



# Effect of surface functionalization of cerium-doped MCM-48 on its catalytic performance for liquid-phase free-solvent oxidation of cyclohexane with molecular oxygen



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## ABSTRACT

Ce-doped MCM-48 (Ce-MCM-48) mesoporous molecular sieve was prepared hydrothermally and its surface was modified with organic groups or fluorine, and their physicochemical properties were characterized by XRD, low-temperature N<sub>2</sub> adsorption, TEM, UV–visible and FT-IR spectroscopies, XPS and contact angle measurement. The results indicated that Ce species were highly dispersed on the MCM-48 materials as Ce<sup>3+</sup> and Ce<sup>4+</sup>. After post-functionalization of Ce-MCM-48, the organic groups or fluorine species have been immobilized on the surface of Ce-MCM-48, but the chemical status of Ce species were hardly changed, and the post-functionalization improved the surface hydrophobicity of the Ce-MCM-48 sample. The catalytic activity testing for the oxidation of cyclohexane with molecular oxygen showed that, Ce-MCM-48 after post-functionalization exhibited the higher cyclohexane conversion and selectivity to cyclohexanol and cyclohexanone, 8.9% cyclohexane conversion with 91.2% selectivity to cyclohexanone and cyclohexanol could be achieved over the Ce-MCM-48 with F-modified catalyst, which was attributed to the proper modification of their surface properties including hydrophobicity and polarity. The F-modified catalyst also showed excellent reusability, and its catalytic performance has no obvious deterioration after being repeatedly used five times.

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## 1. Introduction

Selective oxidation of hydrocarbons is of great importance for the production of fine chemicals and intermediates in chemical industry, such as ketones and alcohols. Among various oxidation reactions of hydrocarbons, the oxidation of cyclohexane has been extensively investigated owing to its importance for industrial production of adipic acid and  $\epsilon$ -caprolactam, which are important chemical intermediates in the manufacture of nylon-6 and nylon-6,6 polymers [1,2]. Many researchers have worked on homogeneous catalysts for the oxidation of cyclohexane [3–5]. Industrial production of cyclohexanone and cyclohexanol (also known as KA-oil) from the oxidation of cyclohexane mostly employed soluble cobalt salt or metal-boric acid as homogeneous catalysts, and was generally operated at ~150 °C and 1–1.5 MPa pressure with low

conversion (<5%) and 70–85% selectivity to KA-oil in order to avoid the formation of excessive amounts of byproducts due to over oxidation [6]. However, homogeneous catalytic processes suffer from the problem of catalyst reusability and pollution issues. Thus, it is desirable to develop more efficient and environment friendly heterogeneous catalysts for the oxidation of cyclohexane with relatively high conversion and selectivity. In recent years, heterogeneous catalysts for the oxidation of cyclohexane have received increasing interest [7–10].

Taking the environmental protection and high-effective atom utilization into consideration, the oxidation of cyclohexane using molecular oxygen as the oxidant is the most competitive undoubtedly [11]. However, it is very difficult to stimulate cyclohexane, inert saturated hydrocarbons, to react with molecular oxygen with high conversion of cyclohexane and selectivity for KA oil simultaneously, because of the deep oxidation of the products [12,13]. In the oxidation of cyclohexane, the starting material (cyclohexane) is hydrophobic and nonpolar while the oxidation

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products (KA oil) are hydrophobic but polar. Thus, the hydrophobic surface can improve the adsorption of hydrophobic reactants and desorption of the products with weak polarity, which can enhance the reactivity of the catalyst. Because the surface properties of catalysts directly affect their catalytic performances [14–18], the surface modification of catalysts is a very important approach to promote their catalytic performances.

The mesoporous silica M41s materials are of great interest as catalyst supports due to their nanoscale periodicity, large surface area and uniform pore size distribution, which can facilitate the mass transfer and the active sites of macromolecular compounds [19–21]. Furthermore, they are excellent substrates for surface modification by virtue of abundance Si–OH groups on the surface.

Herein, this work is to tune the surface properties of cerium-doped MCM-48 material, which provides appealing opportunities for combining the redox of cerium and the proper surface properties, in order to prepare the catalyst with high conversion of cyclohexane and selectivity for KA oil simultaneously.

## 2. Experimental

### 2.1. Chemicals

n-Octyltriethoxysilane (OTES) was purchased from Aladdin Reagent. Other chemical reagents were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd., China. All chemicals were used without further purification.

### 2.2. Synthesis of Ce-MCM-48

The cerium-doped MCM-48 mesoporous material (Ce-MCM-48) was prepared by the following procedures: 9.38 g of TEOS was added into 50 mL of distilled water under vigorous stirring at 35 °C, and then 0.9 g of NaOH and 0.17 g of NH<sub>4</sub>F were added into the solution above under stirring. After 30 min, 0.39 g of Ce(N–O<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was slowly added, followed by adding 10.61 g of CTAB. After stirring for 3 h, the synthesis solution was transferred to a Teflon-lined autoclave and heated at 100 °C for 72 h. The molar composition of the synthesis solution was 1.0 SiO<sub>2</sub>: 0.02 Ce: 0.5 NaOH: 0.1 NH<sub>4</sub>F: 0.65 CTAB: 62H<sub>2</sub>O. The formed solid was collected by filtration, washed with deionized water, dried at 100 °C for 24 h and calcined in air at 550 °C for 6 h to remove the template. The sample synthesized is denoted as Ce-MCM-48. Pure silica MCM-48 (Si-MCM-48) was also prepared with the same procedure as Ce-MCM-48, but no Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added.

### 2.3. Post-functionalization of Ce-MCM-48

Post-functionalization of Ce-MCM-48 was carried out by the reaction between Ce-MCM-48 and OTES to anchor hydrocarbon chains on the surface of Ce-MCM-48. Typically, 0.3 g of Ce-MCM-48 material was suspended in 30 mL of ethanol containing weighed OTES and the mixture was sonicated for 10 min until it became homogeneous. The resulting mixture was continuously refluxed at 78 °C for 12 h, and the final sample was obtained by filtration, washed with ethanol and dried at 60 °C under vacuum for 24 h. This OTES-modified sample was labeled as O-x, x represented the content of C in hydrocarbon chain anchored on the surface of Ce-MCM-48.

Post-functionalization of Ce-MCM-48 with fluorine was prepared as follows [22]: weighed NH<sub>4</sub>F were dissolved in 70 mL of isopropanol under stirring for 1 h. Then 0.6 g of Ce-MCM-48 was added into the solution above and stirred for another 1 h. The prepared mixture was kept under 120 °C in an oven for 24 h. The solid products obtained were filtered and washed with distilled

water and then activated at 200 °C for 3 h under vacuum. This F-modified sample was labeled as F-x, x represented the amount of F anchored on the surface of Ce-MCM-48.

### 2.4. Catalytic activity testing

The oxidation of cyclohexane was carried out in a 50 mL autoclave lined with polytetrafluoroethylene. 4 g of cyclohexane, 20 mg of catalyst and 10 μL TBHP as initiator were introduced into the reactor. After O<sub>2</sub> was charged to 1.0 MPa, the reactor was heated to 140 °C under stirring at 300 rpm. After the reaction, the reactor was thoroughly cooled to avoid the loss of substrate and the reaction mixture was diluted with ethanol to completely dissolve the side products. After the catalyst was separated by centrifugation, an excessive amount of triphenylphosphine (Ph<sub>3</sub>P) was added to completely convert the intermediate cyclohexylhydroperoxide (CHHP) to cyclohexanol. The reaction products were analyzed by Agilent gas chromatograph 7890B equipped with an HP-5 capillary column and a flame ionization detector. Methylbenzene was used as an internal standard substance. In addition, the side products were further identified using Agilent 7890A-5975C gas chromatograph-mass spectrometry (GC-MS). The conversion of cyclohexane was calculated as follows:

$$X(\text{Cyclohexane}) = \frac{n(\text{Cyclohexane})_{\text{initial}} - n(\text{Cyclohexane})_{\text{final}}}{n(\text{Cyclohexane})_{\text{initial}}}$$

$n(\text{Cyclohexane})_{\text{initial}}$  and  $n(\text{Cyclohexane})_{\text{final}}$  were denoted the molar content of cyclohexane in the initial reactant and the final product, respectively.

The selectivity to cyclohexanol (A) and cyclohexanone (K) was calculated respectively as follows:

$$S(\text{Cyclohexanol}) = \frac{n(\text{Cyclohexanol})}{n(\text{Cyclohexane})_{\text{initial}} - n(\text{Cyclohexane})_{\text{final}}}$$

$$S(\text{Cyclohexanone}) = \frac{n(\text{Cyclohexanone})}{n(\text{Cyclohexane})_{\text{initial}} - n(\text{Cyclohexane})_{\text{final}}}$$

$n(\text{Cyclohexanol})$  and  $n(\text{Cyclohexanone})$  were denoted the molar content of cyclohexanol and cyclohexanone in the final product, respectively. The selectivity of KA oil was the total of the selectivity to A and the selectivity to K.

The recycling experiments of the catalyst were carried out and the catalyst was reused five times in the oxidation reaction. After every run, the catalyst was separated from the reaction solution, dried at 100 °C to constant weight in the air.

### 2.5. Characterization of samples

The inductively coupled plasma (ICP) analysis was carried out on an Angilent 725 ES. Elemental analysis of carbon was performed on an Elementar Vario EL III Analyzer. The composition of fluorine-modified samples was measured on a Hitachi S-3400N scanning electron microscope equipped with energy dispersed X-ray detector (EDS). X-ray diffraction (XRD) data were collected on a Bruker D8 diffractometer using Cu K $\alpha$  radiation (40 kV, 40 mA) at room temperature. N<sub>2</sub> adsorption–desorption isotherms of samples were obtained at –196 °C on a Micrometrics ASAP 2020M Sorptometer using static adsorption procedures. Prior to the measurements, the sample was degassed at 120 °C for 12 h. The pore size distribution curves were calculated from the desorption branch by the Barrett–Joyner–Halenda (BJH) method. The internal pore structures of the samples were observed by a high resolution TEM (JEM-2100,

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