

SYNTHESIS, CHARACTERIZATION OF COSALEN/NaY AND THE CATALYTIC PERFORMANCE FOR AEROBIC OXIDATION OF CYCLOHEXANE

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Abstract— N,N'-Bis(salicylidene)ethylenediiminocobalt (Cosalen) was encapsulated into the supercage of microporous NaY zeolite via "ship-in-a-bottle" technique. The impregnated Cosalen complex immobilized on the outer surface of the zeolite was also prepared in order to further prove the encapsulation by the flexible ligand method. The samples were characterized by FT-IR, UV-Vis, XRD, TG/DTA and SEM techniques. The oxidation of cyclohexane using oxygen was chosen to evaluate the catalytic performance of encapsulated complex. The encapsulated Cosalen was stable than the neat Cosalen complex and the conversion of cyclohexane reached 24.4% at 130 °C for 3 h in the CH₃CN solution without adding any inducing agents. The higher selectivity for acid including adipic acid indicated that the encapsulated Cosalen exhibited the ability to produce acid from cyclohexane by one-step reaction.

Keywords— Cosalen, NaY zeolite, oxygen, cyclohexane, oxidation.

I. INTRODUCTION

It is well known that Y-type zeolite can incorporate and immobilize various catalyst complexes in its structure of the large supercage (diameter~1.2Å) and the restricted pore opening (~7.4Å) (Joseph *et al.*, 2001; Fan *et al.*, 2003; Salama *et al.*, 2006). Typical complexes that have been incorporated are metal phthalocyanine complexes, metal porphyrin complexes and metal Schiff base complexes. As such complexes are synthesized in the supercage of zeolite just like building a ship in a bottle, such conformations are often referred to as "ship-in-a-bottle" type catalysts. There have been three main approaches to the preparation of these ship-in-a-bottle chelate complexes, namely, (I) a flexible ligand method (Bowers and Dutta, 1990) (synthesis of the metal complex in situ in the zeolite cavity by reaction of the ligand with the exchanged metal cations), (II) a template synthesis method (Balkus *et al.*, 1994) (condensation of ligand inside a zeolite modified with the metal ion to be complexed), or (III) a zeolite synthesis methods (Varkey *et al.*, 1998) (synthesis of the zeolite in the presence of the preformed metal complexes). In the first approach, the ligand must be able to diffuse freely through the zeolite pores having an advantage to complex with a previously exchanged metal ion. The shaped complex becomes too large and rigid to escape from the cage. The template synthesis method is exemplified by the preparation of intrazeolite metallophthalocyanines in this case because

of the ligands size. The newest zeolite synthesis method has the obvious advantage that the nature of the intrazeolite species is well-defined and no free ligand need to be removed. However, there is a heterogeneous distribution of metal complex in the precursor gel and the complexes cannot be evenly distributed within the zeolite crystals, which have a direct effect on the loadings of the metal complex in the zeolite host.

Encapsulation of transition metal complexes with redox catalytic activity in zeolites is a theme of current research due to their potential use as heterogeneous redox catalysts. N,N'-Bis (salicylidene) ethylenediiminocobalt (Cosalen) is analogue of metalloporphyrin with ability to activate oxygen (Sharma *et al.*, 2004; Das and Punniyamurthy, 2003) by the formation of monomeric metal oxygen adducts (Co-O₂), which was expected to play an important role in the field of aerobic oxidation of hydrocarbons. Whereas the Cobalt Schiff base complex is easily deactivated due to the formation of μ -oxodimers and simple dimmers. To improve the stability of Cosalen complex, N-(4-pyridylmethylidene)-chosten-supported Cosalen was prepared and used for the oxidation of DOPA to its aldehyde (Hu *et al.*, 2001). Silica-supported Cosalen coordinated with chitosan as catalyst has been used for the oxidation reaction of ethanethiol (Ma *et al.*, 2001). Salicylaldehyde -o-phenylenediimine cobalt encapsulated in zeolite-Y catalyzed the oxidation of α -pinene and β -isophorone to isophorone (Joseph *et al.*, 2002). The facts show that the formation of μ -oxodimers and simple dimmers of the metal complex can be effectively prevented by employing the site isolation effect of polymers or inorganic materials.

In this work, we prepared the Cosalen complex encapsulated in NaY zeolite using the flexible ligand method (as the ligand Bis (salicylidene) ethylenediamine (salen) diameter is smaller than the apertures of the NaY zeolite). By the conventional method the ligand is first melt at high temperature and then allowed to diffuse for a long time into the zeolite to complex with ion-exchanged NaY zeolite. It was found that adding t-butyl alcohol as solvent can also realize the encapsulation even at relatively low temperature for shorten periods of time. The synthesized samples were characterized by the technique of FT-IR, UV-Vis, X-ray diffraction (XRD), TG/DTA and scanning electron microscope (SEM). At the same time, the impregnated Cosalen im-

mobilized on the external surface of the zeolite was also prepared to compare with the encapsulated complex. The cyclohexane oxidation was chosen as model reaction to evaluate the catalytic performance of the encapsulated Cosalen complex.

II. EXPERIMENTAL

A. Materials

The zeolite NaY ($\text{SiO}_2/\text{Al}_2\text{O}_3=5.2$) provided by SINOPEC Changling Company, is dehydrated at 200 °C in vacuum for 2 h before use. The ligand $\text{N}_2\text{N}'$ -Bis(salicylidene) ethylenediimine (salen) and Cosalen complex were synthesized according to the literature (Joseph *et al.*, 1999). The other chemicals used were of AR quality. All the solvents (t-butyl alcohol, acetonitrile, methanol, ethyl alcohol) were distilled before use.

B. Sample Preparation

CoNaY Cobaltous acetate (1.75 g) was dissolved in warm distilled water (350 mL) to which NaY zeolite (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 110 °C and used in the followed preparation.

Encapsulated Cosalen/NaY (FL) Salen (0.5 g) was dissolved in t-butyl alcohol (114 mL) and to it CoNaY (1 g) was added and the mixture was stirred for 8 h under reflux at 80 °C in nitrogen flow. The resulted slurry was filtered and the solid was Soxhlet extracted for 48 h with t-butyl alcohol, acetonitrile and methanol, respectively. The obtained solid was further refluxed with 1 mol/L NaCl (50 mL) solution for 16 h to be replaced the uncomplexed Co ions adhering to the outer surface of zeolite by Na^+ . After this, the solid product was filtered and washed with hot water to remove the adsorbed chloride ions (silver nitrate test). The above product was then dried at 110 °C in vacuum for 6 h. The sample thus obtained was denoted as Cosalen/NaY-A (FL). FL is the abbreviation of flexible ligand method.

CoNaY (1 g) was treated with molten salen ligand (2 g) in the autoclave at 150 °C for 24 h under the nitrogen atmosphere. The obtained solid was treated with a similar procedure described above for Cosalen/NaY-A (FL). The resulted product was denoted as Cosalen/NaY-B (FL).

Impregnated Cosalen/NaY (IM) A t-butyl alcohol solution (100 mL) of Cosalen (1 g) was added to a suspension of NaY zeolite (2 g) in t-butyl alcohol and the mixture was stirred at 80 °C for 8 h. After filtration, the product was Soxhlet extracted with t-butyl alcohol and acetonitrile for 12 h, then drying in vacuum at 110 °C for 6 h. The resulted product was denoted as Cosalen/NaY (IM). IM is the abbreviation of impregnation.

C. Characterization of Samples

FT-IR spectra of the solid samples were recorded on a Nicolet 380 instrument in KBr pellets over the range of

400-4000 cm^{-1} under the atmospheric conditions. The electronic spectra were taken on a PE lambda 25 UV-Vis scanning spectrophotometer in the region 200-800 nm. Powder XRD of the samples were carried out using a Rigaku (Model D/Max-2550, Japan), set-up with Cu $\text{K}\alpha$ radiation (40 Kv, 300 mA) and a graphite monochromatic with scan speed 8° /min and scanning in the 2θ range from 3~60°. 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. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves were determined by WRT-3P thermal gravity analyzer and CRY-2P differential thermal analyzer (Shanghai balance instrument factor, China) at a heating rate of 5 °C/min in an air atmosphere. The sample images were observed on the Japan JSM-5600 SEM.

D Catalytic Experiments

The cyclohexane oxidation experiments were carried out in a 250 mL stainless steel autoclave with a Teflon liner. In a typical experiment, reaction mixture containing known amounts of cyclohexane, solvent and catalyst were placed into the autoclave. After sealing, the reactor atmosphere was replaced by a flow of pure oxygen for several minutes, then charged with 0.85 MPa O_2 and heated to the desired temperature and kept at that temperature under constant magnetic stirring. The oxidation was stopped by immersing the hot reactor in a cold ice bath, the reaction mixture was cooled to room temperature and 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 were carried out by GC, which was equipped with AC-10 capillaries (30 mm \times 0.25 mm \times 0.3 μm), and the internal standard was chlorobenzene. The concentration of alkyl hydroperoxide was determined by iodometric titration, and the other products acid and ester by acid-base titration.

III. RESULTS AND DISCUSSION

A. FT-IR spectroscopy

The FT-IR spectra of the samples were shown in Fig. 1. Just as NaY zeolite, CoNaY, the encapsulated Cosalen complex and impregnated Cosalen complex all show the most intensive bands in the regions of 1250-450 cm^{-1} assigned to the lattice vibrations of the zeolite host. This provided information on the integrity of the carrier, as well as the crystallinity of the host zeolite in accordance with the XRD analysis.

An intense band is appearing at 1602 cm^{-1} in IR spectrum of neat complex. This band can be assigned as the characteristic band for azomethine group $\text{C}=\text{N}$ of salen while it is coordinated with Co ion. While zeolite-based materials usually adsorbs H_2O , this band often overlapped with the H-O-H. It is observed new characteristic absorptions after encapsulation in the region

between 1500 and 1350 cm^{-1} , which is absent in the zeolite matrix and also found in the spectrum of impregnated complex and mixture sample. This indicated the presence of Cosalen complex. As for neat complex, C-C stretching modes just appeared in this region. The weak band due to the low concentration in the carrier. It is noticed that no significant shift in the spectrum compared with that of the neat Cosalen, which demonstrated that no free ligand salen existed, it is known that complex made the ligand's absorb peak downward shift in the C=N stretching vibration. If NaY and Cosalen mixed by rubbing, their IR bands incorporated. The Cosalen/NaY (IM) also showed the weak band in the region of 700 and 770 cm^{-1} , which are not obvious in the encapsulated complex. It's also noticed that the spectrum of CoNaY displayed a band at 1400 cm^{-1} due to OH vibration in H_2O molecules coordinated to the Co ions. The persistence of this band after complex indicates that some of Co ions are hitherto coordinated to water molecules (Salama *et al.*, 2006). This band is not apparent in the spectrum of parent NaY zeolite, mixture of NaY and Cosalen and impregnated (IM) sample.

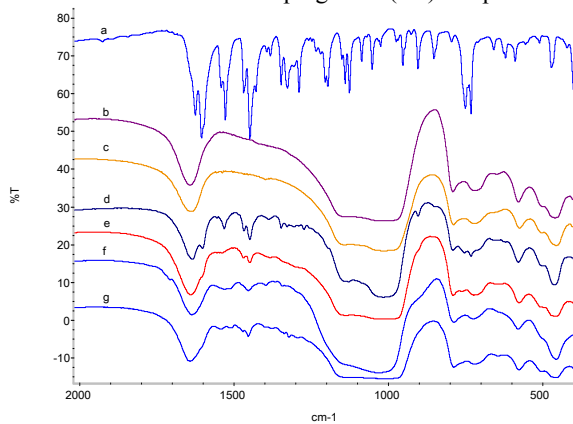


Fig. 1 FT-IR spectra of the samples. (a) Cosalen, (b) NaY zeolite, (c) CoNaY, (d) mixture of NaY and Cosalen, (e) Cosalen/NaY(IM), (f) Cosalen/NaY-A(FL), (g) Cosalen/NaY-B (FL)

B. UV-vis spectroscopy

The UV-vis spectra confirm the incorporation of Cosalen complexes into the zeolite NaY supercages. The only way to remove the complexes from the zeolite is to destroy the molecular sieve lattice. Partial digestion of the zeolites in concentrated H_2SO_4 results in release of the complexes into solution. The band positions from the electronic spectra for these samples are shown in Fig. 2. For the neat Cosalen complex, the main characteristic band assigned to the $\pi-\pi^*$ transition of the π conjugation in framework and benzene ring appearing at 226 nm, the bands at 282 and 347 nm was assigned to the metal-to-ligand charge transfer (MLCT) transition and d-d transition band for the metal atoms. The same bands are present in the UV-vis spectrum of impregnated Cosalen complex, which means the configuration of Cosalen complex had no change when immobilized on the outer surface of the zeolite. The absorb bands for Cosalen/NaY-A (FL) and Cosalen/NaY-B (FL) were

225, 282, 325 nm and 225, 285, 321, 374 nm separately. Some shift of the absorption band with respect to the Cosalen observed indicate that the encapsulation of the complex modifies its electronic and spectral properties to some extent.

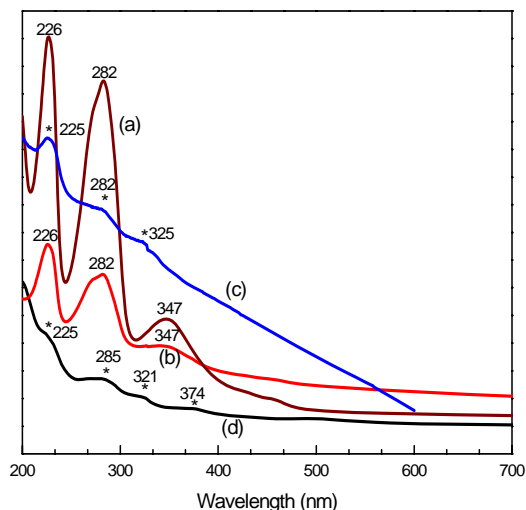


Fig. 2. UV-Vis spectra of the samples. (a) Cosalen, (b) Cosalen/NaY (IM), (c) Cosalen/NaY-A (FL), (d) Cosalen/NaY-B (FL)

C. X-ray diffraction

The powder X-ray diffractions of the parent NaY, CoNaY and Cosalen/NaY are shown in Fig. 3. These samples displayed the expected pattern of hydrated NaY zeolite. It can be assumed that the zeolite framework was not affected to a measurable extent by the presence of the Co-exchanged ions or intrazeolitic complex formation.

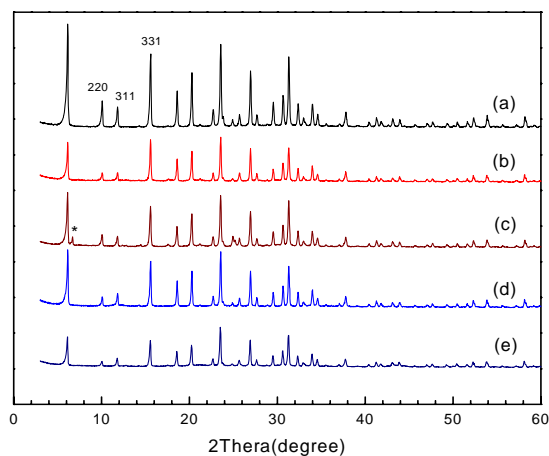


Fig. 3. XRD patterns of the sample. (a) Cosalen, (b) CoNaY, (c) Cosalen/NaY (IM), (d) Cosalen/NaY-A (FL), (e) Cosalen/NaY-B (FL)

It has been observed that empirical derived relationship (Kozlov *et al.*, 1998) exist between the relative 331, 311 and 220 peak intensities and cation location in faujasite type zeolites. Cations are randomly distributed within the lattice if $I_{331} > I_{220} > I_{311}$, but if $I_{331} > I_{311} > I_{220}$, the

cations assume positions at sites I', II. Using these empirical criteria, the diffraction patterns suggest that the large Cosalen complex is probably displaced Co ions from their random positions within the NaY cavities to locations at sites I', II. Site I' is reported as being located in the sodalite cavity while site II at the center of a single six-ring or displaced from this point into a supercage. This would allow more effective coordination between Co ions and salen ligand groups extended into the large cages upon complexation. The XRD analysis proved that through flexible ligand method, the Cosalen has been encapsulated into the zeolite supercage. It is also found that the reduction in the intensities of the peaks was observed for Cosalen/NaY-B (FL) than that for Cosalen/NaY-A (FL). As to impregnated Cosalen/NaY, there is a new diffraction line close to the first line at $6^\circ 2\theta$ (mark on asterisk) assigned to new phase were detected. Obviously, the impregnated sample posses Cosalen complex at the external surfaces.

D. TG-DTA analysis

Thermogravimetry analysis (TG) and differential thermal analysis (DTA) have been used to characterize intrazeolite metal complexes. TG and DTA obtained for the neat, impregnated and encapsulated complex are depicted in Fig. 4. These weight loss peaks below 200°C correspond to desorption of physically adsorbed and occluded water molecules from zeolite at increasing temperature. The neat Cosalen complex shows a weight loss from ca. 300°C . The impregnated Cosalen complex exist an obvious exothermic peak at 300°C indicating the decomposition of the complex, which must exist at the external surface of the NaY zeolite. However, for the corresponding encapsulated complex, there is a continuous weight loss that extends to temperatures above 500°C , which means the thermo stability of Cosalen has been improved after encapsulation.

E. SEM analysis

The images of the samples were observed by scanning electron microscopy (SEM). After Cosalen and NaY mixed by rubbing directly, the SEM show that the surface of the NaY zeolite was covered by some small particle of cosalen complex. The impregnated cosalen/NaY also show the same material on the external surface of the zeolite. The encapsulations of the complexes inside the zeolite cavities were indicated by the absence of extraneous material by SEM. It is also proved that through the thorough washing, the uncomplexed salen ligand and the Cosalen complex absorbed on the surface of the zeolite can be removed completely. Moreover, the image of zeolite with good crystallinity was observed both for Cosalen/NaY-A (FL) and Cosalen/NaY-B (FL). From SEM, the average size of the zeolite particles was estimated to be about $1\ \mu\text{m}$.

F. Catalytic activity

The liquid phase oxidation of cyclohexane was carried out using molecular oxygen as oxidant. The results of comparison tests in the presence of different catalysts were listed in Table 1. It can be seen that the conversion of cyclohexane was only 1.8% without adding any catalyst at 130°C for 3 h in the solution of acetonitrile. When using Cosalen complex as catalyst, the conversion was just 7.9%. As for the distribution of the products, the selectivity of cyclohexanol and cyclohexanone increased when using Cosalen as catalyst as respect to the blank experiment. Both reactions produced large amount of ester. As shown in Table 1, with the exception of blank test, all catalyst showed the ability to decompose the CHHP since only small amount of CHHP was detected after the reaction. It is noted that other Cobalt-based catalyst also showed such performance (Zhou *et al.*, 2005). The impregnated Cosalen complex

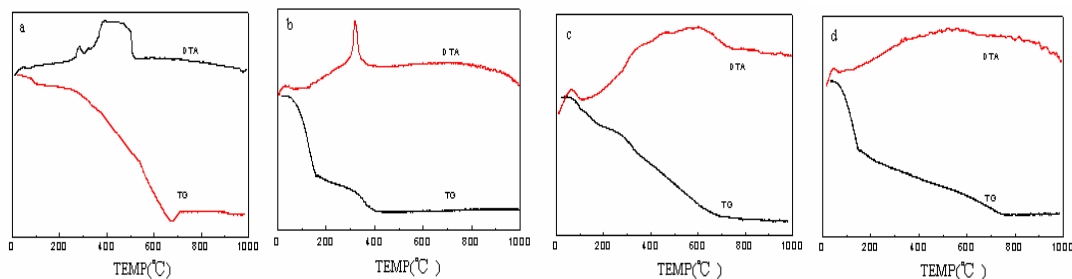


Fig. 4. Thermogravimetry and differential thermal analysis of samples.
(a) Cosalen, (b) Cosalen/NaY (IM), (c) Cosalen/NaY-A (FL), (d) Cosalen/NaY-B (FL)

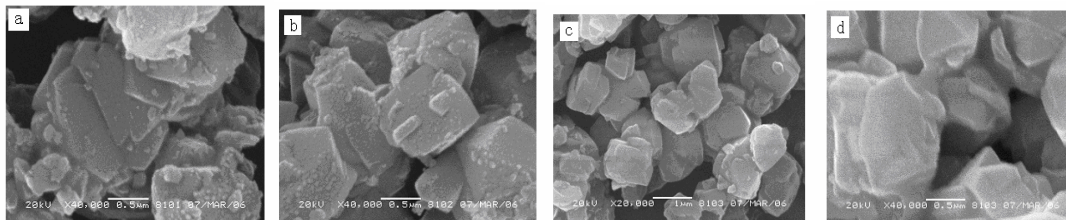


Fig. 5. SEM of the samples

(a) Mixture of NaY and Cosalen, (b) Cosalen/NaY (IM), (c) Cosalen/NaY-A (FL), (d) Cosalen/NaY-B (FL)

Table 1 Results of oxidation of cyclohexane over different catalyst

Catalyst	Co% (Wt%)	Conversion (mol%)	TON ^b	Product distribution (mol%) ^a				
				A	K	CHHP	Acid	Ester
Blank		1.8		17.3	12.7	20.0	19.4	30.6
Cosalen		7.9	305	19.1	22.3	3.4	18.5	36.7
Cosalen/NaY (IM)	2.26	9.5	295	17.5	32.6	5.9	23.9	20.1
Cosalen/NaY-A (FL)	3.14	24.4	544	10.5	29.6	3.9	44.6	11.4
Cosalen/NaY-B (FL)	2.27	21.1	652	8.0	17.5	7.5	40.2	26.8

Conditions: Cyclohexane 0.18 mol, acetonitrile 10 mL, 130 °C, reaction time 3 h, 0.01 g Cosalen or 0.1 g Cosalen/NaY, 0.85 MPa oxygen pressure.

^aA=cyclohexanol, K=cyclohexanone, CHHP: cyclohexyl hydroperoxide, Acid=mainly adipic acid

^bTON: Mole of cyclohexane oxidized per mole of metal calculated using the AAS value. The metal contents in neat complexes were calculated from the respective formula weight.

as catalyst made the amount of the ester decrease to 20.1% compared with the neat Cosalen, and the selectivity of cyclohexanol and cyclohexanone also increased, while the leaching out of the active site from the carrier was also exhibited for the Cosalen/NaY (IM). The analysis of the reaction mixture by AAS really demonstrated the presence of Co ions. The encapsulated complexes showed the higher catalytic activity than the neat complex. The conversion of cyclohexane was up to 24.4% and the total selectivity of cyclohexanol, cyclohexanone and acid clearly improved in the presence of Cosalen/NaY (FL) as catalysts. Fig. 6 shows the effect of reaction time on the oxidation reaction of cyclohexane using CH₃CN as solvent at 130 °C over Cosalen/NaY-A (FL). It can be seen that cyclohexane conversion steadily increased with increasing reaction time. The conversion of cyclohexane reached 30.1% at 4.5 h and then no obvious enhancement. Moreover, the selectivity of CHHP decreased sharply with the increasing time and only small amount of CHHP can be detected in the reaction mixture after 3 h. In addition, the distributions of cyclohexanol and cyclohexanone are almost equal during the reaction time, while the selectivity of acid increased obviously with increasing time and rose to 49.7% at 4.5 h. This result indicated that the rate of oxidizing cyclohexane was slower than that of oxidizing the cyclohexanol and cyclohexanone when the concentration of cyclohexanol and cyclohexanone increased with the reaction. On the other hand, the catalyst carrier might play an important role for the yield of relatively

large amount of acid. The aluminium rich faujasites have a hydrophilic nature, it is anticipated that polar reactants will be preferentially adsorbed compared to apolar molecules like alkanes. So the obtained cyclohexanol and cyclohexanone were more easily adsorbed in the zeolite than cyclohexane, resulting in further oxidation reactions to acid. The HPLC qualitative analysis indicated that most of the acid was adipic acid, a useful and expensive binary acid. It provided the possibility to oxidize the cyclohexane to adipic acid through one-step reaction using such kind of catalyst.

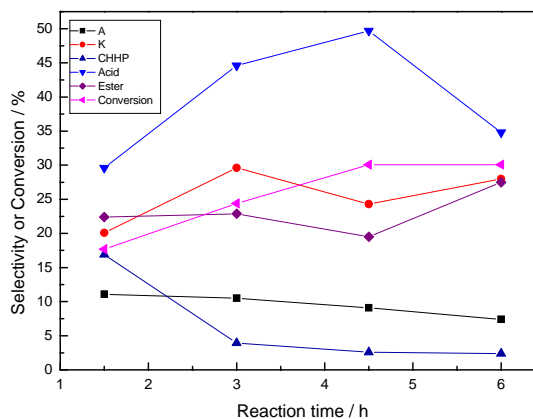


Fig. 6. Reaction time dependence of the conversion and selectivity of the products using Cosalen/NaY-A (FL). Condition: Cyclohexane 0.18 mol, acetonitrile 10 mL, 130 °C, 0.1 g Catalyst, 0.85 MPa oxygen pressure

III. CONCLUSIONS

Cobalt-containing complex of the Schiff base from salicylaldehyde and ethyl diamine has been encapsulated in the intracrystalline voids of NaY zeolite. The complex between the Co exchanged NaY zeolite and salen ligand can be realized in the t-butyl alcohol solution under reflux temperature, which possesses the advantage of low reaction temperature, shortened reaction time and decreased ratio of Co/NaY and salen comparing with the traditional method by reaction of diffusing salen ligand with Co/NaY. In order to further prove the encapsulation, the Cosalen complex incorporated on the surface of the NaY zeolite by impregnation method was also prepared to make a compare. The characterization of FT-IR, UV-Vis, XRD, TG/DTA and SEM indicated that the Cosalen has been encapsulated in the supercage of the NaY zeolite. The cyclohexane oxidation using molecular oxygen was chosen to evaluate the catalytic performance of the immobilized Cosalen. Compared with the neat complex and impregnated complex, the encapsulated Cosalen showed the higher catalytic activity and selectivity for cyclohexanol, cyclohexanone and acid at 130 °C with initial oxygen pressure 0.85 MPa adding CH₃CN as solvent, moreover, the selectivity of acid was obviously higher among the products. The hydrophilic nature of the NaY zeolite carrier might play an important role. It is proposed that improving the ratio of Si/Al of NaY zeolite so that the active site was in the hydrophobic environment may contribute to the selectivity of cyclohexanol and cyclohexanone. Furthermore, it is considered that the Cosalen/NaY (FL) had the potential to produce acid especially adipic acid from cyclohexane by one-step, which is worth of further studies.

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REFERENCES

- Bowers, C. and P.K. Dutta, "Olefin oxidation by zeolite-encapsulated Mn(salen)+ complexes under ambient conditions," *Journal of Catalysis*, **122**, 271-279 (1990).
- Balkus, K.J., A.G. Gabrielov Jr. and S.L. Bell, "Zeolite encapsulate cobalt (II) and copper (III) perfluorophthalocyanines. Synthesis and characterization," *Inorg. Chem.*, **33**, 67-72 (1994).
- Das, S. and T. Punniyamurthy, "Cobalt(II) -catalyzed oxidation of alcohols into carboxylic acids and ketones with hydrogen peroxide," *Tetrahedron Letters*, **44**, 6033-6035 (2003).
- Fan, B.B., W.B. Fan and R.F. Li, "Fe-containing Y as a host for the preparation of a ship-in-a-bottle catalys," *Journal of Molecular Catalysis A: Chemical*, **201**, 137-144 (2003).
- Hu, D.D., Y.L. Cui and X.L. Dong, "Studies on Cosalen immobilized onto N-(4-pyridylmethyl)-chitosan," *Reactive & Functional Polymers*, **48**, 201 (2001).
- Joseph T., C.S. Sajanikumari and S.S. Deshpande, "Oxidation of p-cresol catalyzed by neat and zeolite encapsulated cobalt salen complexes," *Indian Journal of Chemistry*, **38A**, 792 (1999).
- Joseph, T., S.B. Halligudi and C. Satyanarayan, "Oxidation by molecular oxygen using zeolite encapsulated Co(II)saloph complexes," *Journal of Molecular Catalysis A: Chemical*, **168**, 87-97 (2001).
- Joseph T., D.P. Sawant and C.S. Gopinath, "Zeolite encapsulated ruthenium and cobalt schiff base complexes catalyzed allylic oxidation of α -pinene," *Journal of Molecular Catalysis A: Chemical*, **184**, 289-299 (2002).
- Kozlov A., K. Asalura and Y. Iwasawa, "Vanadium(IV) complexes with picolinic acids in NaY zeolite cages synthesis, characterization and catalytic behaviour," *J. Chem. Soc., Faraday Trans*, **94**, 809-816 (1998).
- Ma H.X., D.D. Hu and Y. Fang, "Chitosan coordinated Cosalen and its catalytic activity in oxidation of ethanethiol," *Chinese Journal of Appl. Chem.*, **18**, 290-294 (2001).
- Salama T.M., A.H. Ahmed and Z.M. El-Bahy, "Y-type zeolite encapsulated copper(II) salicylidene-p-aminobenzoic schiff base complex: synthesis, characterization and carbon monoxide adsorption," *Microporous and Mesoporous Materials*, **89**, 251-259 (2006).
- Sharma V.B., S.L. Jain and K. Sain, "Cobalt(II)-schiff base catalyzed aerobic oxidation of secondary alcohols to ketones," *Journal of Molecular Catalysis A: Chemical*, **212**, 55-59 (2004).
- Varkey S.P., C. Ratnasamy and P. Ratnasamy, "Zeolite encapsulate manganese(III)salen complexes," *Journal of Molecular Catalysis A: Chemical*, **135**, 295-306 (1998).
- Zhou L.P., J. Xu and H. Miao, "Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone over Co₃O₄ nanocrystals with molecular oxygen," *Applied Catalysis A: General*, **292**, 223 (2005).

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