

## High Selective Oxidation of Alcohols Based on Trivalent Ion ( $\text{Cr}^{3+}$ and $\text{Co}^{3+}$ ) Complexes Anchored on MCM-41 as Heterogeneous Catalysts

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Cr(III) and Co(III) complexes with acetylacetonate were anchored onto a mesoporous MCM-41 through Schiff condensation. The materials were characterized by XRD, FT-IR, BET, CHN and ICP techniques. Elemental analysis of samples revealed that one C=N bond was formed through Schiff condensation on MCM-41 surface. The catalysts were tested for the alcohol oxidations using *t*-butyl hydroperoxide (TBHP) and  $\text{H}_2\text{O}_2$  as oxidant. The catalytic experiments were carried out at both room temperature and reflux condition. Various solvents such as dichloromethane, acetonitrile and water were examined in the oxidation of alcohols. Among the different solvents, catalytic activity is found more in acetonitrile. Further, the catalysts were recycled three times in the oxidation of alcohols and no major change in the conversion and selectivity is observed, which shows that the immobilized metal-acetylacetonate complexes are stable under the present reaction conditions.

**Key Words :** Alcohol oxidation, Heterogeneous catalyst, MCM-41, Trivalent ions

### Introduction

Homogeneous catalysts cannot be separated from the reaction media and subsequently, cannot be reused. Immobilization of the homogeneous catalysts onto a solid support may be a strategy to overcome this problem.<sup>1-3</sup> MCM-41 has a very high surface area and a regular array of large pore diameter channels. The high concentration of silanol groups is suitable for the immobilization of metal complexes.<sup>4</sup> Up to now, various immobilization methods have been reported to prepare the heterogenized complexes. The one used frequently was to immobilize the active groups onto support through coordination of metal ion to the terminal functional group of a surface-bound linker.<sup>5</sup> Functional groups 3-chloropropyl,<sup>6</sup> 3-aminopropyl,<sup>7</sup> chlorotriphenyl<sup>8</sup> and so on could be grafted onto the internal walls of MCM-41 via Si-O-Si bonds. Jacobs and co-workers<sup>9</sup> reported that sulfonic acid functionalized mesoporous silicates performed well in typical strong acid catalyzed reactions. More recently, several grafting and tethering procedures have been developed to covalently attach transition-metal complexes to organic polymers<sup>10</sup> silica, zeolites and other micro- and mesoporous inorganic materials.<sup>11-14</sup> Transition-metal complexes with Schiff-base ligands are the object of intense research due to their high activity, chemoselectivity and enantioselectivity in a large range of catalytic processes.<sup>15-17</sup> For example, Mn/Co salen complexes have been reported as efficient catalysts for the epoxidation of various olefins.<sup>18-20</sup> The obtained immobilized catalysts are more stable and leaching proof, since covalent bonds are formed between the solid support and the metal complex. The anchoring of acetylacetonate (acac) complexes such as  $\text{Co}(\text{acac})_2$ ,  $\text{Mn}(\text{acac})_2$  and  $\text{Cu}(\text{acac})_2$  onto the surface of amine functionalized MCM-41 has already been reported previously.<sup>21-23</sup> This work reports the successful

anchoring of  $\text{Cr}(\text{acac})_3$  and  $\text{Co}(\text{acac})_3$  onto MCM-41 channels. The resulting material was tested in the aliphatic and aromatic alcohol oxidations, using *t*-butyl hydroperoxide (TBHP) as oxidant. Different reaction parameters such as amount of catalyst, reaction temperature, reaction time, nature of solvent, amount of solvent and type of oxidant are studied. Indeed, results show that trivalent ions, Co(III) and Cr(III), can oxidize the alcohols to aldehyde with a high selectivity as well as divalent ions.

### Experimental

The reagents employed were tetraethyleorthosilicate (TEOS, Merck) as a silicon source, cetyl trimethylammonium bromide (CTAB, Merck) as template and ethylamine (EA, Merck). The parent MCM-41 was synthesized by a room temperature method with some modification in the described procedure in the literature.<sup>24</sup>

**Procedure for MCM-41 Synthesis.** First, 3.33 mL EA was added to 42 mL deionized water and the mixture was stirred at room temperature for 10 min. Next, 1.48 g of the CTAB was gradually added to the above solution under stirring for 30 min. After further stirring for 30 min, a clear solution was obtained. Then, 4.57 mL TEOS was added dropwise to the solution. The pH of the reaction mixture was adjusted to 8.5 by slow addition of HCl solution, 1 M, to the mixture. After 2 h, under slow stirring, the precipitate was separated and washed by centrifugation. The sample was dried at 45 °C for 24 h. The MCM-41 prepared was calcined at 550 °C for 5 h to decompose the surfactant and obtain the pure white powder.

**Preparation of APTES/MCM-41.** The calcined MCM-41 (2 g) was added to a solution of 0.1 mL 3-aminopropyltriethoxysilane (APTES, Merck) in dry toluene (Merck).

This mixture was refluxed for 10 h, with continuous stirring. Finally, the material was filtered, washed with chloroform (Merck) and dried at 80 °C for 8 h. The obtained material was designated as APTES/MCM-41.

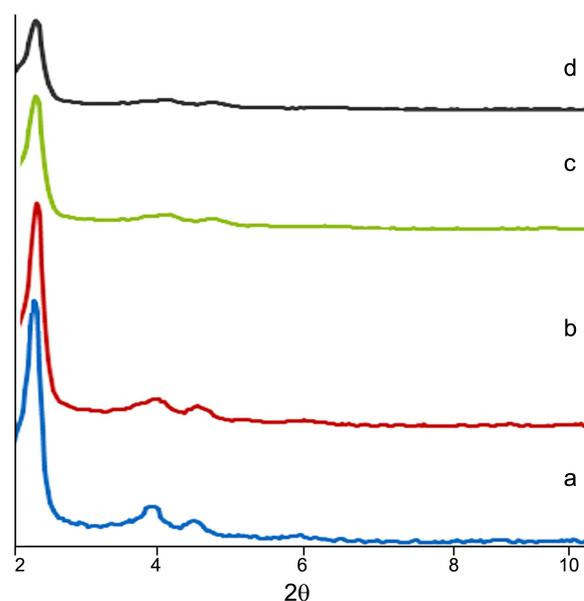
**Preparation of [M(acac)<sub>3</sub>-APETS]/MCM-41, M: Co, Cr.** The modified material APTES/MCM-41 (1g) was refluxed with a solution of metal acetylacetonate in dry toluene, for 12 h. After that, obtained material was Soxhlet extracted with ethanol (Merck), for 14 h and dried at 110 °C for 6 h. The final material will be further on named as [Co(acac)<sub>3</sub>-APTES]/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41.

**Characterization.** X-ray diffraction (XRD) patterns were recorded by a Philips pw1840, X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The patterns were collected in the range 2-10° 2 $\theta$  and continuous scan mode. FT-IR spectra were recorded from KBr pellets (1 wt % sample and 99% KBr) using a Shimadzu FTIR 470 spectrophotometer. <sup>1</sup>H NMR spectra were measured on a Bruker DRX-500 Avance spectrometer and <sup>13</sup>C NMR spectra were obtained on a Bruker DRX-125 Avance spectrometer. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra were expressed in ppm down field from TMS as internal standard. Elemental analyses were performed in an Automatic CHNS-O Elemental Analyser Flash EATM. The metal loading was determined by ICP analysis carried out on a Jobin-Yvon (Ultima) instrument. The reduction in the surface area was measured by BET surface area analysis (Micromeritics Gemini 2360). The oxidation products were further identified by GC-MS analysis (GC capillary HP 6890).

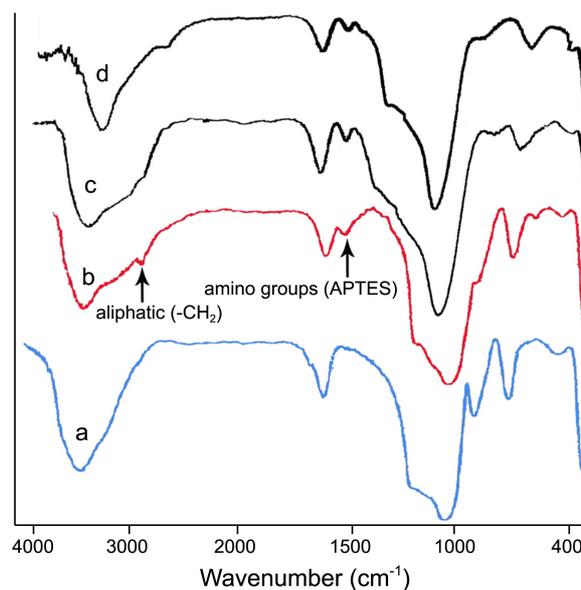
**Catalytic Experiments.** A catalyst (5-25 mg) was placed in the three necked, round-bottomed flask and then 0.3-1 mmol of alcohols (aromatic or aliphatic) and 3 mL of solvent (acetonitrile, dichloromethane and water) were introduced into the reactor through a septum. The catalytic experiments were carried out at room temperature and under reflux condition, under atmospheric pressure and magnetic stirring, using *t*-BHP 70%, (0.1-0.8 mL) or hydrogen peroxide 30% (0.3 mL) as oxidant. The progress of the reaction was followed using thin layer chromatography. After the reaction was run for the desired time, the products were filtered out of the catalyst and then oxidation products were analyzed using a gas chromatograph with a GC capillary column HP 6890 and a FID detector.

## Results and Discussion

The structure of the MCM-41 before and after functionalization was monitored by XRD technique. The XRD of the immobilized complexes were also investigated. Figure 1 shows that the patterns of the chemically modified and complex-immobilized samples are similar to that of the parent MCM-41 sample. In the XRD patterns of the functionalized MCM-41 and immobilized metal complex materials the (100) reflection lost some intensity and both reflections (110) and (200) became weak (Fig. 1(b), (c) and (d)). Indeed, some slight differences in the positions and intensities of the



**Figure 1.** XRD patterns of (a) MCM-41 (b) APTES/MCM-41 (c) [Cr(acac)<sub>3</sub>-APTES]/MCM-41 and (d) [Co(acac)<sub>3</sub>-APTES]/MCM-41.



**Figure 2.** IR spectra of (a) MCM-41 (b) APTES/MCM-41 (c) [Cr(acac)<sub>3</sub>-APTES]/MCM-41 and (d) [Co(acac)<sub>3</sub>-APTES]/MCM-41.

(100) reflection were observed. Chiefly in complex-immobilized samples, the reflections are much weaker due to the presence of the guest species in the pores and occurrence of some disordering. A decrease of specific surface area from 1105 m<sup>2</sup>/g to 760 m<sup>2</sup>/g indicate a successful anchorage of APTES to the MCM-41 walls. In the other hand, immobilized complexes, [Co(acac)<sub>3</sub>-APTES]/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41, have a specific surface area of 490 m<sup>2</sup>/g and 475 m<sup>2</sup>/g, respectively, indicating incorporation of them into the MCM-41 is accompanied by a decrease in surface area and therefore a decrease in pore volume due to pore wall thickness. The IR spectrum of samples is shown in

Figure 2. The broad bands in the range of 3100-3500  $\text{cm}^{-1}$  are due to surface hydroxyl groups. Two strong bands are presented at about 1000-1100  $\text{cm}^{-1}$  and 810  $\text{cm}^{-1}$ , which can be assigned to  $\nu$  (Si-O-Si) and  $\nu_s$  (Si-O-Si) respectively. The band at about 970  $\text{cm}^{-1}$  is attributed to  $\nu$  (Si-OH) vibrations. H-O-H bending vibrations of physisorbed water also observed in the spectrum at about 1622  $\text{cm}^{-1}$ . Figure 2(b) shows the APTES/MCM-41 spectrum. It can be seen that there is an additional band at about 2960  $\text{cm}^{-1}$  due to aliphatic (-CH<sub>2</sub>-) stretching of the propyl chain of APTES. In addition, there is a band at 1600  $\text{cm}^{-1}$  suggesting that the amino groups of APTES anchored to the MCM-41 walls. The decrease observed on the intensity of the band at 970  $\text{cm}^{-1}$  in spectrum Figure 2(b), when compared to that of the unmodified material, is probably due to functionalization of the surface silanol groups. The observed molar ratio 0.7 for N/Cr and 0.8 for N/Co are in close agreement with the expected value of 1.0, which suggested that the amount of undesired residual linkers were negligible and one C=N bond was only formed through Schiff condensation on MCM-41 surface. Two set experiments were performed: (i)

homogenous oxidation using Co(acac)<sub>3</sub> and Cr(acac)<sub>3</sub>; (ii) heterogeneous oxidation using Co(acac)<sub>3</sub>-APTES/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41. Activity of Co(acac)<sub>3</sub> and Cr(acac)<sub>3</sub> was tested on oxidation of primary and secondary alcohol. As expect, both of them can oxidize alcohol to aldehyde in good conversion and yield as well as anchored. Indeed, 90 and 95 percent conversion of oxidation reaction was achieved for 4-chlorobenzyl alcohol and benzhydrol, respectively. Subsequently, catalytic efficiency of anchored complexes was tested for the alcohol oxidations using TBHP and H<sub>2</sub>O<sub>2</sub> as oxidant. The catalytic oxidation was carried out at both room temperature and reflux condition and results are shown in Table 1 and Table 2, respectively. Table 1 reveals that the selective oxidation of benzylic alcohols to aldehyde with immobilized trivalent ion complexes is efficiently promoted in the presence of TBHP. Different types of alcohols, including primary and secondary benzylic and aliphatic alcohols, were efficiently oxidized to their corresponding carbonyl compounds under reflux condition (Table 2). The results show that the catalytic activity of both immobilized complexes at reflux condition is much higher than that of

**Table 1.** Oxidation of benzylic alcohols to their corresponding carbonyl compounds using [Co(acac)<sub>3</sub>-APTES]/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41 at room temperature<sup>a</sup>

[Co(acac) <sub>3</sub> -APTES]/MCM-41				[Cr(acac) <sub>3</sub> -APTES]/MCM-41				
Entry	Yield % <sup>c</sup>	Conversion %	Time (min)	Substrate	Product <sup>b</sup>	Time (min)	Conversion %	Yield % <sup>c</sup>
1	95	100	45	2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-BrC <sub>6</sub> H <sub>4</sub> CHO	35	100	95
2	95	100	35	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4-ClC <sub>6</sub> H <sub>4</sub> CHO	20	100	95
3	72	80	60	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	45	90	92
4	96	100	20	2-MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-MeC <sub>6</sub> H <sub>4</sub> CHO	40	95	90
5	90	95	30	4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	30	100	95
6	95	100	40	PhCH <sub>2</sub> OH	PhCHO	50	100	95

<sup>a</sup>Reactions were performed using 15 mg of catalyst, 0.3 mL TBHP and 3 mL acetonitrile at room temperature. <sup>b</sup>Products were characterized by their physical constants, IR and NMR spectroscopy. <sup>c</sup>GC yields.

**Table 2.** Oxidation of alcohols to their corresponding carbonyl compounds using [Co(acac)<sub>3</sub>-APTES]/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41 at reflux condition<sup>a</sup>

[Co(acac) <sub>3</sub> -APTES]/MCM-41				[Cr(acac) <sub>3</sub> -APTES]/MCM-41				
Entry	Yield % <sup>c</sup>	Conversion %	Time (min)	Substrate	Product <sup>b</sup>	Time (min)	Conversion %	Yield % <sup>c</sup>
1	96	100	10	2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-BrC <sub>6</sub> H <sub>4</sub> CHO	10	100	95
2	95	100	5	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4-ClC <sub>6</sub> H <sub>4</sub> CHO	5	100	95
3	90	85	15	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	30	90	92
4	95	100	15	2-MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	2-MeC <sub>6</sub> H <sub>4</sub> CHO	15	95	90
5	88	90	10	4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	15	100	92
6	96	100	10	PhCH <sub>2</sub> OH	PhCHO	10	100	94
7	-	-	75	CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OH)	Mix <sup>d</sup>	75	-	-
8	22	45	55	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> (OH)	CH <sub>3</sub> (CH <sub>2</sub> )CHO	120	60	58
9	43	65	80	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>	80	50	35
10	95	100	15	PhCH(OH)Me	PhCOMe	30	100	95
11	95	100	8	PhCH(OH)Ph	PhCOPh	18	100	95
12	45	63	85	PhCOCH(OH)Ph	PhCOCOPh	96	100	90
13	-	-	75	PhCH(OH)CH <sub>2</sub> (OH)	Mix <sup>d</sup>	75	-	-
14	96	100	15	C <sub>6</sub> H <sub>11</sub> (OH)	C <sub>6</sub> H <sub>10</sub> O	10	100	95

<sup>a</sup>Reactions were performed using 15 mg of catalyst, 0.3 mL TBHP and 3 mL acetonitrile at reflux condition. <sup>b</sup>Products were characterized by their physical constants, IR and NMR spectroscopy. <sup>c</sup>GC yields. <sup>d</sup>Mixture of products.

room temperature reaction. Benzylic alcohols (Table 2, entries 1-6) successfully converted to their corresponding aldehyde at very short time. While, aliphatic alcohols (Table 2, entries 7-9), were oxidized to aldehyde at longer time reaction than those of benzylic alcohols. Those alcohols (Table 2, entries 7 and 13), including more than one hydroxyl group did not proceed even after prolonged heating. Entries 10-12 corresponded to secondary alcohols have oxidized to ketones in good yields. Also, cyclohexanol as a cycloaliphatic alcohol (Table 2, entry 14) oxidized to cyclohexanone in high yield as well as benzyl alcohol. Since the maximum yields and minimum reaction time was observed with [Co(acac)<sub>3</sub>-APTES]/MCM-41, cobalt immobilized complex was selected as the constant catalyst for investigation the other various parameters on alcohol oxidation. When the oxidation of 2-bromobenzyl alcohol and 1,2-propanediol was performed using 0.1-0.8 mL TBHP, we found that the reaction time decreased as the concentration of hydrogen peroxide increased (Table 3). However, using higher amount of oxidant, aliphatic alcohols were oxidized at higher extent, in the lower reaction time. The large volume of hydrogen peroxide was required for the aliphatic alcohols. In order to assess the stabilities of the complex-immobilized materials, an experiment to find out the extent of chromium or cobalt leaching was carried out. The complex-immobilized materials were separated from the reaction mixtures by filtration after the oxidation reaction, and the filtrates were used for determination of metal ions leaching by ICP emission spectroscopy. No Cr or Co ion was detected in the filtrate of [Co(acac)<sub>3</sub>-APTES]/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41. In addition, a further study on the catalytic reusability of [Co(acac)<sub>3</sub>-APTES]/MCM-41 and [Cr(acac)<sub>3</sub>-APTES]/MCM-41, alcohol oxidations among the prepared complex-immobilized materials, was carried out. After the first catalytic run, the heterogenized catalyst was separated from the reaction solution, washed several times with chloroform to remove any physisorbed molecules, dried at 80 °C and reused in another two catalytic cycles. The catalyst was found to be still active after the third catalytic run, without significant change in the catalytic performance (see Table 4). The nature of the recovered catalyst after reusing three times had been followed by FT-IR spectroscopy and XRD technique,

**Table 3.** Effect of TBHP concentration on oxidation of 2-bromobenzyl alcohol and 1,2-propanediol over [Co(acac)<sub>3</sub>-APTES]/MCM-41<sup>a</sup>

2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH			CH <sub>2</sub> (OH)CH(OH)CH <sub>3</sub>		
TBHP (mL)	Time (min)	Conversion %	Conversion %	Time (min)	TBHP (mL)
0.1	60	100	12	190	0.1
0.2	45	100	20	160	0.3
0.3	10	100	70	120	0.5
0.5	10	100	70	120	0.6
0.8	8	100	72	110	0.8

<sup>a</sup>Reactions were performed using 15 mg of catalyst and 3 mL acetonitrile at reflux condition.

**Table 4.** Recycling experiments over [Co(acac)<sub>3</sub>-APTES]/MCM-41 in acetonitrile, reflux condition

Substrate	Run		
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	10 <sup>a</sup>	10	10
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	5	8	10
4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	10	15	15

<sup>a</sup>Time (min) needed to 100% conversion.

**Table 5.** Nature of the oxidant over [Co(acac)<sub>3</sub>-APTES]/MCM-41, in acetonitrile, reflux condition

Substrate	Oxidant		
	TBHP	H <sub>2</sub> O <sub>2</sub>	-
2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	10 <sup>a</sup>	180	NR <sup>b</sup>
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	5	165	NR

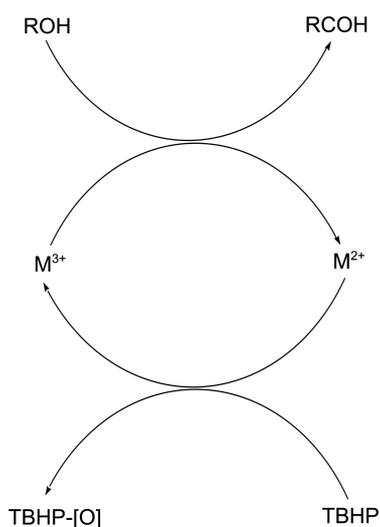
<sup>a</sup>Time (min) needed to 100% conversion. <sup>b</sup>No reaction

no significant changes were observed. This indicated that the complex-immobilized materials with high catalytic performance and stability for the selective oxidation of alcohols was developed by coordinative bonding the complex on surface modified MCM-41. The optimum dosage of catalyst was tested. The reaction time decreased as the catalyst dosage increases from 5 mg to 25 mg per 0.5 mmol of the 2-bromobenzyl alcohol and further increase in the catalyst dosage makes no significant change in reaction time. Effect of the nature of the oxidant shows a maximum conversion for followed by TBHP whereas H<sub>2</sub>O<sub>2</sub> is not found to be effective for the oxidation. In fact, when H<sub>2</sub>O<sub>2</sub> was employed as the oxidant for the oxidation of alcohols, most of H<sub>2</sub>O<sub>2</sub> was decomposed into molecular oxygen and the times of the reaction were quite high. No alcohol conversion was observed in the experiment carried out in the absence of TBHP (Table 5). Various solvents were examined in the oxidation of 2-bromobenzyl alcohol and 4-chlorobenzyl alcohol, and results are shown in Table 6. It can be seen that, acetonitrile is the most suitable solvent for the reaction followed by solvents such as dichloromethane and water. The polarity of acetonitrile was stronger than other solvents. We presume that the strong polarity of solvent may be helpful for the oxidation of alcohols. Evidence for the effective anchorage of the chromium(III) or cobalt(III) acetylacetonate complexes onto the surface of APTES/MCM-41 was first provided by noting that (a) the color of the both complex solution disappears

**Table 6.** Effect of solvent in the oxidation reaction over [Co(acac)<sub>3</sub>-APTES]/MCM-41, reflux

Substrate	Solvent		
	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	H <sub>2</sub> O
2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	10 <sup>a</sup>	25	50
4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	5	35	60

<sup>a</sup>Time (min) needed to 100% conversion.



**Scheme 1.** Plausible mechanism for the oxidation reaction.

during the adsorption reaction, and (b) colorless solutions are obtained when the materials were purified by Soxhlet extraction.

### Conclusion

The anchoring of  $\text{Co}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3$  on MCM-41 was successfully achieved by a post-synthetic method, using APTES as a linking agent. Different characterization techniques such as CHN, ICP, FT-IR, XRD, GCMS and textural analysis showed the evidences that the metal complex was covalently attached to the MCM-41 surface and that its channel structure remained unchanged. The catalysts were tested for the alcohol oxidations using TBHP and  $\text{H}_2\text{O}_2$  as oxidant. The catalytic experiments were carried out at both room temperature and reflux condition with various solvents (acetonitrile, dichloromethane and water). Among different solvents, catalytic activity is found the highest in acetonitrile. The  $[\text{Co}(\text{acac})_3\text{-APTES}]/\text{MCM-41}$  and  $[\text{Cr}(\text{acac})_3\text{-APTES}]/\text{MCM-41}$  catalysts seem to be very stable since it kept its activity when used in three consecutive runs. The aldehyde and ketone are obtained as main products. A plausible mechanism for the oxidation is shown in Scheme 1. At the first  $\text{Co}(\text{III})$  or  $\text{Cr}(\text{III})$  complexes attached on MCM-41 should be reduced to  $\text{Co}(\text{II})$  or  $\text{Cr}(\text{II})$  complexes while alcohol substrates are oxidized to aldehyde. To complete

catalytic cycle, divalent ion complexes should be oxidized to trivalent ion by TBHP. This catalytic cycle will continue until appropriate amount of TBHP exist in reaction media.

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