Immobilized iron Schiff base histidine complexes on Al-MCM-41 and zeolite Y as catalyst for oxidation of cycloalkanes

Faezeh Farzaneh · Samaneh Sohrabi ·
Mina Ghiasi · Mehdi Ghandi · Vahid Daadmehr

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Abstract Iron complexes of *N*-salicylidene-L-histidine with or without bipyridine ligand immobilized on Al-MCM-41 and zeolite Y designated as Fe(sal-L-his)(bipy)complex/Al-MCM-41 or Fe(sal-L-his)complex/Al-MCM-41 and Fe(sal-L-his)(bpy)complex/Y or Fe(sal-L-his)complex/Y respectively, were prepared and characterized by X-ray powder diffraction (XRD), FT-IR, N₂ adsorption/desorption and chemical analysis techniques. Fe(sal-L-his)/Al-MCM-41 and Fe(sal-L-his)(bipy)complex/Al-MCM-41 were found to successfully catalyze the oxidation of cyclohexane, methyl cyclohexane, cyclooctane and adamantane with H₂O₂. The oxidation results and promising catalytic behavior of Fe(sal-L-his)(bipy)complex/Al-MCM-41 for oxidation of cyclooctane with 90 % conversion and excellent selectivity toward the formation of cyclooctanone will be discussed in this presentation.

Keywords Iron Schiff base complex · Al-MCM-41 · Oxidation catalyst · Cycloalkanes

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F. Farzaneh (✉) · S. Sohrabi · M. Ghiasi
Department of Chemistry, University of Alzahra,
Vanak, Tehran, Iran
e-mail: faezeh_farzaneh@yahoo.com; farzaneh@alzahra.ac.ir

M. Ghandi
School of Chemistry, College of Science,
University of Tehran, Tehran, Iran

V. Daadmehr
Magnet and Superconducting Research Lab, Department
of Physics, University of Alzahra, Vanak, Tehran, Iran

1 Introduction

The catalytic oxidation of organic substrates by transition metal complexes is an area of current interest [1]. Transition metal complexes with porphyrin, phthalocyanine and Schiff base ligands have been utilized for oxidation of various hydrocarbons [2–5]. Schiff base ligands are ubiquitous in coordination chemistry where they are used in the synthesis of a large variety of transition metal complexes with a range of structural architectures [6–9]. Among the various metals, iron is the most abundant metal in nature and is indispensable species of nearly all organisms. Nature has developed a number of metalloenzymes such as heme containing as the Cytochrome P-450 and non-heme monooxygenases [10, 11]. There has been significant interest in modeling such enzyme active sites and developing the biomimetic alkane hydroxylation catalyst [12, 13]. In spite of the fact that many investigations and research have been performed on synthesis and biomimetic oxidation chemistry of iron complexes, the design of new iron Schiff base complexes as oxidation catalysts in organic transformations is the subject of recent research [14–17].

Utilization of solid supported liquid phase catalysts (SLPC) would be attractive since they offer the advantages of easy catalyst separation, possible catalyst recycle and sometimes high activity and selectivity [18]. The immobilization of metal complexes within solid supports such as microporous (zeolites) or mesoporous (MCMs) has proven to be an important step in heterogeneous enzymatic catalysis [19–22]. Iron complexes with many type of ligands such as porphyrins, salens, and phthalocyanines have been used for the selective oxidation of hydrocarbons [19–27].

In this study, attempts has been made to immobilize iron (III) complexes of *N*-salicylidene-L-histidine designated as [Fe(sal-L-his)Cl•H₂O] and Fe[(sal-L-his)(bpy)Cl] within

Al-MCM-41 and zeolite Y in order to investigate their catalytic activity on cyclohexane, methyl-cyclohexane, cyclooctane and adamantane oxidations with hydrogen peroxide as oxidant.

2 Experimental

2.1 Materials

All materials were of commercial reagent grade. Iron (III) chloride, methylamine, hexadecyltrimethylammonium-bromide (HDTMABr), tetraethylorthosilicate (TEOS), aluminum hydroxide, 2,2'-bipyridine (bpy), acetone, diethyl ether, salicylaldehyde, L-histidine, sodium acetate, ethanol, acetonitrile, H₂O₂ (30 %), cyclohexane, methylcyclohexane, cyclooctane and adamantane were obtained from Merck Chemical Company and used without further purification. Zeolite Y as powder was purchased from Spag Company.

2.2 Synthesis of Al-MCM-41

The Al-MCM-41 (Si/Al = 50) with molar composition of 1.00 SiO₂: 1.60 MA: 0.215 HDTMABr: 125 H₂O: 0.02 Al₂O₃ was prepared according to the reported method [28]. First, methylamine (2.08 mL) was added to distilled water (42 mL) and the mixture was stirred at room temperature for 10 min. HDTMABr (1.47 g) was gradually added to the above solution under stirring for 60 min, followed by drop-wise addition of TEOS (2.1 g). Aluminum hydroxide (0.06 g) in water (5 mL) was then added and the pH of the reaction mixture was adjusted to 8.5 by slow addition of hydrochloric acid solution (1 M). At this stage, a precipitate was formed. After 2 h, the precipitate was separated and washed by centrifugation. The sample was dried at 45 °C for 12 h. A white powder was finally obtained after calcinations of the solid at 550 °C for 5 h to decompose the surfactant.

2.3 Preparation of [Fe(sal-L-his)Cl•H₂O]

Fe(sal-L-his)Cl•H₂O was prepared according to the modified reported method [29]. Salicylaldehyde (0.010 mol) in ethanol (20 mL) was introduced into histidine (0.010 mol) dissolved in water (20 mL), followed by addition of sodium acetate solution (0.020 mol in 10 mL water). The color of the solution changed to deep yellow. An aqueous solution of FeCl₃ (8.5 mmol, in 10 mL water) was then slowly added to the mixture, while the solution was stirring. The resultant dark red solution was concentrated slowly using a rotary evaporator to obtain a precipitate. The precipitate was separated and washed with acetone and diethyl ether, and then dried at room temperature. CHN elemental analysis calculated (%) for [FeC₁₃H₁₁N₃O₃Cl•H₂O]: C 42.59, H 3.57, N

11.46; Found: C 42.40, H 4.02, N 11.43. The FT-IR and UV-vis spectra of the solid containing peaks respectively at 3,414, 3,016, 1,625, 1,443, 1,201, 553, 455 cm⁻¹ and λ_{max} at 216, 235, 255, 466 nm were identical to those of reported previously [29–31].

2.4 Preparation of [Fe(sal-L-his)(bpy)Cl]

Based on the reported method [29], Fe(sal-L-his)(bpy)Cl complex was prepared by addition of 2,2-bipyridyl (0.01 mol in 20 mL ethanol) to the Fe(sal-L-his)Cl complex (0.01 mmol) and stirring the solution for 2 h. After evaporation of the solvent, acetone was added to the residue and the product was collected by filtration and then drying under vacuum. CHN elemental analysis calculated (%) for [FeC₂₃H₁₉N₅O₃Cl]: C 54.71, H 3.80, N 13.23; Found: C 54.62, H 3.65, N 13.33. The FT-IR and UV-vis spectra of the solid containing peaks respectively at 3,417, 3,024, 1,626, 1,443, 1,195, 538, 456 cm⁻¹ and λ_{max} at 204, 236, 288, 316, 484 nm [32, 33] were identical to those of reported previously.

2.5 Preparation of catalyst

Al-MCM-41 (0.5 g) was added to the complex (0.1 g, 0.27 mmol in 20 mL ethanol). The mixture was refluxed while stirring for 6 h. The solid was filtered, washed with ethanol, Soxhlet extracted with ethanol in order to remove the unimmobilized complex followed by drying at room temperature. The same procedure was used for immobilization within zeolite Y.

2.6 Oxidation reactions

Oxidation reactions were carried out at atmospheric pressure under reflux conditions. Typically, immobilized iron complex/Al-MCM-41 (or iron complex/Y) as catalyst (0.1 g) was added into the reaction flask containing cyclohexane (20 mmol dissolved in 5 mL acetonitrile) with slow stirring. After a few minutes, H₂O₂ (24 mmol, 30 % aqueous solution) was added and the mixture was refluxed for 6 h. The solid was filtered and washed with fresh acetonitrile. The filtrate was then subjected to GC and GC Mass analysis.

2.7 Characterization

The FT-IR spectra of the samples were recorded using Bruker Tensor 27 IR spectrometer in KBr pellets over the range of 4,000–400 cm⁻¹ under the atmospheric conditions. The UV-vis spectra were recorded on a UV-vis Perkin Elmer Lambda 35 spectrophotometer. The amount of iron complexes immobilized within of Al-MCM-41 or zeolite Y was determined by atomic absorption spectroscopy (AAS)

with a GBC spectrophotometer using flame approach, after HF acid dissolution. BET surface areas and pore size distributions were determined by N₂ adsorption/desorption at liquid nitrogen temperature (77 K) using Quanta chrome Nova version 2.2 Analyzer. Prior to adsorption/desorption measurement, the samples were equilibrated by degassing at 110 °C for 3 h. Powder X-ray diffraction (XRD) measurements were performed on a scintillation diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV, 40 mA. Oxidation products were analyzed by a GC and GC Mass model using an Agilent 6890 Series with FID detector, HP-5, 5 % phenylmethylsiloxane capillary and an Agilent 5973 Network, mass selective detector, HP-5 MS 6989 Network GC system, respectively.

3 Results and discussion

3.1 Synthesis and identification of catalysts

Condensation of salicylaldehyde and histidine followed by treatment with FeCl₃·3 H₂O under aerobic conditions afforded the desired iron Fe(sal-L-his)Cl·H₂O complex (compound I, Scheme 1). As seen in the Scheme 1, compound II is obtained after addition of bipy ligand to the compound I solution. The FT-IR, UV–vis and chemical analysis of I and II were consistent with those of the authentic samples [29]. The structure of the complexes has been proposed on the basis of those provided previously [29]. To explore the magnetic properties, computation and optimization of energies and geometries of Fe(sal-L-his)Cl·H₂O and Fe(sal-L-his)(bpy)Cl complexes in doublet, quartet and sextet spin states were also carried out (see the supporting information). It was found that the sextet state for former complex, is 8.9 and 2.5 kcal/mol more stable than the doublet and quartet spin states, respectively. The results of the calculations for the latter complex showed that the intermediate spin state is 2.9 and 7.2 kcal/mol more stable than the high and low spin states in the solvent, respectively. Notably, results obtained through theoretical calculations (Kapa 5.0 and 2.8 emu/gr G 10^{−5}) are in agreement with magnetic properties of the prepared complexes.

3.2 XRD studies

The XRD patterns of Al-MCM-41, Fe(sal-L-his)complex/Al-MCM-41 and Fe(sal-L-his)(bipy)complex/Al-MCM-41 are exhibited in Fig. 1a–c. The presence of a strong peak at $2\Theta = 1.7$ for the (100) reflection is consistent with that reported before [28]. All reflections can be indexed on a hexagonal lattice. No evidence of collapsed Al-MCM-41 structure is observed with the exception of reduction in the peak intensities due to complex immobilization [26, 34].

Scheme 1 Preparation of Fe(sal-L-his)Cl·H₂O (I) and Fe(sal-L-his)(bpy)Cl(II)

Fig. 1 X-ray diffraction patterns of *a* calcined Al-MCM-41, *b* Fe(sal-L-his)complex/Al-MCM-41, *c* Fe(sal-L-his)(bpy)complex/Al-MCM-41

The powder X-ray diffraction patterns of zeolite Y and Fe(sal-L-his)complex/zeolite Y recorded at 2Θ values between 5° and 50° are presented in Fig. 2a–c. Although the XRD patterns of zeolite Y, Fe(sal-L-his)/zeolite Y and Fe(sal-L-his)(bipy)/zeolite Y are very similar but the intensities are weaker in the immobilized complexes (Fig. 2b, c). These observations indicate that the zeolite framework has not undergone a significant structural change during the complex immobilization.

Fig. 2 X-ray diffraction patterns of *a* zeolite Y, *b* Fe(sal-L-his)complex/zeolite Y, *c* Fe(sal-L-his)(bpy)complex/zeolite Y

Fig. 3 N₂ adsorption/desorption isotherms of *a* Al-MCM-41, *b* Fe(sal-L-his)complex/Al-MCM-41 and *c* Fe(sal-L-his)(bpy)complex/Al-MCM-41

3.3 N₂ adsorption/desorption studies

The N₂ adsorption/desorption isotherms of Al-MCM-41, Fe(sal-L-his)complex/Al-MCM-41 and Fe(sal-L-his)(bpy)complex/Al-MCM-41 are shown in Fig. 3a–c. Three well-defined stages may be identified: (1) a slow increase in nitrogen uptake at low relative pressure corresponding to monolayer–multilayer adsorption on the pore walls; (2) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores; (3) a plateau with a slight inclination at high relative pressures associated with multi-layer adsorption on the external surface of the crystals [32–36]. Sharp inflections at 0.2–0.4 for Al-MCM-41 and 0.4–0.7 for immobilized iron complexes are related to the capillary

condensation and confirm the existence of uniform pores [32–36]. Complex intercalated Al-MCM-41 shows lower surface area in comparison to that of the neat Al-MCM-41. The increases observed in pore diameter and lattice parameters may have arisen due to the immobilized complexes within the Al-MCM-41. The same results are obtained for zeolite Y. The iron content percentages of the immobilized complexes are presented in Tables 1, 2, respectively.

3.4 FTIR studies of immobilized iron complexes within Al-MCM-41

The FT-IR spectra of Al-MCM-41, Fe(sal-L-his)complex/Al-MCM-41 and Fe(sal-L-his)(bpy)complex/Al-MCM-41 are given in Table 3. The broad bands appearing at 3,448, 3,446 and 3,432 cm^{−1} may be attributed to the surface silanol and –OH groups of adsorbed water, respectively. Some weak peaks appear at the regions of 2,987–2,900 cm^{−1} due to C–H and N–H vibrations of immobilized complex within Al-MCM-41. The bands at 1,099–1,075 cm^{−1} are due to the asymmetric stretching vibrations of Si–O–Si bridges and those appear at 967–950 cm^{−1} arise from Si–O–Al stretching vibrations. The imine (C=N) functional group of the ligand is clearly observed as intense and well-resolved bands at 1,632 and 1,629 cm^{−1} for immobilized complexes within the Al-MCM-41. The C=C vibrations also appear at the regions 1,450 and 1,400 cm^{−1} (Fig. 4).

3.5 UV–vis spectra studies

The electronic spectra of Al-MCM-41, Fe(sal-L-his)Cl•H₂O complex and Fe(sal-L-his) complex/Al-MCM-41 in ethanol are shown in Fig. 5. The spectrum of Fe(sal-L-his)Cl complex in ethanol solution displays several bands at 216, 235, 255 nm (UV), and 312, 418–495 nm (visible), consistent with those reported before [29]. The first three bands are assigned to interligand transitions, characteristic of the Schiff base due to the salicylaldimine benzenoid π – π^* . The other observed near 312 and 420 nm bands in the absorption spectra must be LMCT [29, 37–39]. After immobilization of Fe(sal-L-his)Cl•H₂O, these bands appear at the regions of 210, 221, 248, 302, 411 and 501 nm, respectively. Similar results were obtained for immobilized Fe(sal-L-his)(bpy) complex (Table 4).

3.6 Magnetization studies

In order to study the magnetic properties, the hysteresis loops of Fe(sal-L-his)complex and Fe(sal-L-his)(bpy) complexes were investigated at room temperature using vibrating sample magnetometry (VSM) and magnetization curves as shown in Fig. 6A, B, respectively. Based on the obtained results, both complex show superparamagnetic

Table 1 Textural parameters, 'd' values, lattice parameters (100) and iron content of Al-MCM-41 samples

Samples	BET (m ² g ⁻¹)	Pore volume (mL g ⁻¹)	Average pore diameter (nm)	d value (Å)	Lattice parameter (Å)	Fe (%)
Al-MCM-41	1,473	0.9601	2.053	37.57	43.38	0.00
Fe(sal-L-his)complex/Al-MCM-41	1,214	1.091	2.140	39.06	45.10	1.07
Fe(sal-L-his)(bpy) complex/Al-MCM-41	1,109	0.9623	2.143	38.43	44.37	0.76

Table 2 Textural parameters, 'd' values and iron content of zeolite Y samples

Material	BET (m ² g ⁻¹)	Pore volume (mL g ⁻¹)	d value (Å)	Fe (%)
Zeolite Y	596	0.03826	14.71	0
Fe(sal-L-his)complex/zeolite Y	549.3	0.04976	14.69	0.97
Fe(sal-L-his)(bpy)complex/zeolite Y	512.8	0.04594	14.64	0.71

Table 3 FT-IR band assignments (cm⁻¹) for Al-MCM-41 and Al-MCM-41 with immobilized complexes

Catalyst	Si-OH	(Si-O-Si) _{asy}	(Si-O-Si) _{as/sy}	(Si-O-Si) _b	C=N	C=C
Al-MCM-41	3,448	1,075	958,801	459	—	—
Fe(sal-L-his)/Al-MCM-41	3,446	1,099	960,802	468	1,632	1,400
Fe(sal-L-his)bpy/Al-MCM-41	3,432	1,077	966,801	461	1,629	1,450

Fig. 4 N₂ adsorption/desorption isotherms of *a* zeolite Y, *b* Fe(sal-L-his)/zeolite Y and *c* Fe(sal-L-his)(bpy) complex/zeolite Y

properties at low field although the Kapa of the former and the latter are 5.00 and 2.80, respectively. The consistency of these results with those of spin multiplicities obtained from theoretical calculations (see the supplementary) is notable [29].

3.7 Reaction conditions

The oxidation reactions were carried out in the presence of Fe(sal-L-his)complex/Al-MCM-41 as catalyst at different

Fig. 5 The UV-vis spectra of *a* Al-MCM-41, *b* Fe(sal-L-his)complex/Al-MCM-41 and *c* Fe(sal-L-his)Cl·H₂O

times using cyclohexane as the representing substrate in order to choose the best reaction time. The results are presented in Fig. 7. As seen, cyclohexane is mostly oxidized within 6 h, beyond which no considerable oxidation occurs during the next 4 h. It was also found that using 0.1 g of catalyst is good enough for running the reactions when cyclohexane is a substrate (Fig. 8).

Oxidation results obtained for cyclohexane, methyl cyclohexane, cyclooctane and adamantane in CH₃CN using H₂O₂ as oxidant in the presence of 0.1 g of Fe(sal-L-his)complex/zeolite Y, Fe(sal-L-his)(bipy)complex/zeolite Y, Fe(sal-L-his)complex/Al-MCM-41 and Fe(sal-L-his)bipy complex/Al-MCM-41 are given in Tables 5, 6, 7 and 8, respectively. Identification of the products was carried out

Table 4 UV–vis data of iron complexes before and after immobilization within nanoreactors of Al-MCM-41

Compound	$\lambda_{\max}$ (ϵ , $M^{-1} \text{ cm}^{-1}$) in ethanol		
	Interligand transition phenyl ring	$\pi \rightarrow \pi^*$ (C=N)	LMCT
Fe(sal-L-his)Cl•H ₂ O	216 (1,466), 235 (1,400)	255 (913)	312 (400), 420 (200), 480 (150)
Fe(sal-L-his)/Al-MCM-41	210, 221	248	302, 411, 468
Fe(sal-L-his)bpyCl	204 (2,562), 234 (2,125)	284 (2,000)	338 (375), 501 (187)
Fe(sal-L-his)bpy/Al-MCM-41	200, 226	256	332, 495

Fig. 6 Magnetization curve of *A* Fe(sal-L-his) complex and *B* Fe(sal-L-his)(bpy) complex, inset Kapa versus magnetic field for *a* Fe(sal-L-his) complex and *b* Fe(sal-L-his)(bpy) complex has been reported **Fig. 7** Effect of time on cyclohexane oxidation with H₂O₂ catalyzed by [Fe(sal-L-his) complex]/Al-MCM-41

by comparison of the GC-Mass spectra with those of the authentic samples. As expected, all catalysts are active with about 47–100 % conversion. We have included the effect

Fig. 8 Effect of the amount of Fe(sal-L-his) complex/Al-MCM-41 on cyclohexane conversion

of [Fe(sal-L-his)ClH₂O]•3H₂O and [Fe(Sal-L-his)(bipy)Cl] as homogeneous catalysts in Table 5 in order to make the comparisons more convenient. It was also found that no significant conversion of cyclohexane was observed with Al-MCM-41 and zeolite Y void of complexes. The catalytic activity of the recovered Fe(sal-L-his)/Al-MCM-41 was similar to that of the fresh catalyst. Notably, no desorption was observed during the course of reactions. Particularly significant is the effect of Fe(sal-L-his)(bpy) complex/Al-MCM-41 as catalyst on cyclooctane oxidation, with 90 % conversion and 85 % selectivity toward the formation of cyclooctanone as the major product (Table 7). The oxidation results of adamantane to adamantane-1-ol, and adamantane-2-one are presented in Table 8. The maximum amount of conversion and selectivity occurs in the presence of Fe(sal-L-his)(bpy) complex/Al-MCM-41 as catalyst (Table 8, entry 20). Compared to other substrates, oxidation reaction of adamantane proceeds less efficiently (98 % conversion within 24 h).

The stability of the Fe(sal-L-his)(bpy) complex/Al-MCM-41 was also studied by recycling the recovered catalyst and determination of the metal content using atomic absorption spectroscopy. The iron content was shown to be 0.755 % with very little change (0.005 %), with respect to the initial catalyst iron content (0.760 %). As shown in Table 5, entry 8, the recovered Fe(sal-L-his)(bpy) complex/Al-MCM-41 catalyzed the oxidation of cyclohexane with a minor decrease in conversion although with the same selectivity toward the formation of the corresponding oxides.

Table 5 Results of cyclohexane oxidation with H₂O₂ in the presence of iron catalysts

Entry	Catalyst	Conversion (%)	Cy-OH ^a (%)	Cy=O ^b (%)	Others ^c (%)	TON
1	Fe(sal-L-his)complex/zeolite Y	65	30	60	10	751
2	Fe(sal-L-his)complex/Al-MCM-41	69	25	63	12	722
3	Fe(sal-L-his)(bpy)complex/zeolite Y	92	28	63	9	1,460
4	Fe(sal-L-his)(bpy)complex/Al-MCM-41	100	27	63	10	1,481
5	[Fe(sal-L-his)Cl•H ₂ O]	47	46	54	–	543
6	[Fe(sal-L-his)(bpy)Cl]	55	30	70	–	873
7	Fe(sal-L-his)complex/zeolite Y ^d	61	24	63	12	639
8	Fe(sal-L-his)(bpy)complex/Al-MCM-41 ^e	95	26	64	10	1,400

Reaction conditions: catalyst (0.1), substrate (20 mmol), H₂O₂ (30 %, 36 mmol), solvent (CH₃CN, 5 mL, under reflux), time (6 h), TON is the mmol of products to the mmol of the iron present in catalyst

^a Cy-OH; cyclohexanol

^b Cy=O; cyclohexanone

^c Others as minor products are 4-hydroxy cyclohexanone and 1,4-cyclohexanedione

^{d, e} Reusability results

Table 6 Results of methyl cyclohexane oxidation with H₂O₂ in the presence of iron catalysts

Entry	Catalyst	Conversion (%)	Me-Cy-OH ^a (%)	Me-Cy=O ^b (%)	TON
9	Fe(sal-L-his)complex/zeolite Y	31	38	62	358
10	Fe(sal-L-his)complex/Al-MCM-41	40	34	66	418
11	Fe(sal-L-his)(bpy)complex/zeolite Y	51	19	81	809
12	Fe(sal-L-his)(bpy)complex/Al-MCM-41	57	20	80	840

Reaction conditions are similar to Table 5

^a Methyl cyclohexanol

^b Methyl cyclohexanone

Table 7 Results of cyclooctane oxidation with H₂O₂ (30 %) in the presence of iron catalysts

Entry	Catalyst	Conversion (%)	Cy-Ol ^a (%)	Cy=O ^b (%)	Others ^c (%)	TON
13	Fe(sal-L-his)complex/zeolite Y	51	10	60	9	589
14	Fe(sal-L-his)complex/Al-MCM-41	68	9	63	5	712
15	Fe(sal-L-his)(bpy)complex/zeolite Y	69	9	82	5	1,095
16	Fe(sal-L-his)(bpy)complex/Al-MCM-41	90	15	85	0	1,075

^a Cyclooctanol

^b Cyclooctanone

^c Unidentified

The final note worthwhile to be emphasize is the high heterogeneous character of the Fe(sal-L-his)(bpy)complex/Al-MCM-41 catalyst used in this work. The experimental evidences ruled out the participation of any leached active species from the solid catalysts in the oxidation reactions.

3.8 Mechanism of catalytic activity

Cyclohexane oxidation using H₂O₂ as oxidant seems to proceed via a radical mechanism initiating from transition metal catalyzed decomposition of H₂O₂. It is generally accepted that Fe^{IV}=O and HO or HOO radicals can be

generated via the reaction between hydroperoxide and the ferric ion (Scheme 2, Eqs. 2a and 2b) [40–43]. The key radical intermediates are obtained through the radical chain reactions (Scheme 2, Eqs. 3, 4 and 5). Cyclohexanol and cyclohexanone are generated via the homolytic (Eq. 6) and heterolytic (Eq. 7) decompositions, respectively. Cyclohexanol and cyclohexanone can also be produced via a Russell termination reaction [44] (Eq. 8).

Compared to Fe(sal-L-his)complex/Al-MCM-41 (Table 5, entry 2), the results presented in Table 5 clearly indicate the enhanced catalytic activity of Fe(sal-L-his)(bpy)complex/Al-MCM-41 (entry 4). The oxidation step (Eq. 2a) is generally

Table 8 Results of adamantane oxidation with H₂O₂ in the presence of iron catalysts

Entry	Catalyst	Conversion (%)	Ad-OH ^a (%)	Ad=O ^b (%)	TON	C ³ -H/C ² -H ^c
17	Fe(sal-L-his)complex/zeolite Y	73	27	73	42	1.11
18	Fe(sal-L-his)complex/Al-MCM-41	82	28	72	65	1.17
19	Fe(sal-L-his)(bpy)complex/zeolite Y	83	28	72	44	1.17
20	Fe(sal-L-his)(bpy)complex/Al-MCM-41	98	30	70	70	1.29

Reaction conditions: catalyst (0.1 g), substrate (1 mmol), H₂O₂ (30 %, 25 mL), solvent (CH₃CN, 15 mL, under reflux), time (24 h), TON is the mmol of products to the mmol of the iron present in catalyst

^a Adamantane-1-ol

^b Adamantane-2-one

^c The selectivity parameter defined by the relative reactivity of tertiary C-H to secondary C-H bonds = (%Ad-OH/4)/(%Ad=O/12)

Scheme 2 Suggested mechanism for the oxidation of cyclohexane

assumed to be facilitated by suitable ligands capable of stabilizing the hypervalent state of the iron-oxo species by resonance. Since Collman and co-workers have reported that oxygen-radical Ph₂NH inhibits an oxidation [45], we used it to have insight into the reaction mechanism. Using an equimolar of trapping agent completely suppressed cyclohexane oxidation based on the GC analysis of the product mixture, which showed that cyclohexane has been left intact.

4 Conclusions

The iron Schiff base complexes immobilized within of Al-MCM-41 and zeolite Y designated as Fe(sal-L-his)complex/Al-MCM-41, Fe(sal-L-his)complex/zeolite Y, Fe(sal-L-his)(bipy)complex/Al-MCM-41 and Fe(sal-L-his)(bipy)complex/zeolite Y, were prepared and characterized. It was found that Fe(sal-L-his)(bipy)complex/Al-MCM-41 successfully catalyze the oxidation of cyclooctane to cyclooctanol and cyclooctanone with 90 % conversion and 85 % selectivity toward the formation of ketone. Similarly, cyclohexanol and cyclohexanone were identified as the major products in the oxidation of cyclohexane. When methyl cyclohexane is used as substrate only methyl cyclohexanol and methyl cyclohexanone are formed. When adamantane is as substrate, the oxidation process is slow relative to the other substrate. These

points together with utilization of H₂O₂ as green oxidant and observation of no metal desorption during the course of reactions are the highlights of this presentation.

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