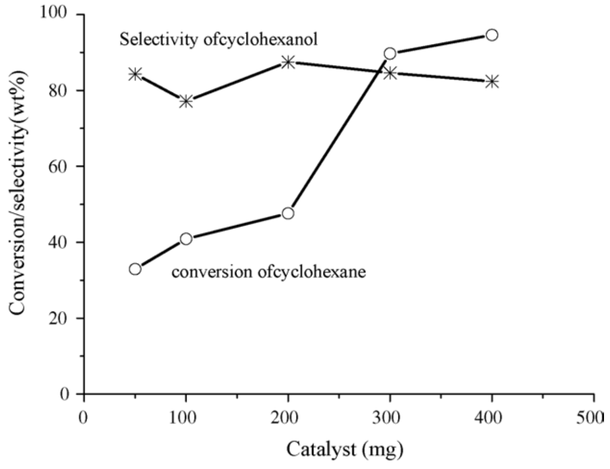

Fig. 7. Effect of catalyst concentration on the conversion and selectivity over Ce-MCM-41. *Reaction conditions*: substrate/oxidant, 0.77; reaction temperature, 373 K; reaction time, 12 h; solvent, acetic acid.

Table 1
Effect of solvents on the cyclohexane reaction

Solvents	Conversion (wt.%)	Selectivity (wt.%)		
		Cyclohexanol	Cyclohexanone	By-products
Acetic acid	94.6	82.4	6.6	11[a]
Methanol	33.4	67.5	29.3	3.2
Acetone	31.9	89.1	10.9	0
Acetonitrile	16.8	48.2	51.5	0.3
Dichloromethane	10.3	52.3	47	0.7

Note: *Reaction conditions*—substrate/oxidant, 0.77; reaction time, 12 h; catalyst, 400 mg; reaction temperature, boiling point of solvents, except for acetic acid at 373 K.

[a] Cyclohexyl acetate.

For comparisons, we have also studied the oxidation of cyclohexane using MCM-41 without the incorporation of Ce as a catalyst under the same conditions with those used for Ce-MCM-41. As expected, MCM-41 did not exhibit any significant activity. Furthermore, even incorporating other metal ions, such as, Fe-MCM-41 prepared using the same procedure as Ce-MCM-41, exhibited significantly lower activity than Ce-MCM-41. Compared with Co-MCM-41 reported in Ref. [6], Ce-MCM-41 also exhibited much higher TON. These comparisons are summarized in Table 2. It is apparent that Ce-MCM-41 exhibits the highest conversion and TON. The high efficiency of Ce-MCM-41 may be explained by the following reasons: firstly, the Ce present in the framework structure of Ce-MCM-41 can impart dual catalytic activity to the catalyst and can form labile oxygen vacancies and the relatively high mobility of bulk oxygen species [8,15,16]. Secondly, Ce-doped mesoporous materials still have monodispersed, single-pore distributed, huge pore vol-

Table 2
Effect of catalysts on the cyclohexane reaction

Catalysts	Conversion (wt.%)	TON	Selectivity (wt.%)		
			Cyclohexanol	Cyclohexanone	Cyclohexylacetate
Ce-MCM-41	94.6	177	82.4	6.6	11
First recycled (Ce-MCM-41)	91.7	171	85.1	11.7	3.2
Second recycled (Ce-MCM-41)	90.2	169	85.6	10.3	4.1
MCM-41	0	0	0	0	0
Fe-MCM-41	58.4	106	67.2	29.2	3.6
Co-MCM-41 [6]	8.1	41	–	–	–

Note: *Reaction conditions*—substrate/oxidant, 0.77; reaction time, 12 h; reaction temperature, 373 K; catalyst, 400 mg; solvent, acetic acid; TON, turn over number (millimole of oxidized products per millimole of metal in the catalyst).

ume and highly ordered mesoporous structures [17] which are excellent activity for catalysis. Thirdly, a complex with peroxy acetic acid was possibly formed in the pores of Ce-MCM-41 which is relatively more hydrophobic and stable than hydrogen peroxide. In short, the synergistic effects among doped cerium, mesoporous framework of MCM-41, acetic acid and hydrogen peroxide make Ce-MCM-41 an effective catalyst for the oxidation of cyclohexane under mild conditions.

To check the stability and recycling ability as well as leaching of cerium ions from Ce-MCM-41 under reaction conditions, recycling experiments were carried out using acetic acid as solvent. The typical recycling procedure was as follows: after the initial reaction, the catalyst was separated from the reaction mixture and washed with acetone and dried at 363 K, followed by the activation at 823 K for 2 h. The reaction was then carried out on the activated recycled catalyst. The results are also summarized in Table 2. It was found that the major product was still cyclohexanol, and the conversion of the cyclohexane and selectivity of cyclohexanol changed little: the conversion from 91.7% at first use to 90.2% at second recycle, while the selectivity was from 85.1% to 85.6%, respectively. All the observations suggest that Ce-MCM-41 is a stable and highly effective catalyst for the cyclohexane oxidation.

4. Conclusions

It can be concluded that Ce-MCM-41 was an efficient and high substrate conversion catalyst for the oxidation of the cyclohexane under relatively mild reaction conditions without adding any initiator. Among the various solvents, acetic acid was found to be more suitable for the high conversion and high cyclohexanol selectivity. The catalyst can be reused once without losing the activity.

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