Zeolite-encapsulated Co(Ⅱ), Mn(Ⅱ), Cu(Ⅱ) and Cr(Ⅲ) salen complexes as catalysts for efficient selective oxidation of benzyl alcohol

F H Li[1], H Bi[1], D X Huang[1], M zhang[2] and Y B Song[1, 3]

[1] College of Science, Shantou University, Shantou, Guangdong, 515063, China
[2] Entry-exit inspection and quarantine bureau, Shantou, Guangdong, 515041, China

[3] E-mail: ybsong@stu.edu.cn

Abstract. Co(Ⅱ), Mn(Ⅱ), Cu(Ⅱ) and Cr(Ⅲ) salen type complexes were synthesized in situ in Y zeolite by the reaction of ion-exchanged metal ions with the flexible ligand molecules that had diffused into the cavities. Data of characterization indicates the formation of metal salen complexes in the pores without affecting the zeolite framework structure, the absence of any extraneous species and the geometry of encapsulated complexes. The catalytic activity results show that CosalcyenY exhibited higher catalytic activity in the water phase selective oxidation of benzyl alcohol, which could be attributed to their geometry and the steric environment of the metal actives sites.

1. Introduction

Transition metal complex-catalyzed oxidation of organic compounds has been extensively investigated in the past decades [1-5]. Metal salen complexes have been reported as efficient catalysts for the epoxidation of various olefins, for their well-established ability to bind oxygen [6]. However, metal alkoxides are sensitive to hydrolysis and the presence of adventitious water can result in the formation of dimmer species. The dimmer species formation caused deactivation of the catalysts and as a consequence the re-used catalysts leads to lower substrate conversion [7-9]. Thus, heterogenization of metal salen-type catalysts, which can avoid the formation of dimerization species, has attracted many researcher attentions [10-12].
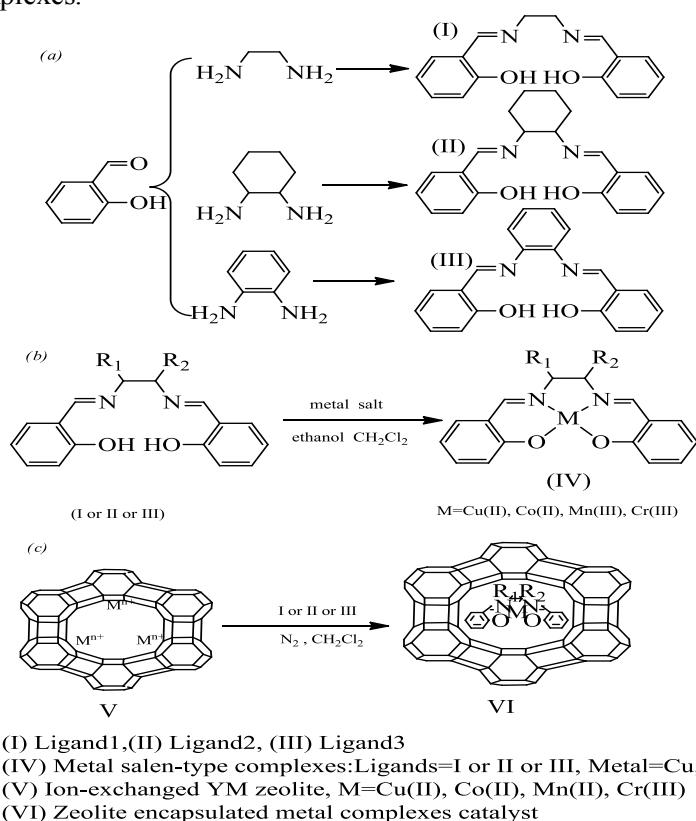
Heterogenization of homogenous catalysts has been an interesting area of research in the academic and industrial, which display potential for practical application. As this method can provide an ideal way for taking the advantages of homogenous catalysts and simultaneously avoid its disadvantages like handling and reusability. Encapsulation in porous solids such as zeolite is an attractive technique for heterogenization, since no leaching is observed when the complex is confined exclusively in the zeolite pores [13-14]. In addition, zeolite-encapsulated complexes promise better control of selectivity of the reaction and higher stability, due to NaY cavity encapsulated metal complexes, avoids direct contact with the metal complexes, reduced dimerization of complexes in the cavity. [15-19]. This nature for the homogeneous catalyst multiphase provides a good thinking and benzyl alcohol oxidation reaction received extensive attention of the academia in recent years. In this work, synthesis, characterization and catalytic activities of zeolite-encapsulated Co(Ⅱ), Mn(Ⅱ), Cu(Ⅱ) and Cr(Ⅲ) salen complexes catalysts for selective oxidation of benzyl alcohol to benzaldehyde were systematically investigated.

2. Experimental

2.1. Materials

$Mn(CH_3COO)_2$, $Co(CH_3COO)_2$, $CrCl_3 \cdot 6H_2O$, $Cu(CH_3COO)_2$, ethanol, hydrogen peroxide and benzyl alcohol were from Sinopharm Chemical Reagent Co, Ltd, while ethylenediamine, O-phenylenediamine,1,2-Diaminocyclohexane and salicylic aldehyde were from Aladdin Reagent Co., Ltd. All these chemicals and reagentsused in present work were of analytical grade and used as received without further purication.The sodium form of Y zeolite (NaY) obtained from Nankai University Catalyst Co, Ltdwas dried at 723 K for 4 h prior to being used as the host material for encapsulating complexes.

(I) Ligand1,(II) Ligand2, (III) Ligand3
(IV) Metal salen-type complexes:Ligands=I or II or III, Metal=Cu, Co, Mn, Cr
(V) Ion-exchanged YM zeolite, M=Cu(II), Co(II), Mn(II), Cr(III)
(VI) Zeolite encapsulated metal complexes catalyst

Figure 1. Preparation of zeolite encapsulated metal salen complexes.

2.2. Preparation of zeolite encapsulated metal salen catalysts

2.2.1. Synthesis of Salen ligands. The ligands were synthesized as following steps [20]. The 10 mmol salicylaldehyde and 20 mmol ethylenediamine (or O-phenylenediamine, 1,2-Diaminocyclohexane) were dissolved in 20 ml ethanol solution, respectively. Under nitrogen atmosphere, the ethanol solution of corresponding diamine was dropwise to the ethanol solution of salicylaldehyde. The resultant mixture was refluxed for 2.5 h at 333 K and then was concentrated to filtration in ethanol solution and dried in vacuum. The resultant corresponding ligand crystals were collected, marked as Ligand 1, Ligand 2 and Ligand 3, respectively, described in figure 1 (a).

2.2.2. Synthesis of metal Salen complexes. The salen ligand compound in dichloromethane solution was heated to reflux under nitrogen atmosphere at 333 K for insertion of metal center, as indicated in figure 1 (b). A solution of Co(II), Mn(II), Cu(II) metal salt were dissolved in 20 ml ethanol solution, respectively. The mixture was added to the ligand dichloromethane solution to reflux for 2 h. The

mixture was concentrated to wash with ethanol to remove the side product and dryness in vacuum, than the corresponding metal-salen complexes were obtained.

2.2.3. Encapsulation of metal salen complexes in Y zeolite. NaY zeolite was ion-exchanged with 0.07 M metal salts solution at 368 K for 24 h and then washed and dehydrated at 673 K for 4 h to obtain CoY, CuY, MnY and CrY zeolites. The anhydrous metal exchanged zeolite was mixed an excess of salen type ligand dissolved in 60 ml CH_2Cl_2 solution, as indicated in figure 1 (c). These solids were heated in sealed glass ampoules for a period of 12 h at 313 K. The resultant mass was soxhlet-extraction with CH_2Cl_2 to remove surface complexes and the free ligand. The extracting in each case was continued for 24 h after the extracting solvent became color less. The purified sample was ion-exchanged with 0.1 M NaCl for 24 h to remove uncoordinated metal ions from the lattice. The zeolite encapsulation complex thus obtained was filtered, washed free of chloride ions and then dried in vacuum.

2.3. Catalytic reaction

The benzyl alcohol oxidation reactions were carried out in a stirred reactor. The vessel was charged with benzyl alcohol (10 mmol), 0.55 mol/L Na_2CO_3 water aqueous solution (30 ml) and catalyst (100 mg). The stirrer was set at 1000 r.p.m and 353K. A certain amount of hydrogen peroxide was dropwise slowly to the reactor, samples from the reactor were taken periodically. The products and the unconverted reactants were analyzed by gas chromatography with a flame ionization detector, using a HP-5 column and decane as the internal standard.

2.4. Characterization

The synthesized materials were characterized by using XRD, FT-IR, DRS UV-vis. XRD experiments were performed using a Bruker-D8 type powder X-ray diffractometer (XRD) operating with Cu Kα radiation (λ=0.154056 nm, 40 kV). The spectra patterns were recorded on a Lambda 950 UV-vis spectrophotometer and a MAGNA-IR 750 Fourier transform infrared spectrometer.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. FI-IR. The FT-IR spectra figure 2 (a) shows the C=N characteristic peaks of Schiff base in the range of 1600-1640 cm^{-1}, 1612 cm^{-1} associated with stretching vibrations of C=N appears. Peaks at 1462 and 1443 cm^{-1} could be ascribed to extension vibration of C=C in benzene, while peak at 1381 cm^{-1} was ascribed to flexural vibration of C-H. All these ligands and metal-salophen complexes exhibit the strong peaks at 1612, 1583, 1525, 1462, 1443 and 1382 cm^{-1} corresponding with reported literature [21]. Peaks at 1323, 1186 and 1151 cm^{-1} were ascribed to the C-O bond, and peak at 750.2 cm^{-1} corresponded with benzene plane deformation absorption. Peaks at 3000 and 2900 cm^{-1} were assigned to extension vibration of C-H and C-H stretching vibration of CH = N respectively [22]. The weak peaks exhibited at 470-500 cm^{-1} and 541 cm^{-1} were assigned to the extension vibration of metal-N (metal include Mn, Cu and Co) and metal-O respectively. The FT-IR spectra of Co(Salen) and CoSalenY in 1600-1200 cm^{-1} range are presented in figure 2 (b). Compared with the spectra of Co(salen), the CoSalenY catalyst exhibit the weak peaks at corresponding peaks. The Co(Salen) were successfully encapsulated in zeolite Y in accordance with the reports [23].
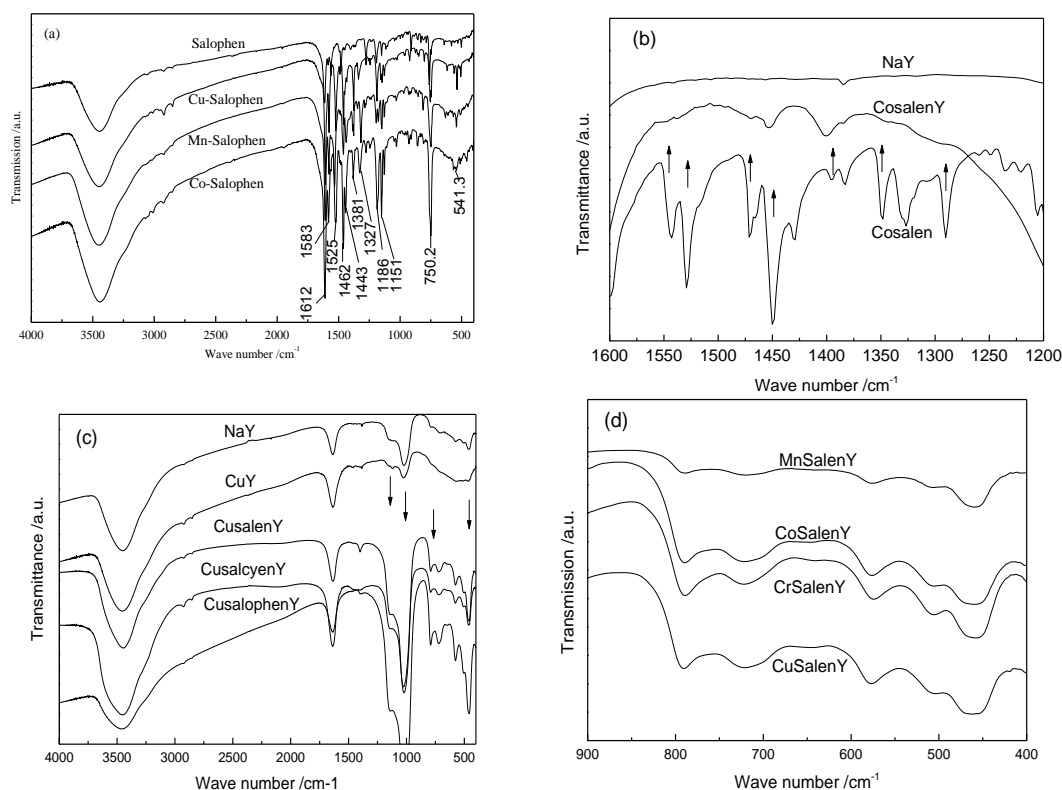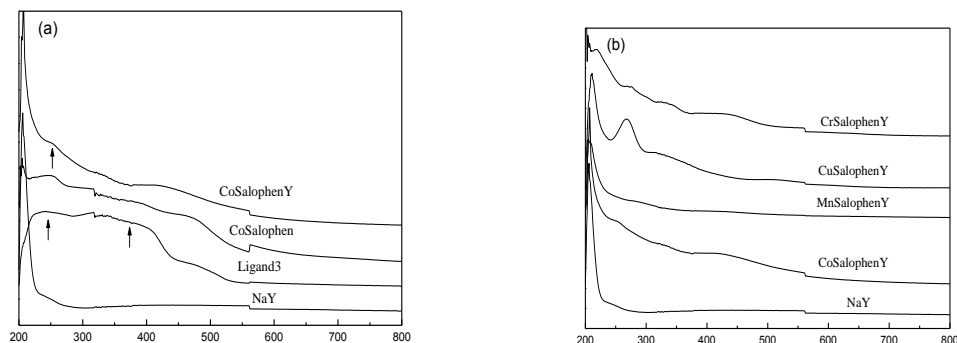
Figure 2. FT-IR spectra of: (a) ligand 3 complexes with different transition. (b) Co(Salen) and CoSalenY; (c) different salen ligand encapsulated in zeolite; (d) different metal complexes encapsulated in zeolite.

The IR spectra of different salen ligand and different metal complexes encapsulated in zeolite exhibit in figure 2 (c) and (d). The sample zeolite encapsulated Cu complexes catalysts exhibit weak peaks in the range of 1650-1520 cm^{-1} corresponding to C=N extension vibrations. The broad bands at the region 1650 and 3400 cm^{-1} are due to lattice water molecules and surface hydroxylic groups. No shift of zeolite lattice bands is observed in the spectra of encapsulated complexes, which implies that the zeolite framework has remained unchanged upon the encapsulated of complexes. The encapsulated metal complexes in the cage could be identified from the bands observed in the region 1200-400cm^{-1} where several peaks at has been observed in 1200, 1000 cm^{-1}, 800-790, 735-715, 580-570, 520, 470-450cm^{-1} as shown in figure 2 (c) and (d). These two results clearly indicate that NaY zeolite structure still remains intact, also further illustrate NaY is suitable for packaging this metal complexes.

3.1.2. DRS UV-vis. The DRS UV-vis electronic spectra are presented in figure 3 (a) and (b). The encapsulated complexes exhibit adsorption bands at 200～310 nm attributable to ligand transition. This indicates the existence of salophen complex in the supercage. The DRS UV-vis spectra of the free and encapsulated Co complexes show intense ligand-metal charge transfer adsorption in the range of 310～420 nm. All the samples exhibit a broad d-d electron transition adsorption at 550～600 nm.

The UV-vis spectra of Co-salophen exhibits a strong peak at ~250 nm, while MnSalophen exhibits a strong peak at ~265 nm and a broad peak at ~420 nm ascribed to the ligand to metal charge transfer transition bonds as shown in figure 3 (b), akin to related metal salen complexes described in the literature. The peaks or broad peak of Co(Ⅱ), Mn(Ⅱ), Cu(Ⅱ) and Cr(Ⅲ)- salen-type complexes in zeolite Y are observed in the region 250～530 nm, while zeolite has no observed. The FT-IR and DRS

UV-vis spectra results manifest the well synthesis of corresponding salen ligand, metal salen complexes and Metal(Salen)Y catalysts.

Figure 3. DRS UV-vis spectra of: (a) Ligand 3, CoSalophen and CosalophenY catalyst, (b) Co(Ⅱ), Mn(Ⅱ), Cu(Ⅱ) and Cr(Ⅲ) salophen complexes catalysts.

3.1.3. XRD. XRD patterns in figure 4 showed that diffraction peak strength corresponding to NaY and Co(Salen)Y in figure 4 (a), in which no change between NaY and Co(salen)Y was observed indicating that NaY zeolite structure did not change. Cu(Salen)Y, Mn(Salen)Y and Cr(Salen)Y in figure 4 (b), (c) and (d) have similar diffraction peaks and peak strength. While the change of difraction peak strength corresponding to Co(salen)Y ($I_{311}>I_{220}$) suggested that some trace of Na$^+$ ions were replace by Co(salen). XRD measurements showed that the encapsulation of Co(salen) in NaY had no obvious inflence on the structure of the zeolitic matrix.
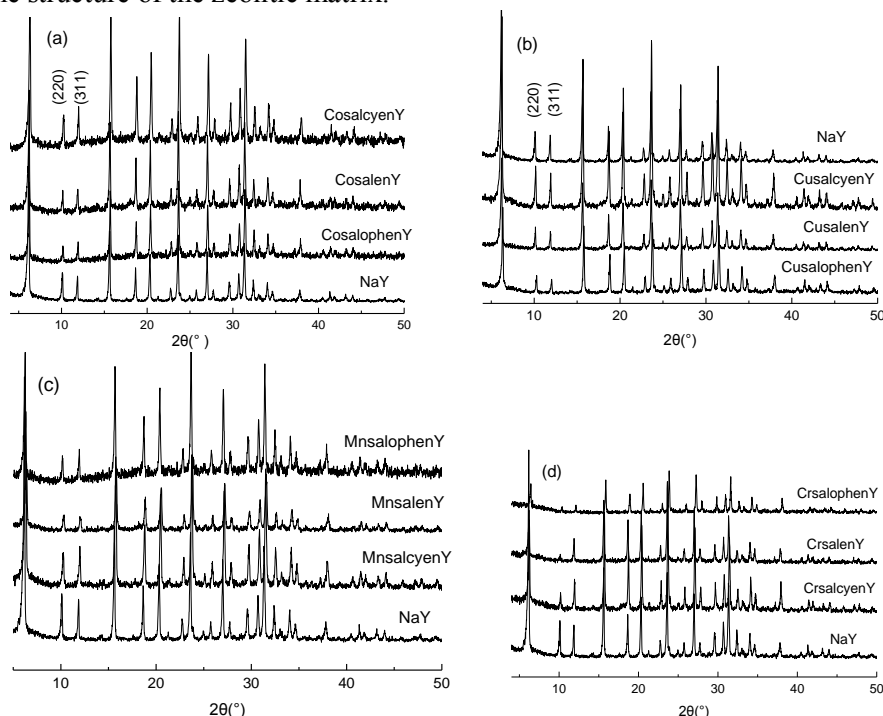
Figure 4. XRD patterns of zeolite encapsulated metal salen type complexes catalysts and NaY. (a) Co(salen) , (b) Cu(salen), (c) Mn(salen), (d) Cr(salen).

3.2. Catalytic activity on oxidation of benzyl alcohol

The oxidation of alcohol is an important reaction in organic chemistry for both laboratory and industrial manufacturing, in particular with the synthesis of aldehydes, which are valuable intermediates in the perfume industry. Here, we discussed the catalytic activity of zeolite encapsulated metal salen-type complex for the selective oxidation of benzyl alcohol to benzaldehyde. The catalytic activity experiments were performed in water phase using 30 ml Na_2CO_3 aqueous as solvents, and H_2O_2 acted as oxidants under 353 K. The catalytic activity of metal complexes and zeolite encapsulation complex was shown in table 1. All of these materials show high selectivity towards benzaldehyde at our selected reaction conditions. The CuSalcyenY shows highest conversion among all encapsulated complexes catalysts, due to the surrounding high electron cloud density of Cu metal atom and the interaction between metal atom and Schiff base ligand, which attribute to the activity of substrate.

Table 1. Encapsulated catalytic in water phase reaction of the conversion and selectivity.

Entry	Catalysts	Conversion (%)	Selectivity(%)	
			Benzaldehyde	Benzoic acid
1	NaY	0	0	0
2	Cusalophen	31.21	100	0
3	Cosalophen	18.76	100	0
4	Mnsalophen	17.15	100	0
5	Crsalcyen	10.22	100	0
6	CusalcyenY	38.14	100	0
7	CusalophenY	37.56	100	0
8	CusalenY	14.89	100	0
9	CosalophenY	15.02	100	0
10	CosalenY	8.84	100	0
11	CosalcyenY	6.62	100	0
12	MnsalophenY	3.21	100	0
13	MnsalenY	0.47	100	0
14	MnsalcyenY	0	0	0
15	CrsalenY	3.83	100	0
16	CrsalophenY	3.23	100	0
17	CrsalcyenY	0	0	0

[a]Reaction condition: 353 K, 10 mmol benzyl alcohol, 30 ml Na_2CO_3 aqueous, 100 mg catalysts, added 10 ml H_2O_2 slowly with stirred at 1000 r.p.m.
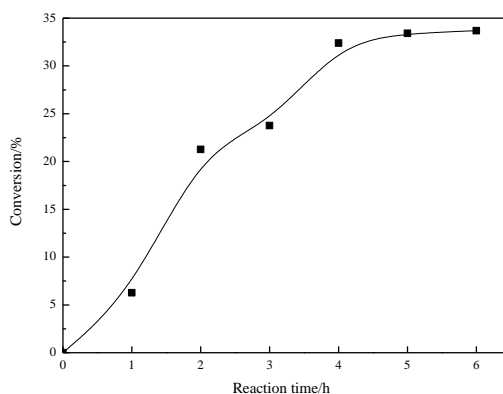
Figure 5. Influence of reaction time on substrate conversion.
[a]Reaction condition: 353 K, 10 mmol benzyl alcohol, 30 ml Na_2CO_3 aqueous, 100 mg catalysts, added 10 ml H_2O_2 slowly with stirred at 1000 r.p.m.

Influence of reaction time was investigated in figure 5. The conversion of benzyl alcohol increase as the reaction time increase in range 1～6 h. Hydrogen peroxide is the preferred oxygen donor in zeolite systems, since they are highly mobile in the pores due to their smaller size. Furthermore, they are cheaper and sufficiently environment-friendly to be used on a commercial scale. The catalytic nature of encapsulated complex catalyst was confirmed by running the reactions in the absence of any catalyst. Hydrogen peroxide alone is unable to oxidize the substrates to a significant extent, indicating that the reactions can perform only when a catalyst promotes them. However, the decomposition of hydrogen peroxide has efficient influence on oxidation of benzyl alcohol.

Table 2. The catalyst of lifetime.

Entry	CoSalenY	CoSalophenY	CoSalcyenY
First run	54.34	32.87	42.32
Second run	47.82	32.67	41.57
Third run	40.65	32.45	41.19
Forth run	22.85	32.22	34.84
Fifth run	19.95	32.14	13.92

[a]Reaction condition: 353 K, 10 mmol benzyl alcohol, 30 ml Na_2CO_3 aqueous, 100 mg catalysts, added 10 ml H_2O_2 slowly in 6 h with stirred at 1000 r.p.m.

In addition, a further study on the catalytic reusability of CoSalenY, CoSalcyenY and CoSalophenY was carried out. After the first catalytic run, the heterogenized catalyst was separated from the reaction solution, washed several times to remove any Physical adsorption of molecular, dried and reused in another four catalytic run in table 2. The CoSalenY and CoSalcyenY begin to loss catalytic activity after three catalytic run, while the CoSalophenY has no much change in the catalytic performance after five catalytic run. This indicated that the zeolite encapsulated metal complex catalysts with high catalytic activity and stability for the selective oxidation benzyl alcohol was developed.

4. Conclusions

Co(Ⅱ), Mn(Ⅱ), Cu(Ⅱ) and Cr(Ⅲ) salen type complexes were synthesized in situ in Y zeolite, and the characterization and catalytic activity on the selective oxidation of benzyl alcohol were systematically surveyed. It has been found that the formation of metal salen complexes in the pores without affecting the zeolite framework structure, the absence of any extraneous species and the geometry of encapsulated complexes. The catalytic activity results show that CoSalcyenY exhibited higher catalytic activity in the water phase selective oxidation of benzyl alcohol. The catalytic behavior could be mainly attributed to the geometry of encapsulated complexes and steric environment of the metal actives sites. To summarize, zeolite encapsulated complexes have interesting catalytic potential particularly with respect to the activity for selective oxidation and stability, and offer further scope to design efficient and environment-friendly catalyst systems.

Acknowledgements

References

[1]   Habibi D and Faraji A R 2013 *Comptes Rendus Chimie.* **16** 888-896
[2]   Noshiranzadeh N, Emami M, Bikas R, et al. 2014 *Polyhedron* **72**: 56-65
[3]   Narita M, Yoon I, Aoyagi M, Goto M, Shimizu T and Asakawa M 2007 *Eur J. Inorg. Chem.* **26** 4229-37

[4]   Zhang X A, Zhou H Q, Su X, Chen X G, Yang C L, Qin J G and Inokuchi M 2007 *J. Alloy Compd.* **432** 247-252

[5]   Chen Y, Liu Y, Zhang X, et al. 2015 *Inorg. Chem. Commun.* **53** 1-3

[6]   Nandi M, Roy P, Uyama H and Bhaumik A 2011 *Dalton Trans.* **40** 12510-518

[7]   Xu Y, Lin L, Kanai M, Matsunaga S and Shibasaki M 2011 *J. Am. Chem. Soc.* **133** 5791-93

[8]   Palopoli C, Bruzzo N, Hureau C, Ladeira S, Murgida D and Signorella S 2011 *Inorg. Chem.* **50** 8973-83

[9]   Zhang Z, Li X, Wang C, Zhang C, Liu P, Fang T, Xiong Y and Xu W 2012 *Dalton Trans.* **41** 1252-58

[10]   Bhunia S, Saha D and Koner S 2011 *Langmuir* **27**: 15322-329

[11]   Purse B W, Tran L H, Piera J, Akermark B and Backvall J E 2008 *Chemistry* **14** 7500-03

[12]   Jain S, Reiser O 2008 *ChemSuChem.* **1** 534-541

[13]   Kowalak, Stanislaw, Ralph C Weiss, and Kenneth J Balkus 1991 *Chem. Commun.* **1** 57-58

[14]   Joseph T, Halligudi S, Satyanarayan C, Sawant D P and Gopinathan S 2001 *J. Mol. Catal. A: Chem.* **168** 87-97

[15]   Johansson M, Purse B W, Terasaki O and Bäckvall J E 2008 *Adv. Synth. Catal.* **350** 1807-15

[16]   Jin C, Fan W, Jia Y, Fan B, Ma J and R L 2006 *J. Mol. Catal. A: Chem.* **249** 23-30

[17]   Xavier K 2004 *Appl. Catal. A: Gen.* **258** 251-259

[18]   Dominguez I, Fornes V and Sabater M 2004 *J. Catal.* **228** 92-99

[19]   Zhan B Z, White M A, Sham T K, Pincock J A, Doucet R J, Rao K R, Robertson K N and Cameron T S 2003 *J. Am. Chem. Soc.* **125** 2195-99

[20]   Huang D X, Song Y B , Fang Y W and Sun C Y 2014 *Adv. Mater. Res.* **881** 292-296

[21]   Johansson M, Purse B W, Terasaki O, et al. 2008 *Adv. Synth. Cataly.* **350** 1807-15

[22]   Ou X, Jiang L, Chen P, et al. 2013 *Adv. Funct. Mater.* **23** 2422-35

[23]   Zhang N and Zhou X F 2012 *J. Mol. Catal. A: Chem.* **365** 66-72