

# Study of Catalyzed Oxidation of Cyclohexane in a Solvent-free System using a unique Combination of two Heterogeneous Catalysts

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**Abstract:** Styrene-maleic anhydride copolymer (SMA) anchored N-Hydroxyphthalimide (NHPI) and Co/ZSM-5 were prepared and characterized by FT-IR, XRD respectively. With two heterogeneous catalysts together in a solvent-free system, the effects of vital process parameters on the oxidation of cyclohexane were studied. Under the optimized conditions, the 26.8% of the conversion of cyclohexane, 71.6%, 10.9% and 2.6% of the selectivity of KA oil (the mixture of cyclohexanone and cyclohexanol), adipic acid and cyclohexyl hydroperoxide (CHHP) were obtained. When the test temperature ranged from 393K to 433K, the reaction rate constant  $K_a$  and reaction temperature  $T$  had an Arrhenius relationship with the linear correlation coefficient of 0.9878, it can be expressed as:  $\ln K_a = -3012/T + 1.279$ . The stability study illuminated the high thermal stability of the two heterogeneous catalysts, being reused for at least five reaction cycles without considerable loss of reactivity.

**Key words:** SMA anchored NHPI; Co/ZSM-5; cyclohexane; heterogeneous oxidation

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The selective oxidation of saturated hydrocarbons is one of the most challenging and promising subjects in oxidation chemistry<sup>[1]</sup>. Of particular importance is the oxidation of cyclohexane due to the large demand for cyclohexanone and cyclohexanol, which are important raw materials for the production of adipic acid and caprolactam<sup>[2]</sup>, so great efforts have been devoted to the oxidation of cyclohexane in the past years<sup>[3-7]</sup>.

In recent years, N-hydroxyphthalimide (NHPI) has been recognized as a valuable catalyst for aerobic oxidation of various organic compounds under mild reaction conditions. Catalytic oxidation reactions generally involve the use of soluble metal salts which are known to catalyze the initiation reaction<sup>[8,9]</sup>.

Despite of good activities and very often excellent selectivity, there are several problems encountered with this catalytic system, particularly catalyst separation, recovery and recycle after reaction. One way to circumvent this problem is to anchor one or more components of the catalytic systems onto a large surface area solid carrier to create new organic inorganic hybrid catalysts.

The incorporation of transition metal ions or complexes into the framework or cavities of zeolites have attracted great interests due to their acidity, redox ability, shape selectivity and recyclable properties<sup>[10,11]</sup>. Metal-containing mesoporous materials such as VMCM-48<sup>[12]</sup>, CoAlPO-5<sup>[13]</sup>, Au-ZSM-5<sup>[14]</sup> and Co-ZSM-5<sup>[15]</sup> are applied to catalyze oxidation of cyclohexane. And metal complexes or metal-containing zeolite are also used as catalysts for this oxidation reaction<sup>[16-19]</sup>. On the other hand, several recycling approaches of NHPI also have been Investigated<sup>[20-22]</sup>.

The aim of the present work was to investigate opportunities for the design of a solvent-free heterogeneous catalytic system, and the performance of the heterogeneous catalysts was studied in the oxidation of cyclohexane.

## 1 Experimental

### 1.1 Materials and Equipments

HZSM-5 was obtained from NanKai University. Maleic anhydride and benzoyl peroxide (BPO) were

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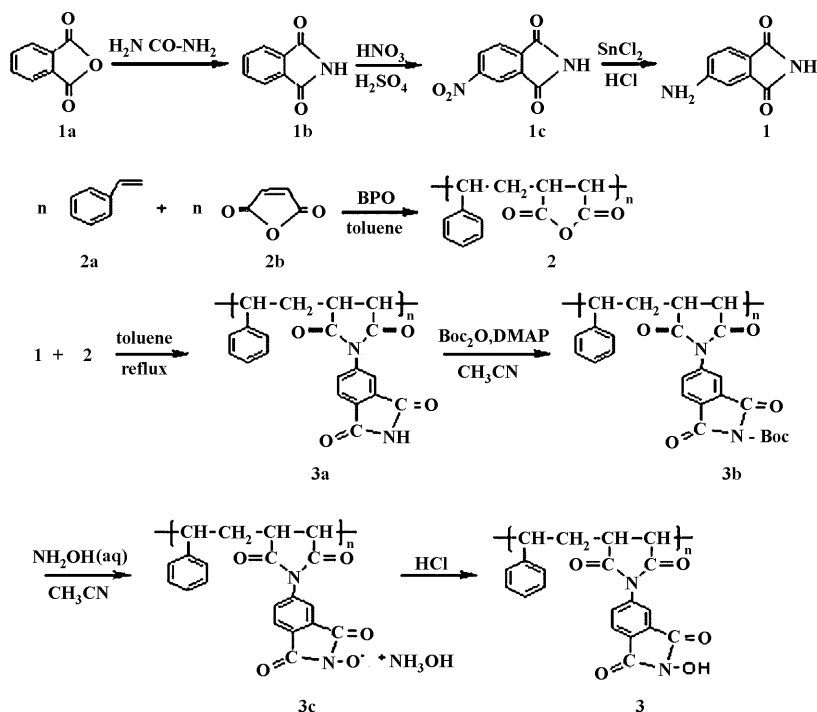
both purified by recrystallization in chloroform and dried to constant in vacuum at 50 °C. Cyclohexane was redistilled before being used. All the other reagents were analytically pure or chemically pure.

IR spectra were recorded on KBr pellet using FTS165 Spectrophotometer. X-ray diffraction (XRD) patterns of HZSM-5 and Co/ZSM-5 were carried out using a Rigaku D/MAX-III C diffractometer with Cu Ka

radiation operating at 30 kV and 25 mA. The products of oxidation were determined by an HP 6890/5973 GC/MS instrument and analyzed by an Agilent 6820 gas chromatograph.

## 1.2 Preparation of catalysts

The procedure for synthesis of SMA anchored NH-PI (SMA-NHPI) was shown in Scheme 1.



Scheme 1 The procedure for the preparation of SMA-NHPI

The phthalic anhydride **1a** was first converted to phthalimide **1b** and then was nitrified to give 4-nitrophthalimide **1c** which was eventually reduced using  $\text{SnCl}_2/\text{HCl}$  as the catalyst to give 4-aminophthalimide **1**.

SMA **2** was prepared by a traditional solution polymerization: distilled toluene (50 mL), destabilized styrene (20 mmol), pure maleic anhydride (20 mmol) and benzoyl peroxide (BPO) (0.16 mmol) was placed in a 250ml three-necked flask fitted with stirrer, thermometer, reflux condenser and inlet of nitrogen, and stirred at room temperature until a clear solution was obtained. The reaction mixture was continuously stirred and heated to 80 °C on a water bath, the copolymer gradually precipitated, after 3 h the mixture was cooled, the white solid polymer filtered off

and dried to constant weight in vacuum at 60 °C. The polymer was redissolved in methyl ethyl ketone and precipitated in methanol.

The procedure for the preparation of the major intermediate **3a** was followed: a solution of **1** (20 mL) in 50ml toluene was added to a toluene solution of **2**, and the reaction mixture was heated under reflux for 6 h. After being cooled to room temperature, the yellow **3a** was filtered off, washed with hot acetone and dried in vacuum at 60 °C. To prepare compound **3**, a suspension of **3a** (10 mmol) in 10ml of anhydrous acetonitrile, at room temperature, were added di-tert-butyl dicarbonate (10.5 mmol), followed by 4-N,N-dimethylaminopyridine (DMAP) (1mol%). After 60 min at room temperature, solvent was removed under reduced pres-

sure. The remaining solid was recrystallized from hexane-ethyl acetate (9:1) to give **3b**. A suspension of **3b** (5 mmol) in 10 mL of acetonitrile at room temperature was added an aqueous solution of hydroxylamine. After stirring the mixture overnight at room temperature, an orange precipitate had formed. Addition of 20 mL of ether allowed the precipitation of all the orange material, which was filtered, washed with ether and dried to give compound **3c** which corresponds to hydroxylammonium salt of compound **3**, then the salt **3c** was dispersed in 30 mL of water and dilute HCl was added until pH 1, finally the mixture was filtrated to obtain SMA-NHPI **3**. The Co/ZSM-5 was prepared according to reference [15].

### 1.3 Oxidation of cyclohexane

The oxidation of cyclohexane was performed in a 600 mL stainless steel autoclave equipped with a magnetic stirrer and an automatic temperature controller. In a typical reaction, 200 mL cyclohexane and SMA-NHPI (1 mol%) and Co/ZSM-5 (0.5 mol%) were added to the autoclave. Oxygen was pressurized into the reactor and the pressure was kept constant by supplying oxygen during the reaction, and then heated to the desired temperature with stirring. When the reaction was completed, the reactor was cooled down to room temperature with flowing tap water and then the pressure was released slowly. The mixture was filtrated, and the liquid phase mixture was distilled to remove cyclohexane to get oxidation products, the solid phase was extracted with ether for three times. Finally, the extraction without ether was combined with oxidation products, and then was analyzed by gas chromatography (GC), and chlorobenzene was used as internal standard. Since cyclohexyl hydroperoxide (CHHP) decomposes in part during chromatographic analysis, CHHP contents were determined by decomposition with PPh<sub>3</sub><sup>[23]</sup>. The formation of acids was investigated by esterification of the reaction mixture with *n*-butyl alcohol and identification of the products by GC-MS.

## 2 Results and discussion

### 2.1 Characterization of catalysts

The structure of SMA-NHPI was characterized by

FT-IR spectroscopy. The compound **1** shows bands at 3 443, 3 358 and 3 240 cm<sup>-1</sup> due to the -NH<sub>2</sub> stretch. The IR spectra of SMA **2** shows bands at 1 790 and 1 710 cm<sup>-1</sup> corresponding to the symmetric and asymmetric carbonyl stretches. The compound **3a** contains NH-stretch at 3 380 cm<sup>-1</sup>. For compound **3**, the broad peak at 3 180 cm<sup>-1</sup> corresponds to N-OH vibrations, the aromatic C-H stretches are seen as a broad multiplet signal around 2 930 cm<sup>-1</sup>, the bands at 1790 and 1 710 cm<sup>-1</sup> respond to the symmetric and asymmetric carbonyl stretches, and the spectral data agrees with its structure (Scheme 1)<sup>[22]</sup>.

The physical and chemical properties of Co/ZSM-5 zeolite were studied by XRD. The XRD of the Co/ZSM-5 displays the same peaks as pure HZSM-5, indicating that the impregnation does not destroy the original structure of HZSM-5 zeolite. That the intensities of corresponding peaks of angle  $2\theta = 22^\circ$ - $25^\circ$  are different is mainly due to different electrovalence to lead charge difference of zeolite.

### 2.2 Oxidation of cyclohexane

2.2.1 Comparison of catalytic activity of various catalysts The results of cyclohexane oxidation by different catalysts were shown in Table 1.

As shown in Table 1, in the presence of NHPI or Co/ZSM-5 alone, less than 10% of cyclohexane was oxidized. Compared with Co(NO<sub>3</sub>)<sub>2</sub>, Co/ZSM-5 significantly facilitated the oxidation of cyclohexane in presence of NHPI, which is ascribed to the enhanced activity by heterogenizing onto a solid support and hydrophobicity of zeolites which favors the adsorption of cyclohexane<sup>[24]</sup>. The catalytic activity of SMA-NHPI is almost same with that of NHPI. This is mainly due to polymer support is cross linked resin having large surface area, and the catalyst particles swell in the reaction medium thereby giving the advantage of high capacity<sup>[25]</sup>. Furthermore SMA-NHPI leads to simplification of reaction work-up and is easily separated from the reaction mass by filtration, so it is employed to investigate the progress of the reaction.

2.2.2 Effect of reaction temperature on the oxidation of cyclohexane Figure 1 showed the changes of KA oil mole mass with reaction time at different temperatures.

Table 1 The results of cyclohexane oxidation by different catalysts

Catalysts (mol%)	Conversion (%)	Selectivity (%)		
		KA oil	Adipic acid	CHHP
NHPI(1)	7.2	68.5	3.9	3.1
Co/ZSM-5(0.5)	9.5	72.1	5.4	2.3
NHPI(1), Co(NO <sub>3</sub> ) <sub>2</sub> (0.5)	18.5	74.6	12.1	2.9
NHPI(1), Co/ZSM-5 (0.5)	26.4	70.5	11.2	2.8
SMA-NHPI(1), Co/ZSM-5(0.5)	26.8	71.6	10.9	2.6

Conditions: cyclohexane 200 mL, 130 °C, 0.8 MPa, 3 h. KA oil: mixture of cyclohexanol and cyclohexanone; CHHP: cyclohexyl hydroperoxide.

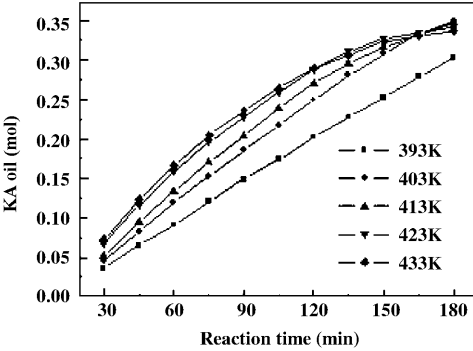


Fig. 1 Change of KA oil mole mass with reaction time at different temperatures

Conditions: cyclohexane 200 mL, 0.8 MPa, SMA-NHPI (1 mol%), Co/ZSM-5 (0.5 mol%).

In the range of test temperatures, the zero-order kinetic relationship between the KA oil mole mass and the reaction time was present. With reaction temperature variation, the reaction rate and time needed to complete the reaction all change. The time to complete the reaction decreased with increasing the reaction temperature, and the observed reaction rate constant  $K_a$  obtained from Fig. 1 increased with the increasing reaction temperature. This is ascribed to its ease to initiate the loop of catalysts at higher temperatures and favorable to force the reaction positively. Moreover, as increasing temperature, CHHP is apt to decompose to cyclohexanol and cyclohexanone, so the mole mass of KA oil increases obviously.

Figure 2 showed that reaction rate constant  $K_a$  and reaction temperature  $T$  had an Arrhenius relationship for which the linear correlation coefficient was 0.9878. The mathematics expression was  $\ln K_a = 3012/T + 1.279$ .

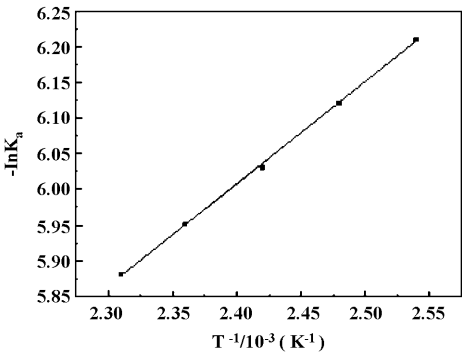


Fig. 2 Relationship between reaction rate constant  $K_a$  and temperature  $T$ .

2.2.3 Effect of oxygen pressure on the oxidation of cyclohexane

Figure 3 showed the effect of oxygen pressure on the oxidation of cyclohexane.

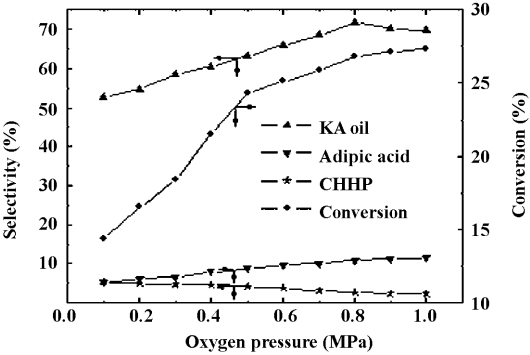


Fig. 3 Effect of oxygen pressure on the oxidation of cyclohexane  
Conditions: cyclohexane 200 mL, 130 °C, 3 h, SMA-NHPI (1 mol%), Co/ZSM-5 (0.5 mol%)

It was clear that the conversion of cyclohexane and the selectivity of adipic acid increased along with the increase of oxygen pressure, then fluctuated slightly over 0.8 MPa, the selectivity of KA oil reached the maximum at 0.8 MPa and subsequently decreased,

while the selectivity of CHHP always decreased during the reaction. In general, the higher the oxygen pressure, the higher the oxygen solubility in the liquid phase. Hence, oxygen in cyclohexane is too low-concentrated to be activated by catalysts, resulting in the lower catalytic activity and conversion. The decreased selectivity of CHHP is ascribed to the decomposition of CHHP at higher oxygen pressure, which is the reason for the increasing selectivity of KA oil as well.

### 2.3 Stability of catalysts

To evaluate the stabilities of those two heterogeneous catalysts in the oxidation of cyclohexane, the catalysts were removed by filtration after specific interval of time and the liquid filtrate was then allowed to react further in the absence of the catalysts. The reaction mixture was analyzed by GC immediately after removal of catalysts and after the total reaction time of 3 h. Furthermore, Co content of Co/ZSM-5 was determined before the reaction and after the reaction, the recovered SMA-NHPI was characterized by FT-IR spectroscopy. No loss of metal could be detected, the IR spectra of fresh and recovered SMA-NHPI were similar, no significant conversion was observed after removing the catalysts, indicating that no active species were present in the supernatant and the two heterogeneous catalysts were stable in the oxidation of cyclohexane.

### 2.4 Recycle of catalysts

Recycling tests with repeated use of the catalysts in five consecutive reactions were carried out. The catalysts were removed from the reaction mixture after 3 h by filtration, washed with ether and dried at 120 °C for 5 h and subjected to the next catalytic run under the same conditions. The results were given in Fig. 4.

It could be seen from Fig. 4 that the reuse of catalysts (five times) did not appreciably decrease the conversion of cyclohexane or the selectivity of products. Chemical analyses of reaction mixture and the used catalysts did not detect the leaching of cobalt from Co/ZSM-5 and the leaching of NHPI from SMA-NHPI, further confirming that the stability and recyclable applicability of the two heterogeneous catalysts for the oxidation of cyclohexane.

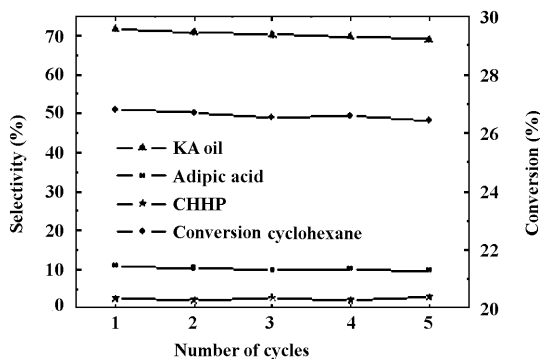


Fig. 4 Recycling studies of the catalytic system  
Conditions: cyclohexane 200 mL, 0.8 MPa, 130 °C, 3 h,  
SMA-NHPI (1 mol%), Co/ZSM-5 (0.5 mol%)

## 3 Conclusions

SMA-NHPI and Co/ZSM-5 were synthesized and applied to catalyze the heterogeneous oxidation of cyclohexane successfully. Compared with homogeneous catalysts, the two heterogeneous catalysts showed good catalytic activity, moreover, led to simplification of reaction work-up and were easily separated from the reaction mass by filtration. The studies of the stability and recycling revealed that the two heterogeneous catalysts were stable and could be reused.

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## 无溶剂体系中非均相催化剂催化环己烷氧化反应研究

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**摘 要:** 本文合成了苯乙烯-马来酸酐共聚物(SMA)桥联 N-羟基邻苯二甲酰亚胺(NHPI)和 Co/ZSM-5 两种非均相催化剂, 用 FT-IR、XRD 进行了结构表征. 考察了这两种非均相催化剂在无溶剂体系中对环己烷的催化氧化行为, 并对各反应因素的影响进行了研究. 结果表明: 在最佳反应条件下, 环己烷的转化率可达 26.8%, 此时 KA 油、己二酸和环己基过氧化氢的选择性分别为 71.6%、10.9% 和 2.6%. 在测试温度范围内, 反应速率常数  $K_a$  和反应温度之间存在 Arrhenius 关系, 相关系数是 0.9878, 数学表达式为  $\ln K_a = -3012/T + 1.279$ . 催化剂的稳定性研究显示两种非均相催化剂都具有很高的热力学稳定性, 可以重复使用五次.

**关键词:** SMA 桥联 NHPI; Co/ZSM-5; 环己烷; 非均相氧化