

## Immobilized Vanadium Compounds within Nanoreactors of Al-MCM-41 as Catalyst for Epoxidation of Alkenes

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### Abstract

$\text{VO}^{2+}$  and its complexes with ethylenediamine (en), acetylacetonate (acac), 2, 2'-bipyridine(bpy) ligands, immobilized within nanoreactors of Al-MCM-41 designated as  $\text{VO}^{2+}/\text{Al-MCM-41}$  or  $\text{VOL}_2/\text{Al-MCM-41}$ , were prepared and characterized by X-ray powder diffraction (XRD), FT-IR, BET nitrogen adsorption-desorption and chemical analysis techniques.  $\text{VO}^{2+}/\text{Al-MCM-41}$  and  $\text{VOL}_2/\text{Al-MCM-41}$  were found to catalyze the epoxidation of *trans*-stilbene, norbornene, and geraniol with aqueous hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in refluxing acetonitrile with 30-80% conversion and up to 98% selectivity toward the formation of the corresponding epoxides. On the other hand, under similar conditions, these alkenes underwent epoxidation with 50 to 99% conversion and up to 100 % selectivity in the presence of  $\text{VO}(\text{acac})_2/\text{Al-MCM-41}$  with *tert*-butylhydroperoxide (TBHP) as oxidant.

**Keywords:** Al-MCM-41; Vanadium complexes; Epoxidation of alkenes; Geraniol

### Introduction

Liquid phase oxidation is performed in two ways in homogeneous and heterogeneous systems. In heterogeneous system, oxidants such as  $\text{H}_2\text{O}_2$  or TBHP are alternate to traditional oxidation employing inorganic oxidants in stoichiometric amounts in industrial organic synthesis [1]. At present, there is a tendency to the replacement of homogeneous process (in which recovery and recycling cause problems) by heterogeneous ones. In order to achieve unique advantages of both homogeneous and heterogeneous systems at large scale, efforts have been focused towards heterogenization of transition metal containing catalysts on different solid supports such as silica [2], polymers [3] microporous [4,5] and mesoporous

materials [6-7]. Micelle-templates inorganic mesoporous silica and related materials have emerged in the past decade as very promising support materials owing to their unique physico-chemical properties (very high surface area, pore volume, and narrow pore size distribution) [8]. Mesoporous molecular sieves of M41S, have been modified by transition metals via post synthesized grafting or tethering [9] or via inclusion of metal during the synthesis (isomorphous substitution) [9,10]. Among different transition metal complexes which have been immobilized within mesoporous materials [6], there have been great attentions to vanadium complexes because of the known excellent catalytic features. Vanadium complexes with nitrogen or oxygen containing ligands have been widely used as model compounds for mimicking the catalytic

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properties of monooxygenases [11,12]. The development of heterogenized vanadium compounds as active oxidation catalysts via immobilization on solid supports such as zeolitic molecular sieves and mesoporous materials in a number of liquid phase oxidations is therefore of great interest to the catalytic chemistry community [4-7,13,14].

In this study, we have prepared the immobilized  $\text{VO}_2^+$  or  $\text{VO}^{2+}$  complexes with en, acac, and bpy ligands within the nanoreactors of Al-MCM-41 as a hydrophobic support and hydrogen peroxide or TBHP as oxidants for oxidation of a number of organic alkenes.

### Materials and Methods

With the exception of vanadyl sulfate and geraniol which obtained from Aldrich, ethylenediamin, acetylacetone, 2,2'-bipyridine, tetraethylammonium hydroxide, cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate, aluminum isopropoxide, ethanol, acetonitrile, dimethyl formamid, 30% aqueous  $\text{H}_2\text{O}_2$ , 80% TBHP in di-*tert*-butyl ether, norbornene, styrene and *trans*-stilbene with commercial reagent grade were purchased from Merck Chemical Company and used without further purification.

### Physical Measurements

FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR Spectrometer. Electronic spectra for solid catalysts were recorded in Nujol on a Perkin Elmer Lambda 35 UV-vis spectrophotometer. The products were analyzed by GC and GC- Mass using Agilent 6890 Series, with FID detector, HP-5, 5% phenylmethylsiloxane capillary and Agilent 5973 Network, mass selective detector, HP-5 MS 6989 Network GC system,

respectively. X-ray powder diffraction (XRD) data were recorded on a diffractometer type, Seifert XRD 3003 PTS,  $\text{CuK}\alpha_1$  radiation ( $\lambda=0.1540$  nm). Nitrogen sorption studies were performed at liquid nitrogen temperature using Quanta chrome Nova 2200, version 7.11 Analyzer. Chemical analysis of samples was carried out with Perkin-Elmer atomic absorption spectrometer (AAS).

### Preparation of Catalysts

#### Synthesis of Al-MCM-41

Al-MCM-41 was synthesized using the previously reported method [15]. Tetraethylorthosilicate (22.3 ml) was mixed with aqueous aluminum isopropoxide solution (0.68g in 5 ml). The mixture was stirred for 30 min and enough 10% aqueous tetraethylammonium hydroxide solution was added with continuous stirring for another 30 min until the gel formation (pH = 11). Cetyltrimethylammonium bromide aqueous solution (7.2g in 60 ml) was then added drop-wise to the mixture so that the gel was changed into suspension. The suspension was transferred into a teflon-lined steel autoclave and heated to 150 °C for 48 h. After cooling to room temperature, the solid was separated by filtration, washed with deionized water and ethanol, and dried in air at 100 °C for 1 h. It was finally calcined under air flowing at 540 °C for 6 h.

#### Synthesis of Vanadium Complexes

$\text{VO}(\text{bpy})_2^{2+}$ ,  $\text{VO}(\text{en})_2^{2+}$  and  $\text{VO}(\text{acac})_2$  complexes were prepared according to the procedure described previously [16,17]. The CHN and FT-IR results of the prepared complexes are given in Tables 1 and 2 respectively. The obtained results are consistent with those of reported before [16, 17].

**Table 1.** Chemical analysis results of  $\text{VO}^{2+}/\text{Al-MCM-41}$  and  $\text{VO}_2/\text{Al-MCM-41}$

Chemical Formula	Found (calculated)			
	V(%)	N(%)	C(%)	H(%)
$\text{VO}(\text{bpy})_2\text{SO}_4$	10.51 (10.73)	11.55 (11.78)	50.22 (50.48)	3.31 (3.36)
$\text{VO}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$	1.89 (1.89)	2.18 (2.08)	9.24 (8.90)	0.81 (0.60)
$\text{VO}(\text{acac})_2$	18.91 (19.08)	-	32.52 (32.67)	5.61 (5.98)
$\text{VO}(\text{acac})_2/\text{Al-MCM-41}$	0.91 (0.91)	-	2.51(2.16)	0.51 (0.30)
$\text{VO}(\text{en})_2\text{SO}_4$	17.92 (18.01)	19.70 (19.77)	16.80 (16.95)	5.60 (5.65)
$\text{VO}(\text{en})_2^{2+}/\text{Al-MCM-41}$	0.34 (0.34)	0.45 (0.40)	0.51 (0.32)	0.21 (0.11)

### Immobilization of Vanadyl Sulfate within Al-MCM-41

Ethanol solution of  $\text{VOSO}_4$  (1.2 mmol in 10 ml) was added to ethanolic suspension of Al-MCM-41 (1 g in 10 ml), and the resultant mixture was refluxed for 8 h. The mixture was then filtered and washed with hot ethanol. The percentage of vanadium was determined by AAS to be 1.60%.

### Immobilization of Vanadium Complexes within Al-MCM-41

$\text{VO}(\text{bpy})_2^{2+}$ ,  $\text{VO}(\text{en})_2^{2+}$  and  $\text{VO}(\text{acac})_2$  (1.2 mmol) in ethanol (10 ml) were added to Al-MCM-41 (1 g) in ethanol (10 ml). The resultant mixtures were refluxed for 8 h. The solids were then filtered and washed with hot ethanol. Chemical analysis of the prepared catalysts are given in Table 1 are consistent with the structures.

### Oxidation of Organic Substrate

#### General Procedure

Oxidation reactions were carried out in a stirring round bottom flask fitted with a water-cooled condenser under atmospheric pressure. Typically, a mixture of catalyst (0.1 g) and substrate (20 mmol, dissolved in 10 ml of acetonitrile) was added to the reaction flask with slow stirring. After a few minutes,  $\text{H}_2\text{O}_2$  (48 mmol, 30% aqueous solution) was added and the reaction mixture was refluxed for 8 h. The solid was then filtered and washed with fresh acetonitrile. The filtrate solution was subjected to GC and GC Mass analysis.

## Results and Discussion

### Textural Properties of the Catalysts

Al-MCM-41 was prepared according to the procedure described previously. As shown in Figure 1, the X-ray powder diffraction pattern of calcined Al-MCM-41 exhibits a strong and two weak peaks. All three XRD reflections can be indexed on a hexagonal lattice. The XRD of calcined Al-MCM-41 is consistent with that of reported Al-MCM-41 XRD [15]. The XRD patterns of  $\text{VO}^{2+}/\text{Al-MCM-41}$  and  $\text{VO}_2/\text{Al-MCM-41}$  are shown in Figure 1. A decrease in the peak intensities is evident in this Figure 1. This change indicates that the Al-MCM-41 pore and surface silanol groups have reacted with vanadyl ions and vanadium complexes (Table 2).

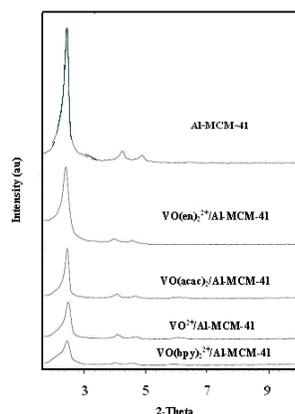
Mesoporous texture of the prepared catalysts was determined by nitrogen sorption analysis.

The specific surface areas of the Al-MCM-41, and the prepared catalysts are given in Table 2. These results

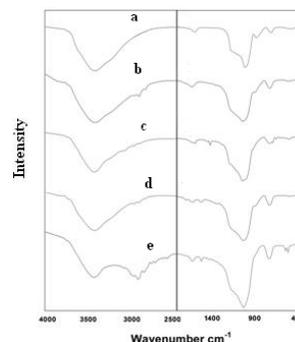
reveal that incorporation of the vanadium compounds lead to specific surface area reduction of the prepared materials.

**Table 2.** Texture parameters of samples obtained from XRD and nitrogen sorption studies

Material	XRD d value (Å)	Lattice parameter (Å)	BET specific surface area ( $\text{m}^2\text{g}^{-1}$ )
Al-MCM-41	36.32	42.08	1054.249
$\text{VO}^{2+}/\text{Al-MCM-41}$	35.57	41.17	920.4030
$\text{VO}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$	36.37	42.09	832.7620
$\text{VO}(\text{acac})_2/\text{Al-MCM-41}$	36.56	42.31	922.1921
$\text{VO}(\text{en})_2^{2+}/\text{Al-MCM-41}$	36.43	42.14	849.72



**Figure 1.** XRD of calcined Al-MCM-41,  $\text{VO}(\text{en})_2^{2+}/\text{Al-MCM-41}$ ,  $\text{VO}(\text{acac})_2/\text{Al-MCM-41}$ ,  $\text{VO}^{2+}/\text{Al-MCM-41}$  and  $\text{VO}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$ .



**Figure 2.** FTIR spectra of (a) Al-MCM-41, (b)  $\text{VO}^{2+}/\text{Al-MCM-41}$ , (c)  $\text{VO}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$  (d)  $\text{VO}(\text{acac})_2/\text{Al-MCM-41}$  and (e)  $\text{VO}(\text{en})_2^{2+}/\text{Al-MCM-41}$

**Table 3.** The FT-IR wavenumbers ( $\text{cm}^{-1}$ ) of Al-MCM-41 and vanadium complexes before and after immobilization within nanoreactors of Al-MCM-41

Catalyst	Si-OH	(Si-O-Si) <sub>sym.</sub>	(Si-O-Si)/ (Si-O-V) <sub>asym.</sub>	Si-O-Si	C-N	C=C	C-H (Stretching)
Al-MCM-41	3422	1080, 1223	960	802	–	–	–
VO <sup>2+</sup> /	3424	1091, 1223	968	805	–	–	–
Al-MCM-41 VO(bpy) <sub>2</sub> SO <sub>4</sub>	–	–	–	–	1602	1442	3079
						1317	3034
VO(bpy) <sub>2</sub> <sup>2+</sup> /	3425	1097, 1238	972	807	1605	1443	3078
Al-MCM-41						1474	3117
VO(acac) <sub>2</sub>	–	–	–	–	–	1556	2969
							3000
VO(acac) <sub>2</sub> /	3445	1088, 1203	969	804	–	1535	2875
Al-MCM-41							2937
VO(en) <sub>2</sub> SO <sub>4</sub>	–	–	–	–	1085	–	2867
							2931
VO(en) <sub>2</sub> <sup>2+</sup> /	3425	1086, 1203	953	810	1085	–	2865
Al-MCM-41							2932

### FT-IR Studies

The FT-IR results of Al-MCM-41 and vanadium complexes before and after immobilization within Al-MCM-41 are given in Table 3. The appearance of broad bands at 3400 to 3500  $\text{cm}^{-1}$  may be attributed to the surface silanols and adsorbed water –OH groups. The absorption bands display at 1080 to 1100 and 1200 to 1223  $\text{cm}^{-1}$  due to asymmetric stretching vibrations of Si-O-Si bridges, and those appear at 950 to 980  $\text{cm}^{-1}$  arise from Si-O-Al, VO-Si and V=O stretching vibrations (Fig. 2) [9, 15].

### Oxidation of Alkenes Catalyzed by VO<sup>2+</sup>/Al-MCM-41 and VO<sub>2</sub>/Al-MCM-41

In order to choose the best reaction time in the presence of 0.10 g of the VO<sup>2+</sup>/Al-MCM-41 catalyst, the oxidation reactions were carried out at different times using *trans*-stilbene as representing substrate. The results are presented in Table 4. It was found that during 8h; about 69% of *trans*-stilbene is converted to stilbene epoxide and benzaldehyde. Further increment of catalyst amount to 0.15 g and then to 0.20 g marginally decreased the conversion to 65 and 61% respectively, at the expense of concomitant decrease in epoxide percentage yield (see Table 5). Increasing the amount of catalyst beyond the optimum amount increases the catalyst surface and makes a suitable media for adsorbing guest molecules either substrate or products. This in turn may result to the decreasing of the total conversion. Thus, 0.10 g of catalyst may be considered sufficient enough to carry out the reaction with good

conversion and selectivity toward the formation of the corresponding epoxide.

The oxidation results of *trans*-stilbene, norbornene and geraniol, with H<sub>2</sub>O<sub>2</sub> catalyzed by VO<sup>2+</sup>/Al-MCM-41, VO(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41, VO(en)<sub>2</sub><sup>2+</sup>/Al-MCM-41 and VO(acac)<sub>2</sub>/Al-MCM-41 are presented in Tables 6, 7 and 8 respectively. The main products of the oxidation reaction of *trans*-stilbene are *trans*-stilbene epoxide and

**Table 4.** Effect of time on *trans*-stilben oxidation in acetonitrile in the presence of VO<sup>2+</sup>/Al-MCM-41

Time (h)	Conversion (%)	Epoxide (%)	Benzaldehyde (%)
4	40	70	30
6	66	70	30
8	69	75	25
10	59	75	25

Reaction conditions: Catalyst (0.1g), substrate (1 mmol), H<sub>2</sub>O<sub>2</sub> (48 mmol).

**Table 5.** Effect of the amount of VO<sup>2+</sup>/Al-MCM-41 on *trans*-stilbene oxidation in acetonitrile

Amount of catalyst (g)	Conversion (%)	Epoxide (%)	Benzaldehyde (%)
0.10	69	75	25
0.15	65	60	40
0.2	61	63	36

Reaction conditions: Catalyst (0.1g), substrate (1 mmol), H<sub>2</sub>O<sub>2</sub> (48 mmol), reaction time (8h).

**Table 6.** Oxidation results of *trans*-stilbene with H<sub>2</sub>O<sub>2</sub> in the presence of different catalysts

Catalyst	Conversion (%)	Epoxide (%)	Benzaldehyde (%)	TON
VO <sub>2</sub> /Al-MCM-41	69	75	25	10
VO(bpy) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	90	70	30	11
VO(en) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	76	76	24	51
VO(acac) <sub>2</sub> /Al-MCM-41	95	46	54	24

Reaction conditions: Catalyst (0.1g), substrate (1 mmol), H<sub>2</sub>O<sub>2</sub> (48 mmol), solvent (refluxing acetonitrile, 10 mL), time (8h); TON is the mmol of product to mmol vanadium present in catalysts.

**Table 7.** Oxidation of norbornene with H<sub>2</sub>O<sub>2</sub> in the presence of different catalysts

Catalyst	Conversion (%)	Epoxide (%)	Ketone (%)	TON
VO <sub>2</sub> /Al-MCM-41	41	13	87	117
VO(bpy) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	67	17	83	168
VO(en) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	30	30	70	400
VO(acac) <sub>2</sub> /Al-MCM-41	60	15	85	300
Al-MCM-41	3	100	-	-

Reaction conditions: Catalyst (0.1g), substrate (20 mmol), H<sub>2</sub>O<sub>2</sub> (48 mmol), solvent (refluxing acetonitrile, 10 mL), time (8 h); TON is the mmol of product to mmol vanadium present in catalysts.

**Table 8.** Oxidation of geraniol with H<sub>2</sub>O<sub>2</sub> in the presence of different catalysts

Catalyst	Conversion (%)	Epoxide <sup>a</sup> (%)	Geranial <sup>b</sup> (%)	Linalool oxide (%)	TON <sup>c</sup>
VO <sup>2+</sup> /Al-MCM41	49	49	30	21	140
VO(bpy) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	80	15	9	76	200
VO(en) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	44	64	2	34	567
VO(acac) <sub>2</sub> /Al-MCM-41	73	15	45	40	365
Al-MCM-41	2	100	-	-	-

Reaction conditions: Catalyst (0.1g), substrate (20 mmol), H<sub>2</sub>O<sub>2</sub> (48 mmol), solvent (acetonitrile, 10 mL), time (8h), <sup>a</sup>3, 7-dimethyl-2, 3-epoxy-6-octene-1-ol, <sup>b</sup>2, 6-octadienal-3, 7-dimethyl, <sup>c</sup>TON: mmol of product to mmol of vanadium complex in Al-MCM-41.

benzaldehyde. This result is partly similar to that reported by Maurya and his co-worker who obtained a mixture of stilbene epoxide, benzaldehyde, benzil and other products using tert-butylhydroperoxide in the presence of oxovanadium (IV) based coordination

polymer as catalyst [3]. Compared to this report, our catalysis system coupled with the green H<sub>2</sub>O<sub>2</sub> converts *trans*-stilbene to the corresponding epoxide with more reactivity and selectivity. As shown in Tables 6, VO(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 and VO(acac)<sub>2</sub>/Al-MCM-41

**Table 9.** Oxidation of norbornene with TBHP in the presence of different catalysts

Catalyst	Conversion (%)	Epoxide (%)	Ketone (%)	TON
VO <sub>2</sub> <sup>+</sup> /Al-MCM-41	74	45	8	211
VO(bpy) <sub>2</sub> <sup>2+</sup> /Al-MCM-41	69	78	10	173
VO(acac) <sub>2</sub> /Al-MCM-41	96	91	4	355
Al-MCM-41	9	100	-	-

Reaction conditions: Catalyst: 0.1, solvent (acetonitrile): 10ml, norbornene: 20mmol, TBHP: 24mmol, time: 8h.

catalysts provide the best results although the former seems to be much better with respect to the production of the stilbene epoxide.

Based on the results given in Table 7, maximum amount of norbornene conversion occur in the presence of VO(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 as oxidation catalyst, but the selectivity for all prepared catalysts is based on the formation of norbornane-2-one. The formation of norbornane-2-one seems likely to have initiated from the hydrolysis of norbornene epoxide due to the presence of high amount of water present in H<sub>2</sub>O<sub>2</sub>.

As shown in Table 8, geraniol is oxidized respectively in low to moderate yield conversions in the presence of VO(en)<sub>2</sub><sup>2+</sup>/Al-MCM-41 and the other three VO<sup>2+</sup>/Al-MCM-41, VO(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 and VO(acac)<sub>2</sub>/Al-MCM-41 catalysts. 2,3-Geraniol epoxide, linalool oxide and geraniol were identified as the oxidation products. Identification of the products was carried out with comparison of the mass spectra with those of authentic samples.

In order to increase the reaction selectivity, the epoxidation of norbornene was carried out in the presence of the prepared catalysts with TBHP as oxidant under similar conditions specified in Table 7. As seen in Table 9, VO(acac)<sub>2</sub>/Al-MCM-41 shows good activity (71%) and selectivity toward the formation of epoxide (96%). Epoxidation results of norbornene, cyclohexene, geraniol and *trans*-stilbene in the presence of VO(acac)<sub>2</sub>/Al-MCM-41 as catalyst are given in Table 10. As seen in this Table, VO(acac)<sub>2</sub>/Al-MCM-41 is very active and selective catalyst for epoxidation of geraniol with 99% conversion and 96% selectivity.

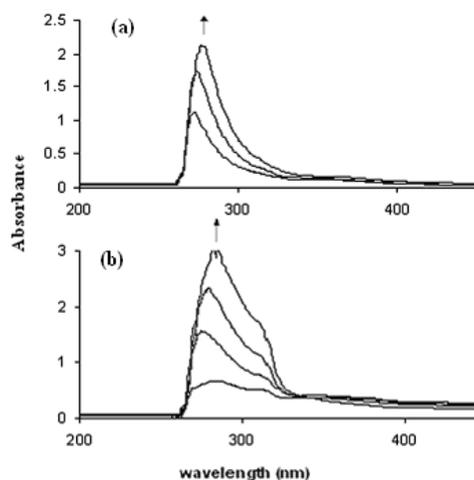
Electronic spectra of VO<sup>2+</sup>/AlMCM-41 ( $\lambda_{max}$  = 237,230nm) and VO(bpy)<sub>2</sub><sup>2+</sup>/Al-MCM-41 ( $\lambda_{max}$  = 236,312, 347nm) confirm the presence of vanadium compounds within nanoreactors of Al-MCM-41. In order to establish the possible reaction pathway of the catalyst during the catalytic action, the changes

appeared in the electronic absorption spectra of VOSO<sub>4</sub> and VO(bpy)<sub>2</sub>SO<sub>4</sub> methanolic solutions due to the reactions with H<sub>2</sub>O<sub>2</sub> were monitored. Based on the

**Table 10.** Results of epoxidation of some olefins with VO(acac)<sub>2</sub>-Al-MCM-41

Substrate	Conversion (%)	Epoxide	Others	TON
Norbornene	96	91	9	480
Cyclohexene	50	60	40	250
Geraniol	99.	98	2	495
Trans-stilbene	90	100	-	23

Reaction condition: solvent for trans stilbene mixture(1:3) DMF and acetonitrile , solvent for other olefins (acetonitrile): 10ml, Trans stilbene: 1mmol and other olefins: 20mmol, TBHP: 24mmol, time: 8h, catalyst: 0.1g.

**Figure 3.** Titration of 10<sup>-4</sup> M solution of (a), VOSO<sub>4</sub> and (b), VO(bpy)<sub>2</sub>SO<sub>4</sub> with 30% H<sub>2</sub>O<sub>2</sub> in methanol.

obtained results (Fig. 3), increases in the band intensities appearing at 237 and 285 nm due to  $\text{VO}(\text{SO}_4)_2$  and  $\text{VO}(\text{bpy})_2$   $\text{SO}_4$  respectively were observed. The same results were obtained after immobilization of vanadium compounds within nanoreactors of Al-MCM-41. These results suggest the formation of peroxo species due to the interaction of vanadium compounds with  $\text{H}_2\text{O}_2$ . This *in situ* generated peroxo species finally transfer oxygen to alkenes to afford the corresponding oxidized products. These observations are consistent with those reported before for some other vanadium complexes [4, 5].

In summary, the immobilized vanadium compounds within nanoreactors of Al-MCM-41 were prepared and characterized. Catalytic activities of these immobilized complexes have been tested for the oxidation of *trans*-stilbene, norbornene and geraniol. It was found that although  $\text{VO}(\text{acac})_2/\text{Al-MCM-41}$ ,  $\text{VO}^{2+}/\text{Al-MCM-41}$  and  $\text{VO}(\text{bpy})_2^{2+}/\text{Al-MCM-41}$  exhibit moderate to high catalytic activities. It was also observed that by changing the oxidant from  $\text{H}_2\text{O}_2$  to TBHP, the activity and selectivity were increased toward the formation of desired epoxides. No desorption was observed during the course of reactions.

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