

Preparation of Zeolite Encapsulated Cobalt Schiff Base and Catalytic Activity in Cyclohexane Oxidation by Oxygen

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Abstract: N,N'-bis(salicylidene) ethylenediiminocobalt (Cosalen) has been successfully encapsulated into Microporous NaY zeolite by the flexible ligand method, which were characterized by FT-IR, UV-Vis, XRD, TG/DTA and BET Surface areas analysis. As catalyst for the oxidation of cyclohexane using oxygen, Cosalen-NaY showed the strong ability to decompose cyclohexyl hydroperoxide (CHHP) and the better selectivity for cyclohexanol, cyclohexanone and adipic acid than the neat complex. The conversion of cyclohexane reached 13.4% at 423 K under oxygen pressure 0.85 MPa for 3 h. After adding CH₃CN as solvent, the conversion was up to 28.3% even at 403 K. Recycling test showed that the catalyst can be used repeatedly with the neglected loss of active site.

Key words: Cosalen; Zeolite; Encapsulation; Oxygen; Cyclohexane oxidation

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The reversible oxygenation of cobalt complex of bis(salicylidene) ethylenediimine (Cosalen) was discovered by Tsumaki in 1938. For its known ability to activate oxygen by the formation of monomeric metal oxygen adducts (Co-O₂), Cosalen was chosen as catalyst in aerobic oxidation of alcohols, phenolic substrates, and benzylic type substrates with the performance mimic of cytochrome P-450^[1~5]. Up to now, catalytic oxidation of C-H bonds in saturated hydrocarbons under mild conditions is still a key step in the functionalization of many organic compounds and continues to be an important challenge for chemists. Molecular oxygen, which is most environmentally benign and economic, would be an ideal ultimate oxidant for oxygenation of hydrocarbons. Cosalen is expected to play an important role in this field. While the cobalt Schiff base is easily deactivated due to the formation of μ -oxo-dimers and simple dimers, which results in the not high stability, difficulty of recover and contaminated products. To improve the stability of Cosalen complex, D. D. Hu etc.^[6] prepared a N-(4-pyridylmeth-

ylidene)-chosten-supported Cosalen used for the oxidation of DOPA to its aldehyde. H. X. Ma etc.^[7] prepared silica-supported Cosalen coordinated with chitosan as catalyst for the oxidation reaction of ethanethiol. Trissa Joseph etc.^[8,9] encapsulated salicylaldehyde-o-phenylenediimine cobalt in zeolite-Y catalyzed the oxidation of α -pinene and β -isophorone to isophorone. The facts show that the formation of μ -oxo-dimers and simple dimers of the metal complex can be effectively prevented by employing the site isolation effect of polymers or inorganic materials.

Y-type zeolite with the cage size of 1.2 nm and small open window of 0.7 nm has been used extensively in the preparation of zeolite encapsulated transition metal complex catalysts. These catalysts could be prepared by the exchange of transition metal salts with Na⁺ of Zeolite-Y and then treated with ligands (flexible ligand method)^[10]. In this work, we prepared the NaY zeolite encapsulated Cosalen with some difference from the literature^[11], and used it as catalysts in oxidation of cyclohexane with dioxygen in the absence of a

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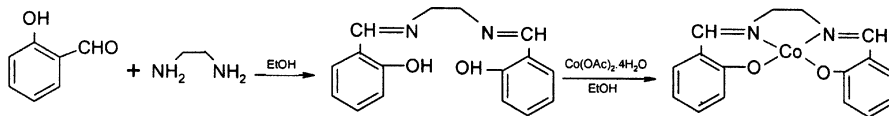
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reducing agent and initiator. The activity of such catalyst appears high. It's also found that the encapsulated cobalt complex can be recycled and reused.

1 Experimental

1.1 Materials

The zeolite NaY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$) was provided by SINOPEC Changling Company, which is de-



Scheme 1 Synthesis of salen and cosalen

mol) dissolved in ethanol (100 mL) is added drop by drop to ethylene diamine solution (4.2 g, 0.07 mol in 50 mL ethanol), The contents were refluxed for half an hour and a bright yellow precipitate of salen was obtained. The yellow precipitate was separated by filtration, washed and dried in vacuum. It was then recrystallized from ethanol to yield salen 15.2 g (mp. 402 ~ 403 K).

Cobaltous acetate (7.54 g, 35 mmol) and salen (8.56 g, 35 mmol) were dissolved in ethanol (200 mL) and refluxed for 2 h in nitrogen atmosphere, on cooling the mixture, after filtration, washed by ethanol to colorless, dried in vacuum at 385 K for 8 h, red brown crystal of Cosalen was obtained.

1.2.2 Synthesis of CoY $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.75 g) was dissolved in warm distilled water (350 mL) to which zeolite NaY (3.75 g) was added and the contents were refluxed for 24 h under the protection of N_2 , a pink colored solid obtained was collected by filtration and this solid was washed several times with hot water. The cobalt-exchanged zeolite was dried in vacuum overnight at 385 K and used in the preparation of catalyst.

1.2.3 Synthesis of Cosalen-NaY by flexible ligand method Salen (3 g) was dissolved in 114 mL of t-butyl alcohol and to it CoY (1 g) was added and this mixture was stirred for 16 h under reflux at 353 K in nitrogen atmosphere. The resulting slurry was filtered and the solid was Soxhlet extracted for 48 h with t-butyl alcohol, methanol and acetonitrile in sequence. This

hydrate under 473 K in vacuum for 2 h before use. The ligand N,N'-bis(salicylidene) ethylenediamine (salen) and cobalt complex has been synthesized and the reaction steps are given below. The other chemicals used were of AR quality.

1.2 Sample preparation

1.2.1 Preparation of salen and Cosalen The stoichiometric amount of salicylaldehyde (17.1 g, 0.14

mol) dissolved in ethanol (100 mL) is added drop by drop to ethylene diamine solution (4.2 g, 0.07 mol in 50 mL ethanol), The contents were refluxed for half an hour and a bright yellow precipitate of salen was obtained. The yellow precipitate was separated by filtration, washed and dried in vacuum. It was then recrystallized from ethanol to yield salen 15.2 g (mp. 402 ~ 403 K).

1.3 Characterization of catalysts

The electronic spectras of the neat and encapsulated complexes dissolved in HCl solution were taken on a PE lambda 25 UV-Vis scanning spectrophotometer. FT-IR spectra of the solid samples were recorded on a PE Spectrum One instrument in KBr pellets over the range of 400 ~ 4 000 cm^{-1} under the atmospheric conditions. Powder of X-ray diffraction of the zeolite encapsulated metal complex catalysts were carried out using a Rigaku (Model D/Max-2550, Japan), set-up with Cu K α radiation (40 kV, 300 mA) and a graphite monochromatic with scan speed 8° /min and scanning in the 2θ range from 3 ~ 50°. Silicon was used to calibrate the instrument. The cobalt content of the samples was measured by atomic absorption spectrometer (AAS-Hitachi Model Z-8000, Japan) after acid (HCl) dissolution of known amounts of the zeolite material. BET Surface area and pore volume of the zeolite-encapsulated catalysts were determined by Tristar 3000 (Micromeritics, USA) at 77 K from nitrogen adsorption. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the zeolite encapsulated metal complexes were recorded on Japan shi-

madzu instrument (Model BT-40).

1.4 Catalytic study

The cyclohexane oxidation experiments were carried out in a 250 mL stainless steel autoclave. In a typical experiment, reaction mixture containing known amounts of cyclohexane, catalyst, (or acetonitrile as solvent) were placed into the autoclave. After sealing, the reactor was replaced by purity oxygen for several minutes at lowest flow rate, then charged with 0.85 MPa of O_2 and heated to the desired temperature and kept at that temperature under constant magnetic stirring. When the reaction was stopped, the catalyst was separated by filtration after the reaction mixture was diluted with 15 g ethanol to dissolve the by-products. The products were analyzed by PE Autosystem Gas Chromatography (GC) and titration. the quantitative analyses of cyclohexanol and cyclohexanone was carried out by GC, which was equipped with AC-10 capillaries ($30\text{ m} \times 0.25\text{ mm} \times 0.3\text{ }\mu\text{m}$), and the internal standard was chlorobenzene. The concentration of cyclohexyl hydroperoxide (CHHP) was determined by iodometric titration, and the other products acid and ester by acid-base titration. Typically, the known amounts of reaction mixture was diluted with 25 mL ethanol and then titrated with 0.1 mol/L NaOH. The solution was refluxed for 1 hour after adding 20 mL 0.1 mol/L NaOH and then titrated with 0.1 mol/L HCl. After the separated catalyst was washed with ethanol three times, dried at 393 K for 6 h and then was used for the recycling study.

2 Results and discussion

2.1 Chemical analysis

The cobalt contents of the encapsulated complex catalysts were estimated by dissolving known amounts of the catalyst in conc. HCl and from these solutions, the cobalt contents were estimated using atomic absorption spectrometer (AAS). The Co content of the catalyst was equal to 1.86 %.

2.2 Catalysts characterization

The FT-IR spectra of the salen, Cosalen, NaY and Cosalen-NaY are shown in Fig. 1. The band at 1638 cm^{-1} in sample (a) was assigned to the $C=N$

vibration indicated the forming of salen. After complexation with the Co ion, this band downward shift to 1625 cm^{-1} in sample (b). It clearly shows that no

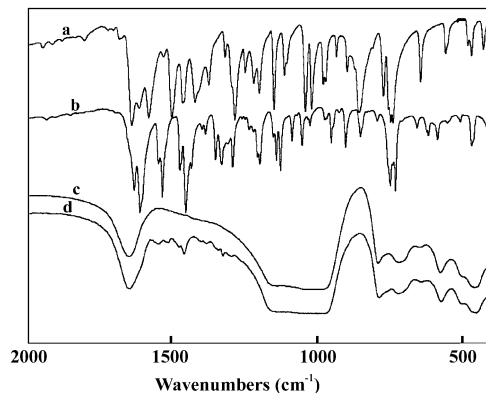


Fig. 1 FT-IR spectra of samples

(a) salen; (b) Cosalen; (c) NaY; (d) Cosalen-NaY absorption band is observed between $1630 \sim 1300\text{ cm}^{-1}$ in the spectrum of NaY, while as to the spectrum of the Cosalen-NaY some bands appear in this region. These bands are attributed to the vibrations of $C=C$ and $C=N$, indicated the presence of Cosalen. Since the Cosalen-NaY sample underwent a thorough extraction, it is not possible for free salen to be embedded in NaY, because uncomplexed salen, with a much smaller line-tic diameter than the pore opening of zeolite Y, can be easily removed during the process of extraction. The bands of all encapsulated complexes are weak in comparison with the neat complexes due to their low concentrations in zeolite cages. The comparison of the spectra indicates the presence of Cosalen inside the zeolite cages.

The UV - Vis spectrum of Fig. 2 confirms the in-

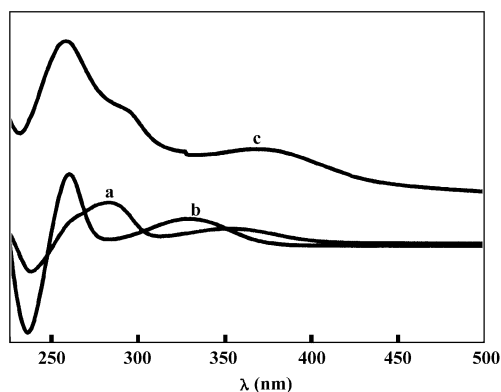


Fig. 2 UV-Vis spectra of sample

(a) salen; (b) Cosalen; (c) Cosalene-NaY

clusion of Cosalen complex within the zeolite cages. The free Cosalen complex has the typical absorptions at 260 and 327 nm. After encapsulation, the absorption peaks still existed suggested the existence of Cosalen in the cage of zeolite, though the peaks have some shift and are broadened which may be attributable to some distort of Cosalen after encapsulated into zeolite NaY.

The surface area and micropore volume of the NaY, CoNaY and Cosalen-NaY are presented in Table 1. The parent zeolite has the largest surface area and

Table 1 Surface area and pore volume of catalysts

Sample	S_A (m ² /g)	V (mL/g)
NaY	756	0.358
CoNaY	644	0.336
Cosalen-NaY	506	0.288

the largest total pore volume. The encapsulation of metal ions and metal salen complexes reduced the surface area and adsorption capacity of zeolite. The lowering of the pore volume and surface area support the fact that Cosalen complexes are present within the zeolite cages and not on the external surface.

Fig.3 compares the X - ray diffraction pattern of

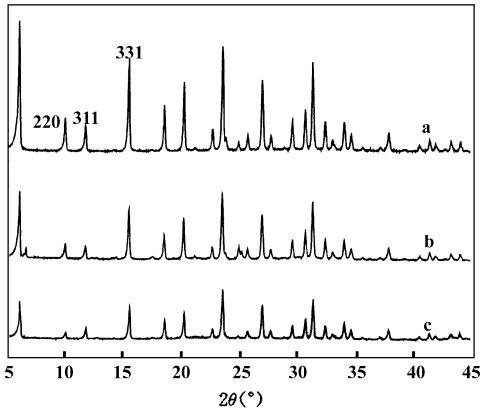


Fig.3 XRD patterns of samples

(a) NaY; (b) CoNaY; (c) Cosalen-NaY

Cosalen-NaY , CoNaY with that of the parent zeolite. It shows that the crystallinity of the zeolite is quite well preserved upon the encapsulation. This indicates that complexing and extraction processes do not have so strong influence on the structure of the parent NaY material. Nevertheless, slight modification occurs, as confirmed by the alteration of the relative intensity of the peaks at 220 and 311 reflections (2θ of about 10 and 12°). Qualitative information about site occupan-

cies can be obtained from comparison of the relative intensities of selected XRD lines. Quayle and Lunsford^[12] suggested that a relationship exist between the relative intensities of 311 and 220 XRD peaks and cation location in faujasite-type zeolites. If $I_{220} > I_{311}$, sodium cations are randomly distributed within the lattice, upon ion exchange with Co^{2+} , and being coordinated to salen, I_{220} becomes lower than I_{311} , the line 222, that could be ascribed to antisymmetric character of the charge distribution with respect to the supercage centre is absent. We presumed, therefore, that the large molecules of the Cosalen complex displace the sodium cations and locate in the supercages.

The TG/DTA curves of Cosalen-NaY are shown in Fig. 4. The endothermic peak observed at temperature

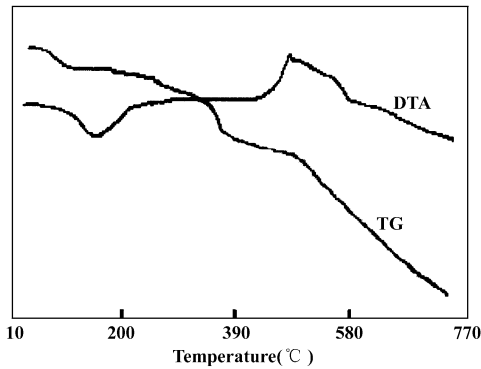


Fig.4 TG/DTA curves of the extracted Cosalen-NaY

below 473 K in the DTA curve is due to the desorption of physically adsorbed and occluded water, whereas the exothermic peak around 748 K is ascribed to the combustion of Cosalen complex encaged in the host. As compared to the neat complex, which decomposes at about 598 K, the thermal stability is greatly enhanced. This gives another piece of strong evidence for the inclusion of Cosalen in NaY.

2.3 Catalytic activity

The liquid phase oxidation of cyclohexane was carried out using molecular oxygen as oxidant, Cosalen encapsulated into zeolite NaY was selected to assess its catalytic properties in this reaction and compared with unsupported Cosalen and the results were shown in Table 2. It can be seen that the conversion of cyclohexane was only 4.4% in blank experiment when parent NaY zeolite was used as catalyst. Cosalen-NaY showed nearly equal activity in oxidation reaction compared

with the unsupported Cosalen. It seemed that there is no obvious induction time to start the reaction. This

Table 2 Results of oxidation of cyclohexane over complex and encapsulated complex

Catalyst	Conversion (%)	Product distribution (%)				
		A	K	CHHP	Acid	Other
NaY ^a	4.4	17.3	36.2	24.4	8.9	13.2
Cosalen ^a	14.8	9.8	18.9	0.4	26.4	44.5
Cosalen-NaY ^a	13.4	5.1	18.4	2.8	52.9	20.8
Cosalen ^b	29.8	4.4	12.5	2.7	36.7	43.7
Cosalen-NaY ^b	28.3	9.1	24.8	0.8	38.2	27.1

A = cyclohexanol; K = cyclohexanone; CHHP = cyclohexyl hydroperoxide; Acid = mainly adipic acid

^a Reaction conditions: 0.18 mol cyclohexane, 0.1 g cosalen-NaY (Co content = 1.86%), 0.85 MPa oxygen pressure, 423 K, 3 h.

^b 0.01 g Cosalen or 0.1 g Cosalen-NaY, (Co content = 3.14%), 403 K, 10 mL CH₃CN as solvent

can be explained that in the case of cobalt salen complex in which cobalt is in divalent state the reaction starts by activation of dioxygen, being particularly active, whereas in the case of other cobalt complexes, it is the activation of the hydrocarbon molecule by the axial ligand, which starts the chain reaction. At the same time, the yield of CHHP over Cosalen and Cosalen-NaY were much lower than those over NaY and this implied that neat and encapsulated complex have stronger ability to decompose CHHP. However, it was of difference as regards the distribution of the reaction products. The one/ol ratio was increased from 1.9 to 3.6 when Cosalen-NaY was used as catalyst. The yield of acid was moderate high due to the relative high conversion of cyclohexane. To some extent, Cosalen-NaY was benefit for the formation of acid especially of adipic acid, which was qualitatively analyzed by HPLC. The selectivity of cyclohexanol, cyclohexanone and acid when used Cosalen-NaY as catalyst was much higher than the one used Cosalen as catalyst. So the carrier may play an important role for this. It is interesting to notice that the catalyst is two times more active after adding the CH₃CN as solvent in the oxidation reaction and the temperature can be decreased to 403 K. The selectivity of cyclohexanol and cyclohexanone is two times higher compared the encapsulated cobalt complex with its unsupported analog. The higher catalytic activity in acetonitrile may be attributed to higher solubility of O₂ and polarity of solvent.

The encapsulated catalyst cosalen in zeolite NaY was recovered and reused. The results presented in

Fig. 5. It can be observed that the activity and selectivity was almost similar to those of the fresh catalyst.

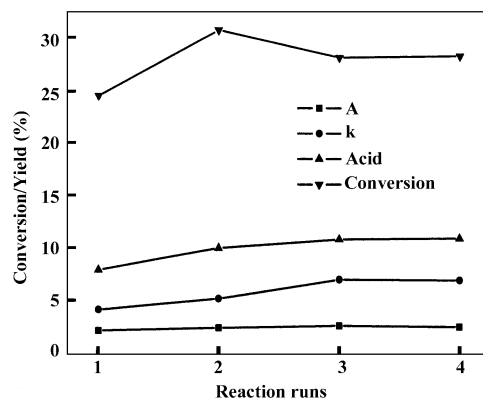


Fig. 5 Recycling studies over Cosalen-NaY
Reaction temperature and time were 403 K and
3.0 h, 0.18 mol cyclohexane ,
10 mL CH₃CN as solvent

Thus, the results indicated the Cosalen-NaY was an efficient, recyclable heterogeneous catalyst for the oxidation of cyclohexane by oxygen.

3 Conclusions

In this work, Cosalen-NaY was prepared by the method of flexible ligand. FT-IR, UV-Vis, Surface area and pore volume, XRD, and TG/DTA characterization showed that Cosalen had been encaged in zeolite Y. The prepared Cosalen-NaY as a catalyst exhibits much higher activity for the oxidation of cyclohexane, which utilized dioxygen as the oxidant under moderate pressure and temperature. The catalyst has the better selectivity for cyclohexanol, cyclohexanone and acid.

Moreover, it shows the potential ability to oxidize the cyclohexane to adipic acid in a single step. The continue efforts should drive for this direction. At the same time, the encapsulated complexes could be recycled and reused with small changes in catalytic activity.

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分子筛负载席夫碱钴配合物的制备 及其催化氧气氧化环己烷

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摘要: 采用柔性配位法将双水杨醛叉乙二胺合钴(Cosalen)封装到了NaY分子筛的超笼中, 采用FT-IR, UV-Vis, XRD, TG/DTA 和 BET 比表面积及孔容分析对负载型配合物(Cosalen-NaY)进行了表征. 在催化氧气氧化环己烷的反应过程中, Cosalen-NaY 能有效地促进环己基过氧化物的分解, 在 0.85 MPa 的氧压下, 150 °C 反应 3 h, 环己烷的转化率达到 13.4%, 在反应体系中加入乙腈作溶剂, 130 °C 下进行反应, 环己烷的转化率提高到 28.3%. 产物中环己醇、环己酮、己二酸的选择性明显高于 Cosalen 为催化剂的反应. 催化剂回收实验表明 Cosalen-NaY 经过三次重复使用后, 没有显著的活性组分流失, 可以重复使用.

关键词: Cosalen; 分子筛; 封装; 氧气; 环己烷氧化