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# Iron(III), cobalt(II) and copper(II) complexes bearing 8-quinolinol encapsulated in zeolite-Y for the aerobic oxidation of styrene

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A series of Fe(III), Co(II) and Cu(II) complexes of 8-quinolinol were encapsulated into the supercages of zeolite-Y and characterized by X-ray diffraction, SEM,  $N_2$  adsorption/desorption, FT-IR, UV-vis spectroscopy, elemental analysis, ICP-AES and TG/DSC measurements. The encapsulation was achieved by a flexible ligand method in which the transition metal cations were first ion-exchanged into zeolite Y and then complexed with 8-quinolinol ligand. The metal-exchanged zeolites, metal complexes encapsulated in zeolite-Y plus non-encapsulated homogeneous counterparts were all screened as catalysts for the aerobic oxidation of styrene under mild conditions. It was found that the encapsulated complexes always showed better activity than their respective non-encapsulated counterparts. Moreover, the encapsulated iron complex showed good recoverability without significant loss of activity and selectivity within successive runs. Heterogeneity test for this catalyst confirmed its high stability against leaching of active complex species into solution. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: zeolite-Y; encapsulation; transition metal complexes; 8-quinolinol; oxidation of styrene

#### Introduction

The oxidation of styrene is of great interest because styrene oxide and benzaldehyde are important and versatile synthetic intermediates in chemical industry.<sup>[1,2]</sup> Currently, a wide range of homogeneous metal complexes for styrene oxidation exist, but most of them suffer from severe deactivation due to easy formation of dimeric peroxo- and  $\mu$ -oxo species. Therefore, much attention has been devoted to the heterogenization of the homogeneous catalysts onto solid supports to increase catalyst stability and allow for catalyst recycling and product separation.<sup>[3-8]</sup> Generally, the homogeneous catalysts are heterogenized either through covalent attachment or encapsulation into porous supports, like MCM-41,<sup>[9]</sup> SBA-15<sup>[10]</sup> and zeolite-Y.<sup>[11-13]</sup> The encapsulation strategy is found to be convenient and advantageous because the metal complex, once formed inside the pore cavity, does not easily diffuse out and enter the liquid phase during catalytic reaction. Faujasite zeolite, including zeolite X and Y, is frequently chosen as a support to encapsulate metal complexes because of its huge supercage of 13 Å with large pore opening of ca 8 Å and three-dimensional pore system desirable for easy reactant accessibility and product diffusion.<sup>[11]</sup>

To encapsulate homogeneous metal complexs into faujasite, three methods have been developed: (i) the template method; (ii) the ship-in-bottle method; and (iii) the flexible ligand method. For method I, preformed transition metal complex is used as a template around which zeolite is crystallized, and thus it requires the metal complex to be stable under harsh zeolite synthesis conditions such as high pH and high temperature. Therefore, there are limited successful examples of encapsulating metal complexes using this approach. For example, Balkus and coworkers synthesized a NaX encapsulated ruthenium perfluorophthalocyanine complex ( $RuF_{16}Pc-X$ ) and it proved to

be efficient for the oxidation of cyclohexane with TBHP.<sup>[14]</sup> Other metallo-phthalocyanine complexes (like iron phthalocyanine, FePc) were also encapsulated into zeolite–Y by the template method. Methods II and III are relatively more adaptive to encapsulation of a wide range of complexes into zeolites. Both approaches have been extensively used to encapsulate Schiff bases, metalloporphyrins, metallophthalocyanines complexes, etc.<sup>[15,16]</sup> Usually, when ligand size is larger than the opening diameter of zeolite channels, method II is used, wherein the ligand is constructed within the micropores of transition metal-exchanged zeolite and then complexed with the resident metal ions.<sup>[17]</sup> On the other hand, when the ligand size is smaller than the opening diameter of zeolite, and the ligand is flexible to diffuse into the zeolite to react with the previously exchanged metals in the zeolite cavity, method III is used.<sup>[18]</sup>

8-Quinolinol, a strong bidentate ligand with a dimeter smaller than 7 Å and its metal complexes larger than 8 Å, can be encapsulated into zeolite Y by method III. However, as far as we know, 8-quinolinol and its encapsulated metal complexes are always ignored, probably due to its moderately conformationally

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flexible structure and their wide application in the field of luminescent materials.<sup>[19]</sup> Little attention has been focused on their catalytic performances except for a pioneering work of MCM-41 encapsulated [Fe(Q)<sub>3</sub>]Cl<sub>2</sub> (Q = 8-quinolinol). The encapsulation significantly improved the catalytic activity of [Fe(Q)<sub>3</sub>]Cl<sub>2</sub> in phenol hydroxylation with  $H_2O_2$  but the leaching of  $Fe(Q)_3$ species occurred due to the same diameters of pore size and pore entrance.<sup>[20]</sup> Moreover, there are few studies examining the leaching process of encapsulated catalysts carefully. Herein, we report the encapsulation of Fe(III), Co(II) and Cu(II) complexes of 8-quinolinol into the zeolite-Y by method III. These encapsulated metal complexes were fully characterized and screened as catalysts for the aerobic oxidation of styrene in the presence of a sacrificial co-reductant isobutyraldehyde. Heterogeneity tests for these catalysts were also performed to investigate their stability against leaching of active complex species into solution.

## Experimental

# Preparation of Metal-exchanged Zeolite, M-Y (M = Fe(III), Co(II) or Cu(II))

Firstly, Na–Y was prepared according to the procedure reported with slight modification.<sup>[21]</sup> In a typical synthesis, 1.6 g of sodium hydroxide and 2.5 g of sodium aluminate (41 wt%) were dispersed in 25 ml of deionized water under constant stirring, and then 18 ml of silica sol (25 wt%) was added. The mixture with a molar composition of  $13.2 \text{ SiO}_2$ –Al<sub>2</sub>O<sub>3</sub>–16.4 Na<sub>2</sub>O–354 H<sub>2</sub>O was stirred at room temperature for 1 h to form gel slurry, and then was hydrothermally crystallized at 100 °C for 24 h. Subsequently, the resultant precipitate was separated from the mother liquor by filtration, washed with deionized water and dried at 150 °C for 12 h.

Metal-exchanged zeolite-Y (M-Y) was prepared as follows: an amount of 2.0 g Na-Y zeolite was suspended in 40 ml distilled water containing 0.32 mmol of metal salt [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O or Cu(CH<sub>3</sub>COO)<sub>2</sub>]. The mixture was stirred at room temperature for 24 h. The M-Y materials were obtained by filtration, washed with hot distilled water till the filtrate was free from any metal ion content and dried for 12 h at 150 °C in air.

# Preparation of Encapsulated Metal Complexes of 8-quinolinol, $MQ_n - Y$ , (Q = 8-quinolinol, n = 2 or 3)

This process was performed with excess 8-quinolinol ligands  $(n_{ligand}/n_{metal} = 3)$ , and allowed the insertion of the ligand in the cavity of the zeolite followed by its complexation with metal ions. The complexation was carried out in MeOH at 80 °C for 24 h. Uncomplexed ligands and the complexes adsorbed on the exterior surface were removed by full Soxhlet extraction with MeOH until the eluate became colorless. The extracted sample was ion-exchanged with aqueous 0.01 M NaCl solution at 80 °C for 8 h to remove uncoordinated metal ions, followed by washing with deionized water until no Cl<sup>-</sup> anions could be detected with AgNO<sub>3</sub> aqueous solution. The MQ<sub>n</sub>-Y samples were then dried at 150 °C for several hours to constant weight. This procedure brought about brilliant color change, suggesting that the properties of pure compounds have been dramatically changed upon encapsulation.

#### Synthesis of Pure Metal Complexes of 8-Quinolinol

The procedures for the preparation of pure metal complexes are as follows: 5 ml of aqueous  $Fe(NO_3)_3 \cdot 9H_2O$  solution (1 M)

was mixed with 2.18 g of 8-quinolinol (15 mmol) in 50 ml of tetrahydrofuran and aqueous  $NH_3 - NH_4^+$  buffer was added to the solution to maintain a pH of 7.0–8.0. In parallel, 5 ml of aqueous  $Co(NO_3)_2 \cdot 4H_2O$  or  $Cu(CH_3COO)_2$  solution (1 m) was mixed with 1.45 g of 8-quinolinol (10 mmol) in 50 ml of tetrahydrofuran. The resulting mixture was stirred and refluxed for 2 h. After cooling, these solid products were separated by filtration, washed with excess ethanol and dried under vacuum. The spectroscopic data of these complexes are given in the Supporting Information.

#### **Catalytic Oxidation**

The oxidation of styrene with air was carried out in a batch reactor. In a typical run, 10 mmol of styrene along with 10 ml of  $CH_3CN$ , 25 mmol of isobutyraldehyde and certain amounts of catalyst were added into a 100 ml two-necked flask equipped with a condenser and an air pump. The reaction was started by bubbling the dry air with a stable flow rate of 80 ml min<sup>-1</sup> controlled by a flowmeter into the bottom of reactor at reaction temperature. After the reaction was finished, the catalyst was filtered, washed with  $CH_3CN$ , dried at 100 °C overnight and reused directly without further purification. The liquid organic products were quantified by using a gas chromatography (Shimadzu, GC-8A) fitted with FID detector and HP-5 capillary column. The liquid organic products were identified by comparison with authentic samples and verified by GC-MS coupling.

### **Results and Discussion**

#### **Morphological and Textural Properties of Materials**

The X-ray powder diffractograms of Na–Y, Fe–Y and FeQ<sub>3</sub>–Y are depicted in Fig. 1 and indicate a well crystalline FAU structure of cubic symmetry.<sup>[22]</sup> The appearance of peaks in iron-exchanged zeolite (Fe–Y) and encapsulated one (FeQ<sub>3</sub>–Y) suggests that the supercages of the zeolite are able to accommodate metal complexes and the crystallinity of the zeolite–Y has been preserved during encapsulation. Only a small decrease was observed in the intensities of the peaks at  $2\theta < 20^{\circ}$  due to the encapsulation of metal complexes. No new peaks assigned to pure iron complexes were detected in the encapsulated zeolite probably due to very



Figure 1. XRD patterns of (a) Na-Y, (b) Fe-Y and (c) FeQ<sub>3</sub>-Y.



Figure 2. SEM images of (a) Fe-Y, (b) FeQ<sub>3</sub>-Y, (c) CoQ<sub>2</sub>-Y and (d) CuQ<sub>2</sub>-Y.

Materials	Chemical composition	BET surface area ( $m^2 g^{-1}$ )	Microporous volume <sup>a</sup> (cm <sup>3</sup> g <sup>-1</sup> )	External surface area (m <sup>2</sup> g <sup>-1</sup> )	
Na-Y	Na <sub>25</sub> [Al <sub>25</sub> Si <sub>167</sub> O <sub>384</sub> ] · 109H <sub>2</sub> O	707.5	0.320	17.7	
Fe-Y	Na <sub>15.7</sub> Fe <sub>3.1</sub> [Al <sub>25</sub> Si <sub>167</sub> O <sub>384</sub> ] · 110H <sub>2</sub> O	599.1	0.255	50.8	
$FeQ_3 - Y$	Na <sub>15.7</sub> Fe <sub>1.0</sub> (FeQ <sub>3</sub> ) <sub>2.1</sub> [Al <sub>25</sub> Si <sub>167</sub> O <sub>384</sub> ] · 110H <sub>2</sub> O	429.8	0.188	16.8	
Co-Y	Na <sub>22.8</sub> Co <sub>1.1</sub> [Al <sub>25</sub> Si <sub>167</sub> O <sub>384</sub> ] · 107H <sub>2</sub> O	645.7	0.296	12.3	
CoQ <sub>2</sub> -Y	Na <sub>22.8</sub> Co <sub>0.2</sub> (CoQ <sub>2</sub> ) <sub>0.9</sub> [Al <sub>25</sub> Si <sub>167</sub> O <sub>384</sub> ] · 107H <sub>2</sub> O	316.2	0.140	16.1	
Cu-Y	$Na_{23,2}Cu_{0,9}[AI_{25}Si_{167}O_{384}] \cdot 111H_2O$	424.7	0.187	32.8	
$CuQ_2 - Y$	Na <sub>23.2</sub> Cu <sub>0.1</sub> (CuQ <sub>2</sub> ) <sub>0.8</sub> [Al <sub>25</sub> Si <sub>167</sub> O <sub>384</sub> ] · 111H <sub>2</sub> O	314.6	0.140	14.2	

low percentage loading. Similar results were also obtained from the XRD patterns of cobalt and copper catalysts (Fig. S1).

SEM micrographs of the modified zeolites exemplified by Fe-Y, FeQ<sub>3</sub>-Y, CoQ<sub>2</sub>-Y and CuQ<sub>2</sub>-Y are depicted in Fig. 2. From these micrographs, Fe-Y possesses the octahedron shape of crystal (Fig. 2a), similar to that of zeolite-Y. The SEM images of FeQ<sub>3</sub>-Y (Fig. 2b), CoQ<sub>2</sub>-Y (Fig. 2c) and CuQ<sub>2</sub>-Y (Fig. 2d) indicate the presence of well-defined zeolite crystals free from any shadow of metal complexes present on their external surface. Both X-ray diffraction and SEM results demonstrate that good crystallinity of zeolites is kept during the encapsulation of metal complexes by method III.

The nitrogen adsorption isotherms for the parent (Na-Y) and modified zeolites  $(M-Y \text{ and } MQ_n-Y)$  are typical of microporous materials (not shown); BET surface areas, micropore volumes and external surface areas were calculated by fitting the adsorption data in the corresponding theories; the values are given in Table 1. As expected, the surface areas and the micropore volumes of M-Yand  $MQ_n-Y$  show an apparent reduction when compared with their respective parent materials. The lowering of the surface areas and pore volumes indicates the presence of metal 8-quinolinol complexes within the cavities of the zeolites and not on the external surface. Similar observations was also found for inclusion of Mn(III) Schiff base complexes into zeolite–Y.<sup>[23]</sup> Nevertheless, the decreasing degree depends on the amount of incorporated complexes as well as their molecular size and geometrical conformation inside the zeolitic host. As a result, compared with their respective M–Y, a reduction by about 30, 25 and 50% was observed upon encapsulation of Fe, Co and Cu complexes of 8-quinolinol into zeolite–Y, respectively. On the other hand, the external surface areas determined from the *t*-plot increase with the incorporation of metal ions by comparing Fe–Y and Cu–Y with Na–Y. This increase can be explained in terms of the zeolite structural deformation occurring during the cation-exchanged process.<sup>[24]</sup>

#### Spectroscopic Characterization

Figure 3 shows the IR spectra of Na-Y, Fe-Y and FeQ<sub>3</sub>-Y. It is evident that framework vibration bands of zeolite-Y dominate



Figure 3. FT-IR spectra of (a) Na-Y, (b) Fe-Y and (c)  $FeQ_3-Y$ .

the spectra below 1200 cm<sup>-1</sup> for all samples. The bands at 462, 572, 692 and 785 as well as 997 and 1138  $cm^{-1}$  are attributed to T-O bending mode, double ring, symmetric stretching and asymmetric stretching vibrations, respectively.<sup>[25]</sup> No shift is observed upon introduction of metal ions and inclusion of metal complexes, further substantiating that the zeolite framework remains unchanged. In spite of this, there is obviously a difference in the range of  $1200-1600 \text{ cm}^{-1}$  among the three samples. It can be seen that the prominent bands, assigned to C-O, C-N and aromatic ring vibrations of ligands, are present at 1276, 1325, 1376, 1466 and 1500 cm<sup>-1</sup> in the spectra of FeQ<sub>3</sub>–Y (Fig. 3c) and FeQ<sub>3</sub> (Fig. S2a). However, these bands are absent in the case of Na-Y and Fe-Y samples. In line with the FeQ<sub>3</sub>-Y sample, the framework IR spectra of other  $MQ_n - Y$  samples (Fig. S3) are also in agreement with their pure analogs (Fig. S2), verifying that various metal complexes have been encapsulated inside zeolite-Y.

The UV-vis spectra of Co-Y, CoQ<sub>2</sub>-Y and CoQ<sub>2</sub> are shown in Fig. 4(A). Clearly, there is a weak and broad adsorption in the region of 400–600 nm for Co-Y, which can be assigned to the overlapping due to  ${}^{4}T_{1} - {}^{4}T_{2}$  and  ${}^{4}T_{1} - {}^{4}A_{2}$  transitions.<sup>[26]</sup> On the other hand, three intense bands were observed for CoQ<sub>2</sub>-Y and CoQ<sub>2</sub> in the regions of 218–320, 320–375 and 550–650 nm, respectively.

These bands are attributed to intra-ligand transition, ligand-tometal change transfer (CT) and d-d transitions, respectively.<sup>[25]</sup> Compared with the pure CoQ<sub>2</sub>, however, these bands in the region of 200–400 nm were blue-shifted upon encapsulation of cobalt complexes in the Na–Y matrix, indicating the restructuring of the ligand after coordination to the cobalt ion fixed in the Na–Y. However, the d–d band considerably red-shifted to 598 nm for CoQ<sub>2</sub>–Y as compared with 577 nm in the spectrum of CoQ<sub>2</sub>. This perhaps originates from the interaction of cobalt complex with zeolite framework, although this complex was located in the supercages in a neutral form. Similar results can be also obtained from iron and copper catalysts (see Fig. 4B and C).

#### Quantification

The Si-Al ratios of modified zeolites are in the range of those expected for faujasite and are almost in the same ratio as in the parent zeolite (not shown). The results of chemical elemental analyses give a Si-Al ratio of ca 6.60, which corresponds to a unit formula  $Na_{25}[Al_{25}Si_{167}O_{384}] \cdot 109H_2O$  for Na-Y and Na<sub>15.7</sub>Fe<sub>3.1</sub>[Al<sub>25</sub>Si<sub>167</sub>O<sub>384</sub>] · 110H<sub>2</sub>O for Fe-Y (Fe and H<sub>2</sub>O contents were estimated by ICP-AES and TG/DSC, respectively; Table 1). The Na and Fe in Fe-Y material give a degree of Na exchange of 37.2%, and the unit cell formula of iron-exchanged zeolites shows an iron dispersion of 3.1 per unit cell. For these exchanged irons, only 32.3% remains in the FeQ<sub>3</sub>-Y, corresponding to a unit cell formula Na<sub>15.7</sub>Fe<sub>1.0</sub>(FeQ<sub>3</sub>)<sub>2.1</sub>[Al<sub>25</sub>Si<sub>167</sub>O<sub>384</sub>] · 110H<sub>2</sub>O (see Tables 1 and 2), indicating that the exchanged irons were not removed by refluxing with 0.01 M NaCl. Similar results are obtained for other modified zeolites and their chemical compositions are also listed in Table 1.

The chemical composition analyses also confirmed the purity and stoichiometry of the pure and encapsulated complexes. The chemical analyses of the encapsulated samples reveal the presence of organic matter with a C : N ratio roughly similar to the theoretical value of 7.80 for pure complexes (Table 2), indicating that the 8quinolinol ligands are intact resident in zeolite Y. Since these ligands were all coordinated to the exchanged transition metal ions in zeolite Y on the condition that the free ligands were fully removed, it is reasonable that the amount of complexed metal ions was determined by that of ligands encapsulated. Therefore, the amounts of metal complexes or ligands encapsulated in zeolite matrix were determined by the N elemental analysis. Nitrogen elemental analysis also reveals that the presence of *ca* 6.3 moieties of 8-quinolinol per unit cell for FeQ<sub>3</sub>–Y and the iron complexes

Table 2.      Selected characteristics of catalysts								
	Mª (mmol g	g <sup>-1</sup> )	C/N analysis (wt%)		%)	H analysis (wt%)		
Catalysts	Exchangeable	As Q <sup>b</sup>	С	Ν	C/N	Total <sup>c</sup>	H in water <sup>d</sup>	H in Q
Fe-Y	0.204	-	-	-	-	1.57	1.57	_
FeQ <sub>3</sub> -Y	0.074	0.150	4.95	0.63	7.90	2.82	1.48	1.34
Co-Y	0.080	-	-	-	-	1.57	1.53	-
CoQ <sub>2</sub> -Y	0.019	0.090	2.05	0.25	8.20	2.64	1.50	1.14
Cu-Y	0.065	-	_	-	-	1.58	1.58	-
CuQ <sub>2</sub> -Y	0.005	0.040	0.89	0.11	8.12	2.02	1.56	0.46

 $^{a}_{.}$  M = Fe, Co or Cu.

 $^{\rm b}$  The amount of metal coordinated with 8-quinolinol (Q).

<sup>c</sup> Estimated by elemental analysis and total amount of H = H in water + H in Q.

<sup>d</sup> Quantification based on TG/DSC results.



**Figure 4.** UV-vis spectra of (A) (a) Co-Y, (b)  $CoQ_2-Y$  and (c)  $CoQ_2$  (inset); (B) (a) Fe-Y, (b)  $FeQ_3-Y$  and (c)  $FeQ_3$  (inset); and (C), (a) Cu-Y, (b)  $CuQ_2-Y$  and (c)  $CuQ_2$  (inset).

formed in the supercages are rationally 1:3 (Fe : Q) stoichiometric compounds. On the other hand, 1.8 and 1.6 moieties of 8-quinolinol per unit cell for CoQ<sub>2</sub> – Y and CuQ<sub>2</sub> – Y demonstrate that the cobalt and copper complexes formed in the supercages are rationally 1:2 stoichiometric compounds. It is also found that the metal

Table 3.	Thermogravimetric analysis data of catalysts						
Materials	Temperature range (°C)	Weight loss (%)	Group Ioss <sup>a</sup>	Type of loss			
Fe-Y	150-280	14.1	nH <sub>2</sub> O	Endothermic			
	150-266	13.3	$nH_2O$	Endothermic			
FeQ <sub>3</sub> -Y	266-750	4.0	Q	Exothermic			
Co-Y	150-270	13.8	$nH_2O$	Endothermic			
	150-263	13.5	$nH_2O$	Endothermic			
CoQ <sub>2</sub> -Y	363-750	3.0	Q	Exothermic			
Cu-Y	150-269	14.2	nH <sub>2</sub> O	Endothermic			
	150-257	14.0	nH <sub>2</sub> O	Endothermic			
CuQ <sub>2</sub> -Y	257-750	3.0	Q	Exothermic			
<sup>a</sup> Q stands for 8-quinolinol.							



Figure 5. TG/DSC curves of Fe-Y (solid lines) and FeQ<sub>3</sub>-Y (dashed lines).

loadings are always higher or similar for the  $MQ_n - Y$  zeolites as compared with the exchanged M-Y (Table 2), suggesting that the encapsulated metal complexes are stable in zeolite matrix and there is no metal leaching during complex encapsulation. This is quite different from the Mn leaching after the introduction of salen ligands into the zeolite – Y as reported in the literature.<sup>[27]</sup>

The differential scanning calorimetry (DSC) data along with the percentage weight loss at different steps and their assignments are presented in Table 3. TG and DSC profiles of two representative samples, Fe-Y and FeQ<sub>3</sub>-Y, are reproduced in Fig. 5. An endothermic loss of intra-zeolite water occurs between temperature 150 and 280  $^{\circ}$ C in Fe–Y and between 150 and 266  $^{\circ}$ C in FeQ<sub>3</sub>–Y,<sup>[28]</sup> although the catalysts were dried at 150 °C. As illustrated in Table 3, 14.1 and 13.3% weight loss of water was detected in Fe-Y and FeQ<sub>3</sub>-Y, respectively, which corresponds to 110 water molecules in their respective unit cell. The second step involves the slow but exothermic weight loss in a wider temperature range due to decomposition of the chelating ligand.<sup>[29,30]</sup> A very small percentage weight loss  $(4.0\% \text{ for FeQ}_3 - Y)$  indicates the presence of only small amounts of metal complexes in zeolite cavities. It is slightly lower than the ligand content estimated by N elemental analysis (6.5%). Similar results can be obtained from cobalt and copper catalysts (see Table 3 and Fig. S4).

Entrapment of metal complexes inside the zeolite cages and not on their external surfaces was previously demonstrated by

rene
n

		M (mmol	Styrene	TOF	Product selectivity (mol%) <sup>c</sup>		
Entry	Catalysts	$g^{-1}$ ) total	conversion (%) <sup>a</sup>	$(h^{-1})^{b}$	So	Bza	Others
1	Fe-Y	0.204	60.6	74.3	30.1	61.7	8.2
2	FeQ <sub>3</sub>	2.048	80.1	89.4	43.2	56.8	0
3	FeQ <sub>3</sub> -Y	0.224	83.4	93.1	24.5	58.2	17.3
4	FeQ <sub>3</sub> -Y (2nd)	0.217	74.2	85.5	37.4	60.7	1.9
5	$Fe-Y + FeQ_3^d$	0.518	66.5	74.7	45.1	51.5	3.4
6	Co-Y	0.080	63.3	197.8	33.2	58.5	8.3
7	CoQ <sub>2</sub>	2.880	51.0	117.0	46.2	53.0	0.8
8	CoQ <sub>2</sub> -Y	0.109	56.7	130.0	39.2	59.6	1.2
9	Cu-Y	0.065	54.2	208.5	30.8	62.8	6.4
10	CuQ <sub>2</sub>	2.840	61.8	441.4	40.4	59.6	0
11	$CuQ_2 - Y$	0.045	89.3	637.9	31.0	59.0	10.0

<sup>a</sup> Reaction conditions: supported catalyst 50.0 mg (FeQ<sub>3</sub> 5.5 mg, CoQ<sub>2</sub> 2.0 mg and CuQ<sub>2</sub> 1.0 mg using the same molar concentration of metal ions as compared with FeQ<sub>3</sub> – Y, CoQ<sub>2</sub> – Y and CuQ<sub>2</sub> – Y), styrene 1.14 ml (10 mmol), CH<sub>3</sub>CN 10 ml, flow of air 80 ml min<sup>-1</sup>, isobutyraldehyde 2.28 ml (25 mmol), temperature 80 °C and duration 8 h.

<sup>b</sup> TOF (turnover frequency): moles of substrate converted per mole metal ion per hour.

<sup>c</sup> So, styrene oxide; Bza, benzaldehyde; and Others, include benzoic acid, phenylacetaldehyde and 1-phenylthane-1,2-diol.

 $^{d}$  Fe – Y, 18.0 mg and FeQ<sub>3</sub>, 3.7 mg.

nitrogen adsorption and SEM analyses. However, TG/DSC analysis can substantiate this result more accurately. Taking into account the content of Na in the zeolite and the fact that only 1% of the cationic exchange sites are on the external surface of the zeolite,<sup>[27,31]</sup> it can be calculated that, if all the external ionic exchange sites of the zeolite were completely occupied by transition metal ions followed by the complete complexing with 8-quinolinol, the weight loss due to the combustion of these complexes present on the surface would be about 0.14% for FeQ<sub>3</sub>-Y, 0.13% for CoQ<sub>2</sub>-Y and 0.15% for CuQ<sub>2</sub>-Y, respectively. Actually, a Q weight loss of 3.0–4.0% was found, and thus most of the coordination compounds should be in the cavities of the zeolite.

#### **Catalytic Properties**

To ensure a fair comparison, the molar ratios of metal ions to styrene were the same in the pure and encapsulated complexes for each reaction and relevant control experiments were performed. Table 4 summarizes the catalytic results for the aerobic oxidation of styrene over various catalysts. Except for Na-Y (not listed), all the metal-exchanged zeolites and metal complexes whether encapsulated or not exhibit activity. This shows that the active sites are exchanged metal ions and encapsulated metal complexes. Actually, according to the elemental analysis, the majority of the exchanged transition metals in  $MQ_n - Y$  are coordinated with 8-quinolinol, i.e. 67.7% for FeQ3-Y, 81.8% for CoQ<sub>2</sub>-Y and 88.9% for CuQ<sub>2</sub>-Y. This demonstrates that the activity of  $MQ_n - Y$  is mainly conducted by the encapsulated metal complexes, not exchanged metal ions. Both FeQ<sub>3</sub>-Y and CuQ<sub>2</sub>-Y are more active than their corresponding metalexchanged zeolites and pure metal complexes. The mechanical mixture of Fe-Y (18.0 mg) and FeQ<sub>3</sub> (3.7 mg) shows 66.5% styrene conversion under the same reaction conditions, which is lower than that obtained from FeQ3-Y, although the total amount of iron was equivalent to that of FeQ<sub>3</sub>-Y. It is probable that there exists synergism between the exchanged metal ions and encapsulated metal complexes. However, Co-Y is more active than the resulting  $CoQ_2-Y$  and shows a higher TOF value (Table 4, entries 6 and 8). The activity reduction of  $CoQ_2-Y$  may be ascribed to the constraints and steric hindrance after encapsulation of cobalt complexes in the zeolite supercages.

The encapsulated metal complexes show many advantages over their homogeneous counterparts. Firstly, the catalytic activity of  $MQ_n - Y$  is always found to be better than their respective nonencapsulated complexes (Table 4, entries 2, 3, 7, 8, 10 and 11). The reason for the higher activity of encapsulated complexes is the site-isolation of the metal complexes.<sup>[32]</sup> Secondly, the pure complexes were completely destroyed during the first run since the color was significantly changed. Taking CoQ, for example, during the reaction, the color of solution changed from light yellow to dark brown. This may be related to the irreversible deactivation due to formation of  $\mu$ -oxo and  $\mu$ -peroxo dimeric and other polymeric species, especially when using oxidant.<sup>[33]</sup> On the other hand, zeolite encapsulated metal complexes did not undergo any color change during the reaction and could be easily separated and reused. As illustrated in Table 4, the recycled FeQ<sub>3</sub>-Y displays similar activity and product distribution as compared with the fresh one.

To further verify the heterogeneity of the zeolite encapsulated catalysts, leaching tests for FeQ<sub>3</sub>-Y, CoQ<sub>2</sub>-Y and CuQ<sub>2</sub>-Y catalysts were performed. We filtered the catalyst at the reaction temperature (80 °C), e.g. the FeQ<sub>3</sub>-Y after 1.0 h (24.9% styrene conversion). At this time, half the volume was filtered and the resulting clear solution was allowed to react. The percentage of leaching was estimated by comparing the time-conversion plot of the twin reactions with and without solid. It was found that styrene could just be converted at a very low rate (Fig. 6a) and this trend is almost parallel to the blank experiment (not shown). The filtrate neither shows any activity towards oxidation reaction nor does the ICP-AES analysis show the presence of iron in the filtrate. However, as for CoQ<sub>2</sub>-Y and CuQ<sub>2</sub>-Y catalysts, it was found that, after the hot filtration, the mother liquor reacted further at roughly the same rate as that observed when the catalyst was not filtered (Fig. 6b



**Figure 6.** ( $\hat{a}$ - $_i$ ): Time-conversion plot for aerobic oxidation of styrene in combination with isobutyraldehyde as co-reductant. ( $\hat{a}$ - $\hat{a}$ ): Heterogeneous reaction check by continuing the reaction after removing the catalyst after 1.5 h (removing FeQ<sub>3</sub> – Y after 1.0 h). Reaction conditions: 10 mmol of styrene, 10 ml of CH<sub>3</sub>CN, 25 mmol of isobutyraldehyde, 50 mg of catalyst (a, FeQ<sub>3</sub> – Y; b, CoQ<sub>2</sub> – Y and c, CuQ<sub>2</sub> – Y), flow of air 80 ml/min and temperature 80 °C.

and c), which leads to the inevitable conclusion that all of the observed activity can be attributed to homogeneous Co(II) or Cu(II) species leached from the zeolite. According to the literature,<sup>[34]</sup> we suppose that the remarkable leaching occurring for CoQ<sub>2</sub>-Y and CuQ<sub>2</sub>-Y can be attributed to the change in the unstable coordinate environment of the active sites during the reaction.

Additionally, we found that the acidic nature of hydrophilic zeolite was reflected in the product distribution. The catalytic results over homogeneous complex catalysts show that benzaldehyde (Bza) is the major oxidation product, followed by styrene oxide (So), similar to the literature.<sup>[35,36]</sup> The encapsulated complexes show similar product distributions to the homogeneous counterparts, except for the presence of phenylacetaldehyde and 1-phenylethane-1,2-diol, formed via ring opening of phenyloxirane on acid sites. Lower styrene oxide selectivity for  $MQ_n - Y$  and M-Y is also connected with this ring opening reaction, suggesting that the acidity of the zeolite support decreases the selectivity to phenyloxirane. Comparing these results with our earlier data on the epoxidation of styrene over tethered iron Schiff base complexes on SBA-15 under identical reaction conditions.<sup>[37]</sup> we observed that here the selectivity to phenyloxirane was lower, further indicating that the acidity of the zeolite probably accelerates further isomerization of styrene oxide to phenylacetaldehyde. However, this selectivity to styrene oxide is still higher than that obtained by zeolite-Y encapsulated Mn complexes,<sup>[23]</sup> which can probably be explained by the higher Si-Al molar ratio of zeolite-Y in this study associated with lower acidity.

### Conclusions

Fe(III), Co(II) and Cu(II) complexes of 8-quinolinol were successfully encapsulated in the supercages of zeolite–Y by a flexible ligand method, as evidenced by FT-IR, UV–vis spectroscopy, N<sub>2</sub> adsorption/desorption techniques. The loadings of metal and ligand were quantified by ICP-AES, TG/DSC and CHN elemental analysis, and the internal location of active species was demonstrated. The structural integrity of zeolite throughout the encapsulation procedure was confirmed by XRD and SEM studies. These encapsulated metal complexes displayed better activity than their corresponding homogeneous analogs due to the site-

isolation as well as the synergism effect between the exchanged metal ions and encapsulated metal complexes. Leaching tests confirmed only  $FeQ_3-Y$  was stable against leaching of active species into solution and can be recycled without significant loss of activity and selectivity within successive runs. Moreover, the selectivity to benzaldehyde was higher than to styrene oxide in all cases due to the acidic nature of zeolite matrix.

#### **Supporting information**

Supporting information may be found in the online version of this article.

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#### References

- [1] G. D. Yadav, A. A. Pujari, Org. Process Res. Dev. 2000, 4, 88.
- [2] B. S. Lane, K. Burgess, Chem. Rev. 2003, 103, 2457.
- [3] A. Corma, H. Garcia, Chem. Rev. 2002, 102, 3837.
- [4] T. Sato, J. Dakka, R. A. Sheldon, J. Chem. Soc. Chem. Commun. 1994, 16, 1887.
- [5] M. A. Camblor, A. Corma, A. Martinez, J. Perez Parienta, J. Chem. Soc. Chem. Commun. 1992, 8, 589.
- [6] G. Tozzola, M. A. Mantegazza, G. Ranghino, G. Petrini, S. Bordiga, G. Ricchiardi, C. Lamberti, R. Zulian, A. Zecchina, J. Catal. **1998**, 179, 64.
- [7] A. Singh, T. Selvam, J. Mol. Catal. A: Chem. **1996**, 113, 489.
- [8] B. F. Sels, D. De Vos, P. A. Jacobs, Tetrahedron Lett. 1996, 37, 8557.
- [9] T. Joseph, D. Srinivas, C. S. Gopinath, S. B. Halligudi, *Catal.Lett.* **2002**, 83, 209.
- [10] T. Joseph, S. B. Halligudi, J. Mol. Catal. A: Chem. 2005, 229, 241.
- [11] R. A. Sheldon, I. W. C. E. Arends, A. Dijksman, Catal. Today 2000, 57, 157.
- [12] C. R. Jacob, S. P. Verkey, P. Ratnasamy, *Micropor. Mesopor. Mater.* 1998, 22, 465.
- [13] G. J. Hutchings, Chem. Commun. 1999, 999, 301.
- [14] K. J. Balkus, M. Eissa, R. Levado, J. Am. Chem. Soc. **1995**, 117, 10753.
- [15] N. Herron, *Inorg. Chem.* **1986**, *25*, 4714.
- [16] C. Bowers, K. P. Dutta, J. Catal. 1990, 122, 271.
- [17] D. Srinivas, S. Sivasanker, Catal. Surv. Asia 2003, 7, 121.
- [18] R. Vijayalakshmi, S. K. Kulshreshtha, *Micropor. Mesopor. Mater.* **2008**, *111*, 449.

- [19] H. S. Wang, J. H. Huang, S. J. Wu, C. Xu, L. H. Xing, L. Xu, Q. B. Kan, Mater. Lett. 2006, 60, 2662.
- [20] C. B. Liu, Y. K. Shan, X. G. Yang, X. K. Ye, Y. Wu, J. Catal. 1997, 168, 35.
- [21] M. M. Htay, M. M. Oo, Wld Acad. Sci. Eng. Technol. 2008, 48, 114.
- [22] J. A. Kaduk, J. Faber, *The Rigaku J.* **1995**, *12*, 14.
- [23] M. Salavati-Niasari, Micropor. Mesopor. Mater. 2006, 95, 248.
- [24] J. Sebastian, K. Mohan, R. V. Jasra, J. Catal. **2006**, 244, 208.
- [25] C. Jin, W. B. Fan, Y. J. Jia, B. B. Fan, J. H. Ma, R. F. Li, J. Mol. Catal. A: Chem. 2006, 249, 23.
- [26] X. Y. Qi, G. J. Wang, X. K. Ye, Y. Wu, *Chem. J. Chin. Univ.* **1996**, *17*, 939.
  [27] M. Silva, C. Freire, B. de Castro, J. L. Figueiredo, *J. Mol. Catal. A: Chem.* **2006**, *258*, 327.
- [28] M. R. Maurya, S. J. J. Titinchi, S. Chand, J. Mol. Catal. A: Chem. 2003, 201, 119.
- [29] P. K. Saha, B. Dutta, S. Jana, R. Bera, S. Saha, K. Okamoto, S. Koner, Polyhedron 2007, 26, 563.

- [30] Y. Yang, Y. Zhang, S. J. Hao, Q. B. Kan, Catal. Commun. 2010, 11, 808.
- [31] E. Páez-Mozo, N. Cabrimas, F. Lucaccioni, D. D. Acosta, P. Patron, A. L. Cmestra, P. Ruiz, B. Delmon, J. Phys. Chem. **1993**, 97, 12819.
- [32] Y. Yang, Y. Zhang, S. J. Hao, J. Q. Guan, H. Ding, F. P. Shang, P. P. Qiu, Q. B. Kan, Appl. Catal. A: Gen. 2010, 381, 274.
- [33] X. L. Wang, G. D. Wu, J. P. Li, N. Zhao, W. Wei, Y. H. Sun, Catal. Lett. 2007, 119, 87.
- [34] T. Kovalchuk, H. Sfihi, V. Zaitsev, J. Fraissard, J. Catal. 2007, 249, 1.
- [35] V. Indira, S. B. Halligudi, S. Gopinathan, C. Gopinathan, *React. Kinet. Catal. Lett.* 2001, 73, 99.
- [36] Á. Zsigmond, A. Horváth, F. Notheisz, J. Mol. Catal. A: Chem. 2001, 171, 95.
- [37] Y. Yang, J. Q. Guan, P. P. Qiu, Q. B. Kan, Transition Met. Chem. 2010, 35, 263.