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STYRENE OXIDATION BY COPPER(II) COMPLEXES SALEN-TYPE ENCAPSULATED INTO NaY ZEOLITE

KATALITYCZNE UTLENIANIE STYRENU W OBECNOŚCI KOMPLEKSÓW MIEDZI(II) TYPU SALEN OSADZONYCH NA ZEOLICIE NaY

The copper(II) complex with a Schiff-base salen-type ligand has been encapsulated in the nanopores of a NaY zeolite by using two different methodologies, the flexible ligand and in situ complex preparation methods. The encapsulated and non-encapsulated copper(II) complexes were screened as catalysts for styrene oxidation by using TBHP as the oxygen source in acetonitrile solvent. Under the optimized conditions, the catalysts exhibited moderate activity with higher selectivity to benzaldehyde. Both heterogeneous catalysts were found to be reusable after the catalytic cycle, but with some loss of activity.

Keywords: Copper(II) complexes, Schiff base, NaY zeolite

Osadzenie kompleksu miedzi(II) z zasadą Schiffa typu salen na zeolicie typu NaY zostało przeprowadzone za pomocą dwóch metod „flexible ligand” i „in situ”. Katalityczne właściwości otrzymanego kompleksu oraz jego heterogenizowanych analogów badano w reakcji utleniania styrenu w obecności TBHP. Jako rozpuszczalnik stosowano acetonitryl. Testowane katalizatory wykazują średnią aktywność katalityczną z tendencją wytwarzania aldehydu benzoowego. Oba heterogenizowane katalizatory mogą być wykorzystywane ponownie bez utraty aktywności katalitycznych.

1. Introduction

Epoxides are important synthetic intermediates for a large number of bifunctional alcohols that can be prepared conveniently from the corresponding alkenes [1]. In oxidation of styrene benzaldehyde is formed as by product. This is of great interest due to the importance in the manufacture of both bulk and fine chemicals [2].

Various transition metal compounds (Cu, Fe, Co, V and Mn) have been reported as active catalysts for the epoxidation of olefins in homogeneous phase. However, homogeneous catalysts have some disadvantages in that they can decompose during the course of the reaction and are not easily recovered after the reaction for reuse. Many strategies have been adopted to heterogenize homogeneous catalysts to increase catalyst stability and allow for catalyst recycling and product separation.

Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts [3, 4] especially in oxidation reactions [5, 6]. The Schiff base complexes were immobilized on polymeric organic materials [7], then supported on porous solid such as alumina [8], silica [9], clays [10] or encapsulated in the pores of zeolite-Y [11]. There are certain disadvantages with polymeric supports due to their vulnerability to some chemicals and solvents. Immobilisation of metal complexes into the nano-cavity of zeolite is often termed as “zeolite encapsulated metal complexes” (ZEMC).

Encapsulated molecules in zeolite are characterised by isolation from other molecules by zeolite lattice [12], low mobility [13] and steric restriction. Moreover, encapsulation of metal complexes in porous materials typified by zeolites leads to size restriction and severe leaching of catalysts. The advantages of immobilised metal complexes promoted our research groups to investigate the catalytic properties of the complexes entrapped within the nano-cavities of zeolite-Y [14].

2. Experimental

2.1. Materials and reagents

NaY zeolite (CBV100, Si/Al ratio = 2.83) in powder form, was obtained from Zeolyst International. The powder was calcinated at 500°C during 8 h under dry air stream prior to use. All chemicals and solvents used were purchased from Aldrich: copper(II) acetate monohydrate, tetrahydrofuran (THF), acetonitrile, tert-butylhydroperoxide solution - 5.0-6.0 M in decane (TBHP), chlorobenzene (PhCl), styrene (St), Styrene oxide (So), Benzaldehyde (Bza). Trifluoroacetic (TFA) acid was purchased from ACROS.

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2.2. Characterization methods

Powder X-ray diffraction patterns (XRD) were recorded using a Philips Analytical X-ray model PW1710 BASED diffractometer system. The solids samples were exposed to the Cu $K\alpha$ radiation at room temperature in a 2θ range between 5 and 65° . The analyses of XRD were made using X'pert HighScore Plus software (PANalytical B.V) computer software. The latest available ICSD [15], ICDD [16] and IUCr/COD/AMCSD [17], databases were utilized. The GC-FID chromatograms were obtained with a SRI 8610C chromatograph equipped with CP-Sil 8C capillary column. Nitrogen was used as the carrier gas. The identification of reaction products were confirmed by commercial samples and by GC-MS (Varian 4000 Performance).

2.3. Preparation of the catalysts

The synthesis and characterisation of free ligand 1.5-bis((E)-5-chloro-2-hydroxybenzylideneamino)-1H-imidazole-4-carbonitrile ($H_2imida-salen$) and its copper(II) complex were reported elsewhere [18]. Briefly, 2-hydroxy-5-chloro-benzaldehyde and trifluoroacetic acid were added to a suspension of the 1.5-diamino-4-cyanoimidazole in ethanol, under stirring, at room temperature. The yellow solid was filtered and washed.

The synthesis of free complex, $[Cu(imida-salen)]$ was carried out in THF. Cu(II) acetate monohydrate and the Schiff base were solubilised in the same solvent. The solution was refluxed for 2 h and a brown solid was separated by filtration (Fig. 1).

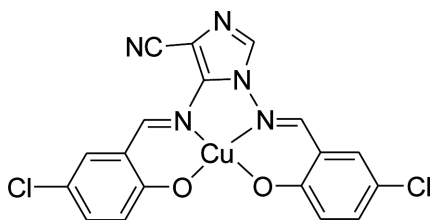


Fig. 1. Molecular structure of the $[Cu(imida-salen)]$ complex

The preparation procedure for the zeolite based catalysts was described elsewhere [18]. Method A: A solution of the $H_2imida-salen$ ligand and copper(II) acetate monohydrate in THF was added to NaY zeolite suspension in the same solvent under constant stirring. The solid fraction was filtered and Soxhlet extracted. The new catalyst is denoted as $CuL'@NaY_A$, where L' is a product of the ligand clivagem namely: salicylideneamine.

Method B: The previously copper-exchanged ($Cu-NaY$) zeolite was suspended in a solution of $H_2imida-salen$ ligand and THF. The new material was filtered, washed and dried. The solid was Soxhlet extracted. The new catalyst denoted as $CuL@NaY_B$, where L is $H_2imida-salen$.

All the compounds and heterogenised catalysts were fully characterised in [18].

2.4. Oxidation of styrene

Oxidation of styrene was studied at room temperature under constant stirring. Briefly, 0.1 g (1.0 mmol) of styrene, 0.1

g (1.0 mmol) of PhCl (internal standard) and 0.10 g of heterogeneous catalyst were mixed in 5.0 mL of acetonitrile, TBHP (0.3 mL, 1.65 mmol, of 5.5 M in decane) was progressively added to the reaction medium at a rate of 0.05 mL min^{-1} . During the experiments, 0.1 mL aliquots were taken from solution with a hypodermic syringe, filtered through $0.2 \mu\text{m}$ syringe filters and directly analyzed by GC. After the reaction cycle, the catalysts were washed, dried and characterised.

3. Results and discussion

Characterisation methods confirmed that $CuL@NaY_B$ the *imida-salen* ligand retains its integrity in zeolite matrix and the resulting complex has the same coordination sphere as the free complex. For $CuL'@NaY_A$, the ligand is cleaved and the encapsulated copper(II) complex is different from the free complex, i.e., the copper(II) is coordinated by two bidentate Schiff base molecules. This was confirmed by different analytical methods such as elemental analysis, EPR and Raman [18]. The stability of the complex with bidentate ligand was confirmed by DFT method.

Results of X-ray diffraction studies on both $CuL@NaY_B$ and $CuL'@NaY_A$ are shown in Fig. 2 and Fig. 3, respectively. One can see in Fig. 2 and Fig. 3 presence of silicon oxide that was used as a reference standard. In this connection it is worth nothing that low quartz (Fig. 2) or α -quartz (Fig. 3) is the specific name of "ordinary" quartz. The "low" refers to the fact that this is the stable silica polymorph at low temperature as opposed to the very similar β -quartz that is stable only beyond $T = 573^\circ\text{C}$. Crystallographic information files used for phase analysis were ICSD – 31228 and ICSD – 39830, respectively.

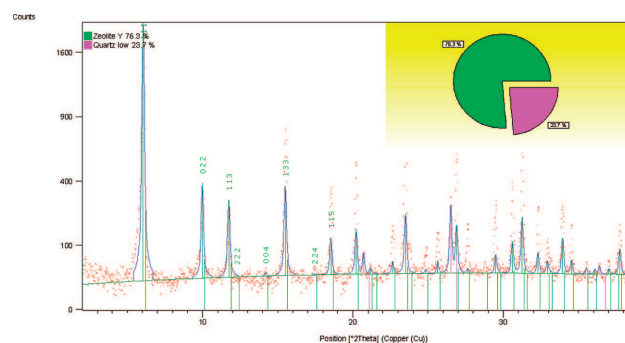


Fig. 2. X-ray diffraction pattern of $CuL@NaY_B$

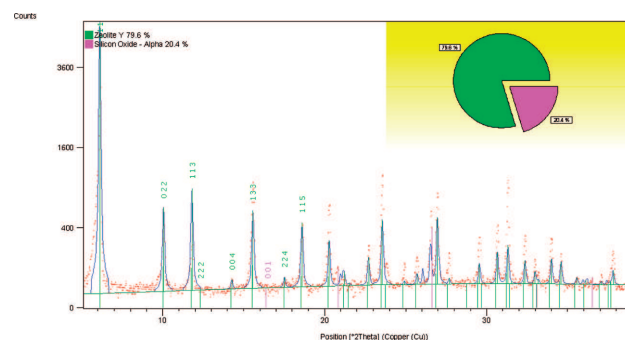


Fig. 3. X-ray diffraction pattern of $CuL'@NaY_A$

Calculations performed for zeolite Y (as a model structure a crystallographic information file published as PDF

00-038-0328 or ICSD code 66409 was utilized) made it possible to ascribe a space group $Fd-3m$ (227) of cubic symmetry to the material under study. It was found that elementary cell parameters were as follows: $a = 24.644(1)$ Å and $a = 24.648(2)$ Å for CuL@NaY_B and CuL@NaY_A respectively.

However, results of XRD measurements suggested different copper localisation in both materials. As evidence of different copper localization one can take the intensity ratio of the 022 and 133 diffraction peaks. In case of CuL@NaY_B relative intensity of 022 diffraction line was $I_{022}/I_{111} = 18.26\%$ and relative intensity of 133 diffraction line was $I_{133}/I_{111} = 13.42\%$. In case of CuL@NaY_A relative intensity of 022 diffraction line was $I_{022}/I_{111} = 12.01\%$ and relative intensity of 133 diffraction line was $I_{133}/I_{111} = 17.03\%$. It is worth noting that for not modified zeolite Y (ICSD code 73929) the $I_{022}/I_{111} = 11.48\%$ and $I_{133}/I_{111} = 10.08\%$. Thus, in case of CuL@NaY_A material 'inverse' relation of relative intensities of diffraction peaks took place.

According to our simulations performed for zeolite Y (crystallographic information file ICSD code 73929) with PowderCell [19] computer program the 'inversed' relation of relative intensities of 022 and 113 X-ray diffraction lines takes place when second position of Na^+ ion characterized with Wyckoff symbol 32e and fractal positions $x = 0.05450(30)$; $y = 0.05450(30)$; $z = 0.05450(30)$ (ICSD code 73929) is occupied with Cu^{2+} ion. Therefore, it is reasonable to conclude that for CuL@NaY_B material a part of this copper could be located in framework sites that are inaccessible for the ligand [18, 20].

These heterogeneous catalysts were studied in oxidation of alcohols with moderate conversion towards oxidation of phenol and cyclohexanol [18]. To explore the applicability of Schiff base based heterogeneous catalysts they were examined in the oxidation of styrene, (Table 1). In order to establish the role of complex, blank experiments in the presence of parent zeolite and in the absence of catalyst under the same experimental conditions were also investigated. The results obtained showed that the TBHP has no ability to oxidize the styrene without catalyst. The catalytic activity of parent zeolite was also very low (Table 1).

Oxidation of the styrene catalysed by neat and heterogenised complexes, under experimental conditions, yields styrene oxide and benzaldehyde. No other products such as: 1-phenylethane-1,2-diol, benzoic acid and phenyl acetaldehyde were detected. These are common products and have been identified by others [21]. Styrene oxide, is the minor product and it is in accordance with previous publications [21, 22, 23]. For better comparison, in this study the amount of complex used in homogeneous test corresponds Cu(II) loading in heterogenised catalysts. Under the experimental conditions used, the product distribution is the same as in the homogeneous oxidation of styrene with benzaldehyde as the major oxidation product, followed by styrene oxide. Both heterogeneous catalysts have similar epoxide styrene yield and selectivity, although lower than that observed for the homogeneous reaction. At the end of the catalytic cycle, the materials were easily separated from the reaction medium. No further styrene conversion occurred upon removal of the heterogeneous catalyst from the reaction medium, subsequent to 24 h of reaction. This indicates that styrene oxidation is catalysed essentially by

the encapsulated metal complexes, and that almost no leaching of the active species occurred during the catalytic cycle.

TABLE 1
Catalytic results for the oxidation of styrene catalyzed by the encapsulated and free copper(II) complexes

Catalyst	T^a	%C ^{b,c}	Selectivity ^{b,d}		$\eta^{b,e}$	
			So	Bza	So	Bza
NaY	48	<3	ND	100	ND	<3
[Cu(imida-salen)] ^f	24	40	41	59	16	24
CuL@NaY _A ^g	24	35	28	72	10	25
CuL@NaY _B ^h	48	36	34	66	12	24

a) Reaction time at which the substrate conversion starts to become constant; b) Determined by GC against internal standard; c) Styrene conversion (%C) calculated as: $\%C = \frac{[A_{(St)} / A_{(PhCl)}]_{t=0h} \times [A_{(St)} / A_{(PhCl)}]_{t=xh}}{100 \times [A_{(St)} / A_{(PhCl)}]_{t=0h}}$; d) Product selectivity (%S) calculated as: $\%S = \frac{A_{(product)}}{A_{(product)} + A_{(other\ reaction\ products)}} \times 100$, where A stands for chromatographic peak area; e) Product yield (% η) calculated as $\% \eta = \%C \times \%S / 100$; f) Cu loading = 9.4×10^{-4} mmol, g) Cu loading = 1.0×10^{-3} mmol/g, h) Cu loading = 2.0×10^{-3} mmol/g.

Indirect comparison of recently reported solid copper-based catalysts with the catalysts presented here for their activities in the oxidation of styrene in the presence of tBuOOH shows that the catalysts used in this study show lower activity than copper Schiff base complexes supported on MCM-41 or MCM-48 [24, 25, 26]. On the other hand the heterogeneous catalysts prepared show similar activity to supported copper porphyrin complex on MCM-41 [27].

The recyclability of the heterogeneous catalysts was also evaluated. After the catalyst was used, it was recovered by filtration, washed several times with EtOH and ACN, and subsequently dried at 100°C then reused. The catalysts were used two times without significant change in their catalytic activity.

4. Conclusion

Two heterogeneous catalysts based on copper(II) complexes with the 1,5-bis((E)-5-chloro-2-hydroxybenzylideneamino)-1H-imidazole-4-carbonitrile (H_2 imida-salen) ligand were tested as catalysts for styrene oxidation. All heterogeneous catalysts show moderate conversion towards oxidation of styrene under optimized reaction conditions. Significant selectivity towards benzaldehyde formation (>60%) was observed for all catalysts. No copper leaching was observed during reaction cycle.

REFERENCES

- [1] J. Huang, T. Akita, J. Faye, T. Fujitani, T. Takei, M. Haruta, *Angew. Chem. Int. Ed.* **48**, 7862 (2009).
- [2] Y. Yang, S. Hao, P. Qiu, F. Shang, W. Ding, Q. Kan, *Reac. Kinet. Mech. Cat.* **100**, 363 (2010).
- [3] P.G. Cozzi, *Chem. Soc. Rev.* **33**, 410 (2004).

- [4] C. Baleizão, H. Garcia, *Chem. Rev.* **106**, 3987 (2006).
- [5] T. Katsuki, *Coord. Chem. Rev.* **140**, 189 (1995).
- [6] M. Islam, P. Mondal, S. Mukherjee, M. Mobarak, A. Sigha Roy, S. Mondal, S. Sarkar, *J. Chem. Technol. Biotechnol.* **85**, 460 (2010).
- [7] K.C. Gupta, A. Kumar Sutara, C.-C. Lin, *Coord. Chem. Rev.* **253**, 1926 (2009).
- [8] M. Salavati-Niasari, A. Amiri, *Appl. Catal. A: Gen.* **290**, 46 (2005).
- [9] E.M. Serwicka, J. Połtowicz, K. Bahranowski, Z. Olejniczak, W. Jones, *Appl. Catal. A: Gen* **275**, 9 (2004).
- [10] (a) I. Kuźniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, *J. Mol. Catal. A: Chem.* **278**, 82 (2007); (b) I. Kuźniarska-Biernacka, C. Pereira, A.P. Carvalho, J. Pires, C. Freire, *J. Braz. Chem. Soc.* **20**, 1320 (2009); (c) I. Kuźniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, *Cat. Lett.* **134**, 63 (2010); (d) I. Kuźniarska-Biernacka, C. Pereira, A.P. Carvalho, J. Pires, C. Freire, *Appl. Clay Sci.* **53**, 195 (2011).
- [11] (a) I. Kuźniarska-Biernacka, O. Rodrigues, M.A. Carvalho, I.C. Neves, A.M. Fonseca, *Appl. Organomet. Chem.* **26**, 44 (2012); (b) I. Kuźniarska-Biernacka, A.M. Fonseca, I.C. Neves, *Inorg. Chim. Acta.* **394**, 591 (2013). (c) I. Kuźniarska-Biernacka, O. Rodrigues, M.A. Carvalho, P. Parpot, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves, *Eur. J. Inorg. Chem.* 2768 (2013); (d) I. Kuźniarska-Biernacka, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves, *J. Catal.* **278**, 102 (2011).
- [12] W. Turbevill, D.S. Robins, P.K. Dutta, *J. Phys. Chem.* **96**, 5024 (1992).
- [13] W.H. Quayle, J.H. Lunsford, *Inorg. Chem.* **2**, 97 (1982).
- [14] (a) I. Kuźniarska-Biernacka, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves, *J. Catal.* **278**, 102 (2011); (b) I. Kuźniarska-Biernacka, O. Rodrigues, M.A. Carvalho, I.C. Neves, A.M. Fonseca, *Appl. Organomet. Chem.* **26**, 44 (2012); (c) I. Kuźniarska-Biernacka, A.M. Fonseca, I.C. Neves, *Inorg. Chim. Acta.* **394**, 591 (2013); (d) B. Silva, H. Figueiredo, V.P. Santos, M.F.R. Pereira, J.L. Figueiredo, A.E. Lewandowska, M.A. Banares, I.C. Neves, T. Tavares, J. Hazar, *Mater.* **192**, 545 (2011); (e) H. Figueiredo, M.M.M. Raposo, A.M. Fonseca, I.C. Neves, C. Quintelas, T. Tavares, *Stud. Surf. Sci. Catal.* **158**, 1073 (2005).
- [15] ICSD Database, FIZ Karlsruhe, (URL: <http://www.fiz-karlsruhe.de>).
- [16] International Centre for Diffraction Data, 12 Campus Boulevard, Newton Square, PA 19073-3273 U.S.A.; (URL: <http://www.icdd.com>).
- [17] IUCr/COD/AMCSD Database (URL: <http://www.crystalimpact.com/matcg>).
- [18] I. Kuźniarska-Biernacka, M.A. Carvalho, S.B. Rasmussen, M.A. Bañares, K. Biernacki, A.L. Magalhães, A. Rolo, A.M. Fonseca, I.C. Neves, *Eur. J. Inorg. Chem.* 5408 (2013).
- [19] W. Kraus, G. Nolze, Powder cell - a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns, *J. Appl. Crystallogr.* **29**, 301 (1996).
- [20] H. Figueiredo, B. Silva, M.M.M. Raposo, A.M. Fonseca, I.C. Neves, C. Quintelas, T. Tavares, *Microporous Mesoporous Mater.* **109**, 163 (2008).
- [21] M.R. Maurya, A.K. Chandrakar, S. Chand, *J. Mol. Catal. A: Chem.* **270**, 225 (2007).
- [22] Y. Yang, S. Hao, P. Qiu, F. Shang, W. Ding, Q. Kan, *Reac. Kinet. Mech. Cat.* **100**, 363 (2010).
- [23] S.M. Islam, A.S. Roy, P. Mondal, S. Paul, N. Salam, *Inorg. Chem. Commun.* **24**, 170 (2012).
- [24] S. Jana, B. Dutta, R. Bera, S. Koner, *Langmuir* **23**, 2492 (2007).
- [25] P. Roy, K. Dhara, M. Manassero, P. Banerjee, *Inorg. Chem. Comm.* **11**, 265 (2008).
- [26] A. Sakhivel, W. Sun, G. Raudaschl-Sieber, A.S.T. Chiang, M. Hanzlik, F.E. Kühn, *Catal. Comm.* **7**, 302 (2006).
- [27] P. Karandikar, M. Agashe, K. Vijayamohan, A.J. Chandwarkar, *Appl. Catal. A* **257**, 133 (2004).

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