



# Epoxidation of Alkenes with Molecular Oxygen Catalyzed by Immobilized $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{bpy})_2\text{Cl}_2$ Complexes within Nanoreactors of Al-MCM-41

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**Abstract:** Cobalt complexes with different ligands such as bipyridine, and acetylacetonate were immobilized within nanoreactors of Al-MCM-41, designated as  $\text{Co}(\text{acac})_2/\text{Al-MCM-41}$  and  $\text{Co}(\text{bipy})_2^{2+}/\text{Al-MCM-41}$ . The immobilized complexes were characterized by XRD,  $\text{N}_2$ -adsorption desorption, FT-IR and UV-Vis techniques. It was found that  $\text{Co}(\text{bipy})_2^{2+}/\text{Al-MCM-41}$  and  $\text{Co}(\text{acac})_2/\text{Al-MCM-41}$  successfully catalyze the oxidation of norbornene, styrene, cis-stilbene, trans-stilbene, and cyclohexene with 68% to 100% conversion and 41% to 90% selectivity toward the corresponding epoxides. No desorption was observed during the course of reactions.

**Keywords:** Cobalt complexes, Immobilization, Al-MCM-41, Epoxidation, Molecular oxygen.

## Introduction

Catalytic oxidation is a key technology for converting petroleum feedstocks to useful chemicals such as alcohols, carbonyl compounds and epoxides. Epoxides are important synthetic intermediates for the synthesis of oxygen containing natural or unnatural compounds<sup>1-2</sup>. Many transition metal complexes such as Co, Ti, Mn, V and Mo have been used as catalyst for high selectivity epoxidation of cyclic olefins<sup>2</sup>. Cobalt complexes as the efficient oxyfunctionalization catalysts of alkenes and alkanes have been the subject of intense research in the last two decades. Different types of cobalt complexes such as Cobalt (II) Schiff base complexes<sup>3-4</sup>, cobalt(II) porphyrines<sup>5</sup> and metallophthalocyanines of cobalt complexes<sup>6-7</sup>, have been prepared and used for epoxidation reactions. Methods including incorporation of cobalt species within microporous or mesoporous frameworks<sup>8-9</sup> and fixation of active cobalt complexes on appropriate supports could provide selective and stable catalysts with facile recovery and recycling<sup>10-13</sup>. Immobilization of Co (salen) and Co perfluorophthalocyanine on MCM-41 and on modified MCM-41 have been studied for oxidation of alkenes and alkanes<sup>14-17</sup>.

In this study, attempts have been made to prepare the alkenene epoxidation catalyst via immobilization of bipyridine and acetylacetonate cobalt(II) complexes within Al-MCM-41 as anionic based lattice with positive charge, would be a good candidate for immobilization of different cobalt complexes.

## Experimental

FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR Spectrometer using KBr pellets. The UV-Vis measurements were performed on a double beam UV-Vis Perkin Elmer Lambda 35 spectrophotometer. X-ray powder diffraction (XRD) data were recorded on a Seifert XRD 3003 PTS diffractometer with Cu  $\kappa\alpha_1$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). Nitrogen sorption studies were performed at liquid nitrogen temperature (77 K) using a Quanta chrome Nova Win 2, version 2.2. Oxidation products were analyzed by GC and GC-MS using an Agilent 6890 series with FID detector, HP-5, 5% phenylmethylsiloxane capillary and an Agilent 5973 Network, mass selective detector, HP-5 MS6989 Network GC system, respectively. Atomic absorption data obtained by double beam GBC (909).

### *Preparation of catalysts*

The Al-MCM-41 (Si/Al=50) was prepared according to previously reported method<sup>18</sup>. Co(bpy)<sub>2</sub>Cl<sub>2</sub>·3H<sub>2</sub>O and Co(acac)<sub>2</sub> complexes were prepared according to the previously described procedure<sup>19-20</sup>. Al-MCM-41 (0.5 g in 5 mL methanol) was added to the desired complex (0.1 g in 5 mL methanol). The mixture was refluxed for 24 h while stirring. The solid was filtered, washed with hot methanol and the resultant Co(acac)<sub>2</sub> /Al-MCM-41 or Co(bipy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 were dried in air at room temperature. The percentage of cobalt determined by AAS, were 0.15% and 0.49% respectively.

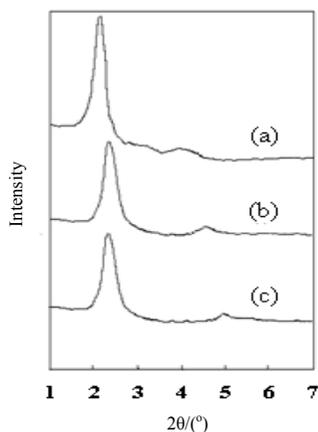
### *Catalytic epoxidation, general procedure*

All epoxidation reactions of the alkenes were carried out in a round bottom flask equipped with a magnetic stirrer and a water-cooled condenser under atmospheric pressure. Typically, a mixture of catalyst (0.2 g) and substrate (20 mmol, dissolved in 10 mL CH<sub>3</sub>CN) was added to the reaction flask with slow stirring. After a few minutes, isobutyraldehyde (24 mmol) was added and the mixture refluxed for 12 h under O<sub>2</sub> atmosphere. The solid was then filtered and washed with fresh solvent. The filtrate was subjected to GC and GC mass analysis.

## Results and Discussion

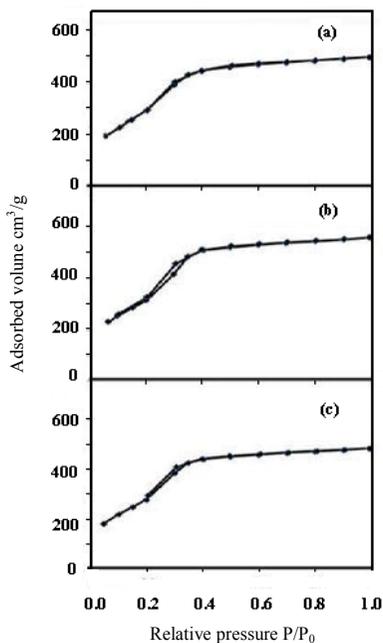
### *Spectral characteristics*

The XRD patterns of calcined Al-MCM-41, Co(acac)<sub>2</sub>/Al-MCM-41 and Co(bpy)<sub>2</sub> complex/Al-MCM-41 are shown in Figure 1. The XRD pattern of Al-MCM-41 was consistent with that reported before<sup>18</sup>. As seen, the peaks  $d_{100}$  of Co(acac)<sub>2</sub>/Al-MCM-41 and Co(bpy)<sub>2</sub> complex/Al-MCM-41 shift to higher angles with lower intensities. These changes indicate that the pore surface silanol groups of Al-MCM-41 have reacted with Co(acac)<sub>2</sub> and Co(bpy) Cl<sub>2</sub><sup>21-22</sup>.



**Figure 1.** XRD patterns of (a) Al-MCM-41, (b)  $\text{Co}(\text{acac})_2/\text{Al-MCM-41}$  and (c)  $\text{Co}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$ .

The nitrogen adsorption-desorption isotherm plots of Al-MCM-41,  $\text{Co}(\text{acac})_2/\text{Al-MCM-41}$  and  $\text{Co}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$  (Figure 2) are consistent with mesoporous alumina (type IV). The type IV isotherm indicates that at low pressure  $P/P_0$ , adsorption takes place as a thin layer on the walls (monolayer coverage). In addition, the height of inflection in nitrogen adsorption isotherm plots of  $\text{Co}(\text{acac})_2/\text{Al-MCM-41}$  and  $\text{Co}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$  are smaller than that of Al-MCM-41. It is attributed to the reduced surface area from 1343 to 1247 and 1279  $\text{m}^2/\text{g}$  respectively (Table 1). Thus, it can be concluded that the complexes are included into the Al-MCM-41 pores<sup>23</sup>.



**Figure 2.** Nitrogen adsorption-desorption isotherms : (a) Al-MCM-41, (b)  $\text{Co}(\text{acac})_2/\text{Al-MCM-41}$  and (c)  $\text{Co}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$ .

**Table 1.** Texture parameters samples taken from XRD and nitrogen adsorption studies.

Sample	$d_{100}(A^0)$	$a_0(A^0)$	$S_{BET}, m^2/g$	$V_{BJH}, mL/g$	$D_{BJH}(A^0)$
Al-MCM-41	38.4	44.3	1343	0.9	22.3
Co(acac) <sub>2</sub> /Al-MCM-41	35.32	40.78	1247	0.81	21.21
Co(bpy) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	35.85	41.39	1279	0.82	20.89

<sup>a</sup> $a_0$ : Lattice parameter,  $V_{BJH}$ : pore volume, <sup>c</sup> $S_{BET}$ : surface area, <sup>d</sup> $D_{BJH}$ : average pore diameter.

The FT-IR spectra of Al-MCM-41, Co(acac)<sub>2</sub>/Al-MCM-41 and Co(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 are given in Table 2. The broad band appearing at 3500 to 3400 cm<sup>-1</sup> may be attributed to the surface Si-OH, Al-OH and -OH groups of adsorbed water. The bands at 1100 and 967 to 950 cm<sup>-1</sup> are due to the asymmetric and symmetric stretching vibrations of Si-O-Si and Si-O-Al bridges respectively<sup>14,18-24</sup>. The stretching frequency of the C=O and C=N groups of the immobilized Co(acac)<sub>2</sub> and Co(bpy)<sub>2</sub> complexes within the Al-MCM-41 appear at 1591 and 1631 cm<sup>-1</sup> respectively<sup>26-27</sup>. Some of the complexes vibrations could not be observed probably because it is masked by strong and broad Si-O-Si band position in the region of 1390-900 cm<sup>-1</sup>. The observation of three new bands in the C-H stretching vibrations range at 2960, 2932 and 2857cm<sup>-1</sup>, consistent with C-H of the free Co(acac)<sub>2</sub> complex bands suited at 3000, 2971, and 2923cm<sup>-1</sup> suggest that the Co(acac)<sub>2</sub> complex is immobilized in the support. The same results are observed for immobilized Co(bpy)<sub>2</sub>Cl<sub>2</sub> complex.

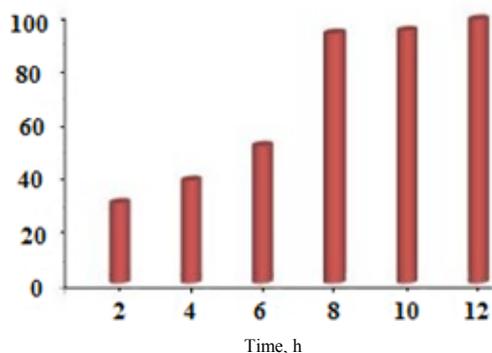
**Table 2.** FT-IR band assignments in wavenumbers (cm<sup>-1</sup>) obtained for Al-MCM-41 and immobilized cobalt complexes within the nanoreactors of Al-MCM-41.

Catalyst	$\nu_{OH}$ (Si-OH)	$\nu_{CH}$ (CH <sub>2</sub> )	$\nu_{CO}$ or CN	$\nu_{as}$ (Si-OSi)	$\nu_{sy}$ (Si-OSi)
Al-MCM-41	3427	-	-	1074-957	805
Co(acac) <sub>2</sub> / Al-MCM-41	3445	3254-2993	1523-1591	1074-957	799
Co(bipy) <sub>2</sub> / Al-MCM-41	3421	3300-3050	1631	1080-953	812

### *Epoxidation of alkenes catalyzed by Cobalt complexes/Al-MCM-41*

Optimization of the epoxidation reaction times were carried out in the presence of 0.1 g of the cobalt complex/Al-MCM-41 as catalyst using trans-stilbene as the representing substrate. The results are presented in Figure 3. As seen, trans-stilbene is mostly oxidized during 8 h, beyond which no further oxidation occurs during the next 4 h.

Since the epoxidation of alkenes by O<sub>2</sub> is an important research direction, we described to examine this reaction with the combination O<sub>2</sub> and isobutyraldehyde as oxidant and co-reductant in the presence of Co(acac)<sub>2</sub>/Al-MCM-41 and Co(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 as catalysts. Identification of the products was carried out by comparison of product mass patterns with those of the authentic samples.



**Figure 3.** The effect of time on epoxidation of trans-stilbene using cobalt (acac)<sub>2</sub>/Al-MCM-41 as catalyst.

As seen in Table 3, the oxidation reactions of norbornene, styrene, cis-stilbene, trans-stilbene, cyclohexene have proceeded with 68% to 100% conversion and 90% to 41% selectivity toward the corresponding epoxides using Co(acac)<sub>2</sub>/Al-MCM-41 as catalyst. The oxidation result carried out in the presence of Co(bipy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 as catalyst are given in Table 4.

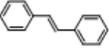
**Table 3.** Epoxidation results of some olefins with molecular oxygen in the presence of Co(acac)<sub>2</sub>/Al-MCM-41 as catalyst.

Substrate	Conversion, %	Epoxide, %	TON
 trans-stilbene	99	80	60
 cis-stilbene	99	79 <sup>b</sup>	60
 styrene	93	41 <sup>c</sup>	1120
 cyclohexene	100	61 <sup>d</sup>	1204
 norbornene	90	90	819

<sup>a</sup>mmol of product(s) per mmol of complex per h, <sup>b</sup>trans (79%), <sup>c</sup>benzaldehyde as the side product was formed, <sup>d</sup>a mixture of 2-cyclohexene-1-ol and 2-cyclohexene-1-one was formed as the side products.

The last worthwhile point to be emphasized is the highly heterogeneous character of the cobalt complex/Al-MCM-41 catalysts used in this work. Experimental evidence ruled out the effect of the participation of any active species, leached from the solid catalysts in the epoxidation reactions. Oxidation reactions of trans-stilbene under the effect of the recovered Co(acac)<sub>2</sub>/Al-MCM-41 and Al-MCM-41 void of complexes as catalysts were found to proceed with 85% and 5% conversion toward the corresponding epoxide.

**Table 4.** Epoxidation results of some olefins with molecular oxygen in the presence of  $\text{Co}(\text{bipy})_2^{2+}/\text{Al-MCM-41}$  as catalys.

Substrate	Conversion, %	Epoxide, %	TON <sup>a</sup>
 trans-stilbene	87	70	171
 cis-stilbene	97	73 <sup>b</sup>	173
 styrene	94	58 <sup>c</sup>	3686
 cyclohexene	100	79 <sup>d</sup>	3921
 norbornene	68	97	2666

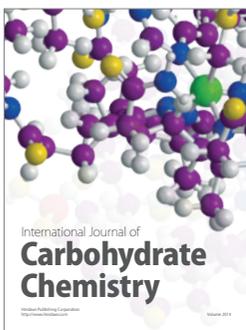
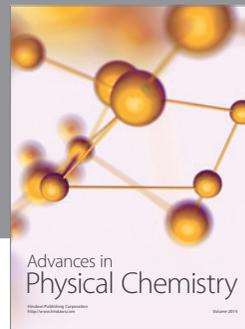
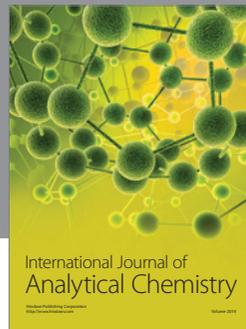
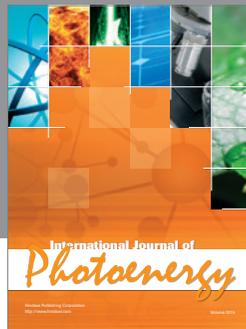
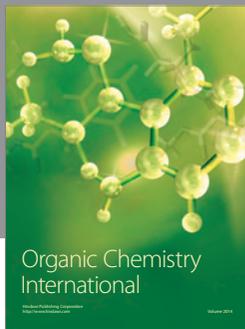
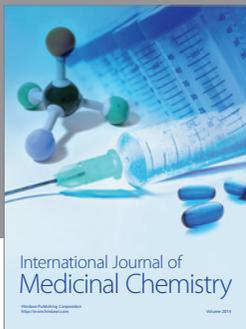
<sup>a</sup>mmol of product(s) per mmol of complex per h, <sup>b</sup>a mixture of trans (73%) and cis (27%) was formed, <sup>c</sup>benzaldehyde as the side product was formed, <sup>d</sup>a mixture of 2-cyclohexene-1-ol and 2-cyclohexene-1-one and 1,2 cyclohexanediol were formed as the side products.

We believe that epoxidation mechanism under our catalysis system is similar to that studied by Nam *et al.*<sup>26</sup> for the epoxidation of olefins using cobalt(II) porphyrins or cobalt (II) cyclams complexes as catalysts (Scheme 1). As seen in Scheme 1, path a, isopropylacyl radical generated in situ via electron transfer from aldehyde to  $\text{L}_n\text{Co}^{2+}$  affords the corresponding peroxide radical in reaction with  $\text{O}_2$ . Subsequent addition of this radical to alkenes such as stilbene, styrene, cyclohexene and norbornene followed by back electron transfer from complex radical anion to peroxy radical intermediates regenerates the catalyst with the formation of the corresponding epoxide and isobutyric acid. Several points need to be elaborated with respect to the results depicted in Tables 3 and 4:

- Either cis or trans-stilbene affords the corresponding trans-epoxide. This seems to be due to the higher thermodynamic stability of trans-epoxide in which the phenyl groups are located anti with respect to each other.
- Oxidation of styrene gives a mixture of styrene epoxide and benzaldehyde. As depicted in Scheme 1, path b, styrene epoxide seems to have partly undergone further oxidation to benzaldehyde as the main byproduct. Such process has been observed previously by us and others<sup>27-28</sup>.
- Since cyclohexene contains active allylic hydrogens, there seem to be a competition reaction available to it, in which it behaves as an acyl radical scavenger, regenerating the isopropyl aldehyde by hydrogen atom transfer. The in situ generated cyclohexene radical in turn in reaction with  $\text{O}_2$  affords 2-cyclohexene-1-ol and 2-cyclohexene-1-one as the byproducts (Scheme 1, path c).
- Although norbornene contains allylic hydrogens, it cannot have a competition reaction similar to cyclohexene, due to the formation of a highly unstable bridgehead radical intermediate (Scheme 1, path d)<sup>29</sup>. Therefore, norbornene epoxidation proceeds conclusively, affording the corresponding epoxide in 90 to 97% yields (Tables 3 and 4).



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