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Catalytic oxidation of cyclohexane to KA oil by zinc oxide supported manganese 5,10,15,20-tetrakis(4-nitrophenyl)porphyrin

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ABSTRACT

A series of manganese metalloporphyrins were prepared and tested in cyclohexane oxidation. It has been found that the manganese 5,10,15,20-tetrakis(4-nitrophonyl) porphyrin (Mn-TNPP) presents better catalytic performance. The Mn-TNPP was then immobilized on different supports, and characterized by UV–vis, FT-IR, XRD, TG/DTG and ICP. Among these supported Mn-TNPP catalysts, Mn-TNPP/ZnO exhibits the best selectivity to KA oil and higher turnover number in cyclohexane oxidation. The influence of the reaction conditions and the recycle of the catalysts are discussed. Mn-TNPP/ZnO catalyst presents the average cyclohexane conversion of 7.17%, KA oil selectivity of 91.18%, and the average catalytic turnover number of 6.53×10^4 after six times of recycle under 150 °C and 1.0 MPa.

1. Introduction

Cyclohexane oxidation is a very important reaction in chemical industry. The oxidation products of cyclohexanone and cyclohexanol (KA oil) are raw materials to produce caprolactam, adipic acid and nylon [1–3]. However, it is very difficult to activate the C—H bonds in inert cyclohexane, which results in the poor cyclohexane conversion of 3–5% and the selectivity to KA oil of 75–80% in the industrial cyclohexane autocatalytic oxidation process [4,5]. A large number of researchers have engaged in the study of C—H activation in hydrocarbons and have obtained many achievements [6–8].

In the past few decades, looking for a kind of highly efficient catalysts in cyclohexane oxidation has become a major goal for scientists [9–11]. Biomimetic oxidation of hydrocarbon as a new catalytic system is gradually maturing and has been attracting more attention. Like cytochrome P-450, metalloporphyrins have many advantages in the oxidation of hydrocarbon, such as mild condition, high turnover numbers and high selectivities [12–15]. The cenral metal has a great influence on the activity of the metalloporphyrins, and the studies have shown that the manganese exhibit a better catalytic activity in the activation of C—H [16,17]. However, the metalloporphyrins are easier to aggregate or decompose at a relatively high temperature during the oxidation reaction, and it is very difficult to recover or reuse [18,19]. Thus, immobilization of the metalloporphyrins on stable supports has become the most effective way to overcome the above drawbacks. It is interesting to find that the catalytic performance is not degraded when the metalloporphyrin active component was immobilized on the support. The catalytic effect is definitely improved and not significant reduced after repeated use several times [20–22]. Therefore, it is attractive to look for a better type of immobilized metal porphyrins in cyclohexane oxidation.

In this paper, several substituted manganese porphyrins (Mn-T(p-Cl)PP, Mn-D(p-Cl)D(p-Br)PP, Mn-T(p-Br)PP, Mn-TNPP) were synthesized and tested in cyclohexane oxidation. The Mn-TNPP shows better catalytic performance and it is chosen to prepare a series of supported Mn-TNPP catalysts. These prepared catalysts were characterized by UV–vis, FT-IR, XRD, TG/DTG, ICP, and tested in cyclohexane oxidation.

2. Experimental

2.1. Reagents

Zinc sulfate heptahydrate (99%), Aluminum nitrate nonahydrate (98%), NH_3 aqueous (NH_3 27%), Zirconia (99.95%), the other solvents and reagents were all obtained from Aladdin. No impurities were found in the cyclohexane by GC analysis before use.

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2.2. Substituted manganese metalloporphyrins

All reagents and solvents used for the synthesis of porphyrin were of analytical grade and were obtained commercially. Mn-T(p-Br)PP, Mn-D(p-Cl)D(p-Br)PP and Mn-T(p-Cl)PP were synthesized by modifying the reported procedures [23–25]. The Mn-TNPP was synthesized according to the following procedures [26], The 5,10,15,20-tetrakis(4-nitrophonyl) porphyrin (1.26 mmol) was dissolved and refluxed in DMF (100 mL). Then, manganese acetate (6.3 mmol) was added in four portions within 15 min. The evolution of the reaction was monitored by thin layer chromatography. The solvent was evaporated by rotary evaporation after the reaction was completed. The mixture was filtered and washed with water. Then it was purified by column chromatography (alumina, CH_2Cl_2/methanol = 10:1.5). After the solid was vacuum-dried, the Mn-TNPP compound was obtained with the yield of about 90%.

2.3. Preparation of the supported catalysts

Mn-TNPP/Boehmite, Mn-TNPP/Kaolin, Mn-TNPP/ZrO_2 and Mn-TNPP/$Zr(OH)_4$ were synthesized by modifying the reported procedures [20,27]. Mn-TNPP/ZnO was prepared by the following procedure [28], Zinc sulfate heptahydrate (0.25 mol) was added to 500 mL of deionized water in a three-necked flask with high stirring for 1 h. Then, NH_3 aqueous (1.10 mol) was added to adjust the pH to 8.0, after filtration, the filter cake was dissolved in 250 mL ethanol and 0.023 mmol of the Mn-TNPP ethanol solution were slowly added into the above suspension and stirred for another 40 min, and the mixture was heated to 65 °C with rapid stirring for 12 h. After cooling to room temperature, the suspension was filtrated and washed with distilled water, and the cake was vacuum-dried at 170 °C for 24 h and then washed in a Soxhelt apparatus for 48 h with 280 mL of CH_2Cl_2 to remove the weakly adsorbed metalloporphyrin on the surface. Finally, the solids were dried at 70 °C for 10 h.

2.4. Characterization of the TNPP, Mn-TNPP and Mn-TNPP/ZnO

UV–vis spectra was obtained by UV-2550 spectrophotometry with a scan range of 300–800 nm for TNPP, Mn-TNPP and the supported manganese metalporphyrin complexes using 1 cm quartz cuvette.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 spectrometer in the range 400–4000 cm^{-1}, the samples were ground into fine powders, mixed with KBr, and then were pressed into thin pellets to assay their spectra.

X-ray diffraction (XRD) patterns for powder samples of Mn-TNPP/ZnO were collected on a Japan Rigaku D/Max 2550 VB^{+} 18 kW X-ray diffractometer under the conditions of 40 kV, 30 mA, Cu Kα radiation. Scans were performed from (2θ) 5 to 90 at a rate of 2 min^{-1}.

TG/DTG curves for Mn-TNPP/ZnO were recorded by a TGA/DCS using air as purge gas (40 mL min^{-1}) over a temperature range of 30–600 °C and with a heating rate of 10 °C min^{-1}.

Inductively coupled plasma (PS-6 ICP-AES) was used to measure the content of manganese in the supported metalloporphyrins.

2.5. Procedures for the catalytic test

Cyclohexane oxidation was carried out in a 50 mL autoclave reactor with a magnetic stirrer in the absence of solvent. Typically, cyclohexane (188 mmol) and catalysts were added into the autoclave reactor. And the reactor was sealed and heated to the setting temperature. Then it was pressurized to the setting pressure with the molecular oxygen under stirring. After the reaction, the reactor was cooled to the ambient temperature in an ice-water bath. The mixture was dissolved in ethanol and the catalysts were removed by filtration. The catalysts were washed by ethanol, dried and then recycled in the next reaction. The cyclohexanol and cyclohexanone in the product were analyzed by gas chromatography by using chlorobenzene as the internal standard. The total acid and ester in the product was analyzed by the chemical titration method.

3. Results and discussions

3.1. Characterization of the catalysts

3.1.1. UV–vis spectra of TNPP, Mn-TNPP and Mn-TNPP/ZnO

UV–vis spectra of the TNPP, Mn-TNPP and Mn-TNPP/ZnO are shown in Fig. 1. The spectra of TNPP exhibit one Soret band at 425 nm and four *Q* bands at 518 nm, 552 nm, 594 nm and 650 nm, which indicats that the TNPP was successfully synthesized [29]. There is one of apparently features that the numbers of *Q* band reduces to one or two with the metal entered into the porphyrin center. When Mn-TNPP was immobilized onto the ZnO support, the UV characteristic Soret peak was red-shifted from 480 nm to 475 nm. The red-shift phenomenon is similar to the literatures [30,31], this means that the Mn-TNPP molecules were set on the surface of the ZnO crystals and interacted with the oxygen atom, thus formed a new stable structure.

3.1.2. FT-IR spectra of ZnO, Mn-TNPP and Mn-TNPP/ZnO

The FT-IR spectra of Mn-TNPP, ZnO and Mn-TNPP /ZnO are shown in Fig. 2. From the spectra of Mn-TNPP, the sharp bands at 1348 cm^{-1} and 1520 cm^{-1} are assigned to the symmetric and asymmetric stretching vibration of the –NO_2 group, and the band at 825 cm^{-1} indicates that the nitro group is in the para position of the benzene ring. The bands at 1598 cm^{-1} and 3110 cm^{-1} are come from the phenyl vibration inside the porphyrin, it exhibits that the nitrobenzene was introduced into the porphyrin molecules. The sensitive metal bands appear at 1408 cm^{-1}, 1010 cm^{-1} and 509 cm^{-1}, it indicates that the metalloporphyrin was successfully synthesized [26,32,33]. For the Mn-TNPP/ZnO (a) and ZnO (b), the spectra are broadly similar. The ZnO vibrations bands appear at 420 cm^{-1} and 602 cm^{-1}, and the wide band at 990 cm^{-1} and 1108 cm^{-1} are assigned to the vibrations of the O–H groups from the $Zn(OH)_2$, which exists in the ZnO structure [34]. Compared with the ZnO, the bands at 3320 cm^{-1} and 3563 cm^{-1} are disappeared in Mn-TNPP/ZnO, it maybe result from the introduction of the active components. Meanwhile, a new peak at 518 cm^{-1} appears in the Mn-TNPP/ZnO, it may be assigned to the ZnO-Mn-TNPP vibration, and it indicates the coordination of the oxygen atom of ZnO to Mn-TNPP.

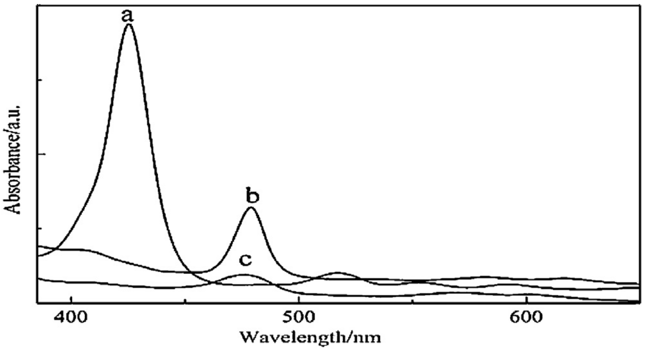

Fig. 1. Ultraviolet–visible spectra: TNPP (a), Mn-TNPP (b) and Mn-TNPP/ZnO (c).