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Immobilized Vitamin B_{12} within nanoreactors of MCM-41 as selective catalyst for oxidation of organic substrates

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Abstract

The immobilized Vitamin B_{12} (Vit-B_{12}) within the nanoreactors of MCM-41 as molecular sieves was characterized by X-ray powder diffraction (XRD), FT-IR, chemical analysis and nitrogen adsorption–desorption. XRD and N_2 adsorption–desorption isotherms showed that the well ordered hexagonal structure of MCM-41 is presented and surface area, pore volumes and pore diameters decrease after immobilization of Vit-B_{12} within nanoreactors of MCM-41. It was found that Vit-B_{12}/MCM-41 successfully catalyzes the oxygen transfer of *tert*-butylhydroperoxide (TBHP) to norbornene and *trans*-2-hexene-1-ol and formation of the corresponding epoxides with 90% reactivity and 100% selectivity. Moreover, cyclohexane, cyclohexene and cyclohexanol are converted to the corresponding alcohols and ketones. On the other hand, styrene undergoes oxidative degradation with the formation of benzaldehyde and benzoic acid.

Keywords: MCM-41; Nanoreactors; Vitamin B_{12}; Oxidation catalysts

1. Introduction

The selective oxidation of organic compounds is still a challenge in chemical industries and catalytic researches [1–3]. The cobalt catalyzed oxyfunctionalization of alkenes and alkanes has been the subject of intense research in the last two decades [4,5]. Different types of cobalt complexes, such as cobalt(II)–Schiff base complexes [6,7], cobalt(II) porphyrins [8,9], perflurinated metalloporphyrin of cobalt complexes, cobalt phthalocyanines, have been prepared and used for oxidation reactions. These materials, which efficiently catalyze the oxidation of organic substrates, are good biological model [10–13]. In order to heterogenize homogeneous catalysis systems, the most studied cases have been concentrated on the framework of substituted cobalt in aluminophosphates [14–17]. Thomas et al. obtained good results with Co-APO-18 as a catalyst for the oxidation of alkanes [18,19]. The fixation of active complexes of cobalt onto the appropriate supporters could provide selective and stable catalysts with facile recovery and recycling. Sorokin and Tuel have shown that covalent anchoring of different transition metal complexes of phethalocyanine onto the silica gel was a promising strategy to prepare heterogeneous catalysts for organic compounds [20]. Immobilization of trimeric cobalt complex on the surface of MCM-41 is another catalyst [21]. Hexagonal mesoporous materials such as MCM-41 offer new opportunities for organometallic and enzymatic type compounds incorporated or immobilized in MCM-41 [22]. Since MCM-41 molecular sieves contain a large number of silanol groups at the surface of their channels, a wide variety of reactive transition metal complexes can be anchored on the surface by reaction with silanol groups [23].

Recently, the immobilized Co(salen) and Co(perchlorophthalocyanine) complexes within the channels of MCM-41 have been studied for oxidation reactions of alkenes [24–26]. In this study, we have prepared the immobilized Vitamin B_{12} (Vit-B_{12}) within the nanoreactors of MCM-41 as catalyst for oxidation of a number of organic substrates. In fact, coenzymes such as B_{12} with apoenzyme (protein) together acts as holoenzyme in living systems. We thought that immobilized Vit-B_{12}/MCM-41 with polar Si–OH groups on the surface of MCM-41 is a good artificial host for simulation of proteineouas environment.

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2. Experimental

2.1. Materials

All materials were of commercial reagent grade. Cobalt chloride ($CoCl_2 \cdot 6H_2O$), sodium hydroxide, cetyltrimethylammonium bromide (CTAB), fumed silica (99.8% metal free), Vitamin B_{12}, methanol, ethanol, acetonitrile, TBHP (80% in di-*tert*-butylhydroperoxide), norbornene, cyclohexane, cyclohexene, cyclohexanol, styrene, *trans*-2-hexene-1-ol and diphenylamine were purchased from Merck chemical company.

2.2. Physical measurements

FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR Spectrometer. 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 Rigaku D/MAX-2550/PC diffractometer (Japan) with Ni filter and Cu Kα radiation at 40 KV and 30 MA.

2.3. Preparation of catalyst

2.3.1. Synthesis of MCM-41

MCM-41 was synthesized as reported previously [27]. For this purpose, 0.6 g of sodium hydroxide in 10 g deionized water was added to a solution of cetyltrimthyl ammonium bromide (7.89 g in water). After stirring for 3 h, a solution of fumed silica (1.8 g in 20 ml water) was added to the surfactant solution. The prepared gel was then kept for 24 h at room temperature. The molar composition of the final gel was 30 SiO_2, 5.2 CTAB, 7.5 NaO_2 and 2500 H_2O. Finally, the gel mixture was placed in a Teflon-lined stainless steel autoclave, and kept at 100 °C for 72 h. The solid product, washed with deionized water and then dried at 100 °C for 3 h and calcinated at 500 °C for 6h.

2.3.2. Immobilizing of Vitamin B_{12} within MCM-41 (Vit-B_{12}/MCM-41)

In order to immobilize Vit-B_{12} within MCM-41, 1 g Vit-B_{12} in 5 ml methanol was slowly added to 5 g of MCM-41 in 5 ml methanol. The mixture was kept under reflux condition for 1 h. The solid product was then washed with hot methanol and dried at room temperature.

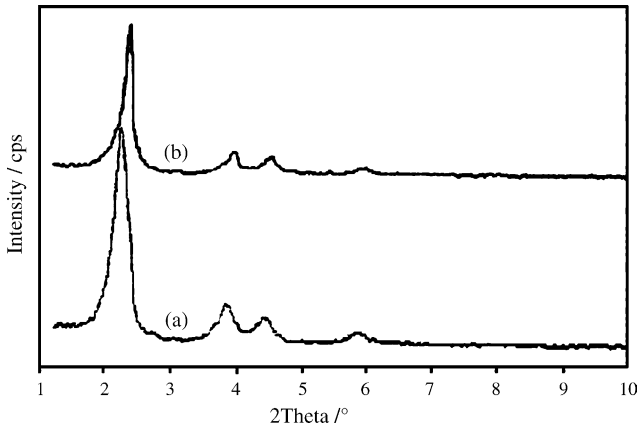


Fig. 1. XRD of: (a) calcined MCM-41 and (b) Vit-B_{12}/MCM-41.

2.4. Oxidation of organic substrates

2.4.1. General procedure

Oxidation reactions were performed in a stirring round bottom flask fitted with a water-cooled condenser. Reactions were carried out at atmospheric pressure under reflux conditions in different solvents. Typically, 0.2 g of Vit-B_{12}/MCM-41 catalyst and 20 mmol of substrate in 3 ml of solvent was added to the reaction flask with slow stirring. After a few minutes, TBHP (24 mmol) was added to the reaction mixture at room temperature and refluxed. The solid was filtered after 8 h and washed with fresh solvent. The filtrate solution was then subjected to GC and GC mass analyses.

2.4.2. Oxidation of cyclohexene in the presence of diphenylamine radical scavenger

The general procedure was repeated using cyclohexene as the organic substrate in the presence of Ph_2NH (20 mmol).

3. Results and discussion

MCM-41 was prepared according to the procedure described previously. Fig. 1a shows the X-ray powder diffraction pattern of calcined MCM-41. It exhibits a strong and three weak peaks. All four XRD reflections can be indexed on a hexagonal lattice. The XRD of calcined MCM-41 completely consistent with MCM-41 spectrum [27]. The XRD pattern of Vit-B_{12} within MCM-41 is shown in Fig. 1b. As is seen, the peak 1 0 0 in this case shifted to a higher angle (Table 1) and the d_{100} intensity has also been decreased. These changes indicate that the pore surface silanol groups of the MCM-41 were reacted with Vit-B_{12}.

Table 1
Physicochemical characterization of calcined MCM-41 and Vit-B_{12}/MCM-41

Samples	Calcined		BET surface area (m^2g^{-1})	Pore size (Å)	Wall thickness (Å)
	d-spacing value	Unit-cell parameter			
MCM-41	35.14	40.62	1212	24.9	10.9
Vit-B_{12}/MCM-41	33	38.15	930	24.6	11.9

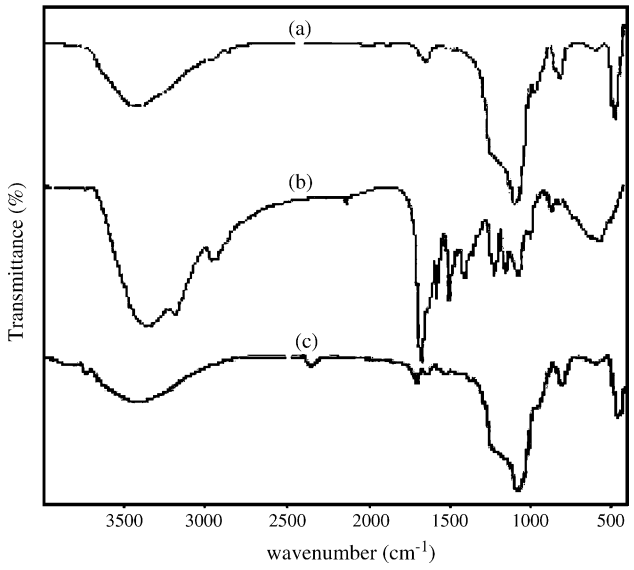


Fig. 2. FT-IR spectra of: (a) calcined MCM-41, (b) Vit-B_{12} and (c) Vit-B_{12}/MCM-41.

In order to see whether the MCM-41 surface hydroxyl groups have reacted with Vitamin B_{12} molecule, we have shown the FT-IR spectra of MCM-41 and Vit-B_{12}/MCM-41 in Fig. 2. The intensity of the absorption peak at 3500 cm^{-1} belonging to the acidic Si–OH groups has decreased due to condensation with immobilized Vit-B_{12} amino groups. That the absorption peak at 960–980 cm^{-1} has not completely disappeared after Vit-B_{12} immobilization shows that some hydroxyl groups inside pores not accessible to Vit-B_{12} molecules are left intact [28].

The nitrogen adsorption–desorption isotherm plots for MCM-41 and Vit-B_{12}/MCM-41 are shown in Fig. 3. The type IV isotherms [29] indicate that, at low relative pressures p/p_0, adsorption takes place as a thin layer on the walls (monolayer coverage). Sharp inflections, at 0.24–0.410 (for MCM-41) and 0.25–0.37 for Vit-B_{12}/MCM-41 related to the capillary condensation and confirm the existence of uniform pores. In addition, the height of inflection in the nitrogen adsorption isotherm plots for Vit-B_{12}/MCM-41 is smaller than MCM-41. It is attributed to the reduced pore volume (Fig. 4), which reflects the decreasing of surface area (Table 1). This effect can be attributed to the inclusion of Vit-B_{12} into pores of MCM-41.

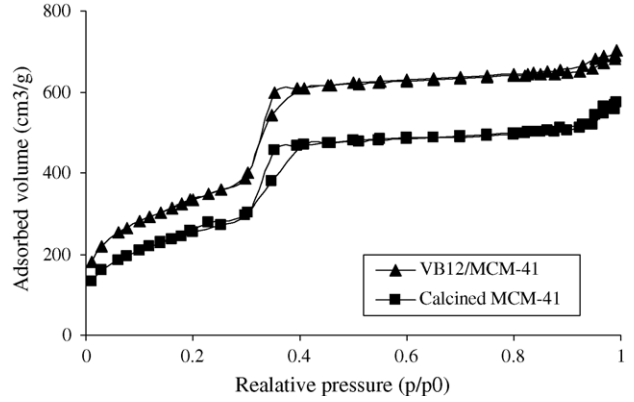


Fig. 3. N_2 adsorption of: calcined MCM-41 and Vit-B_{12}/MCM-41.

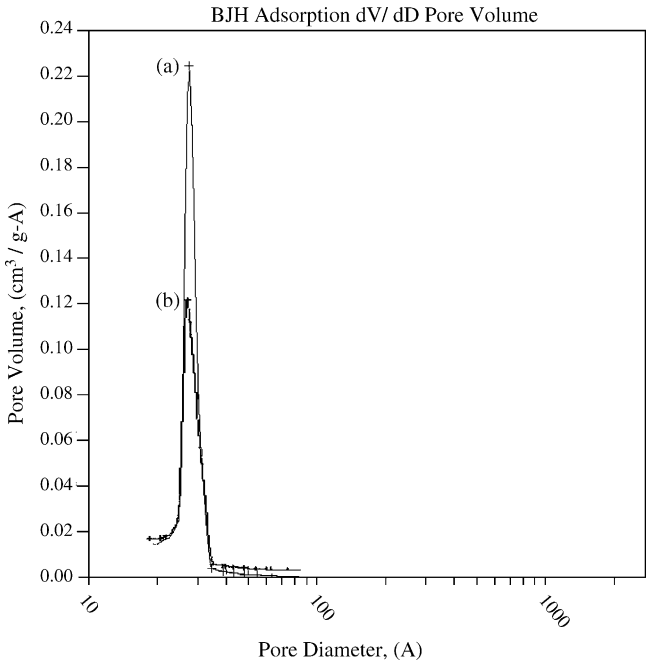


Fig. 4. Pore size distribution of: (a) calcined MCM-41 and (b) Vit-B_{12}/MCM-41.

Table 2
Effect of time on norbornene epoxidation in acetonitrile in the presence of Vit-B_{12}/MCM-41

Time (h)	Conversion (%)
4	81
6	85
8	90

Reaction condition: Catalyst, 0.2g; substrate, 20 mmol; TBHP, 24 mmol.

To choose the best oxidation solvent in the presence of Vit-B_{12}/MCM-41 as catalyst, the oxidation reactions were carried out in different solvents using norbornene as the representing substrate. The results are presented in Table 2. It is evident that acetonitrile provides the best oxidation medium for high substrate conversion and 100% selectivity toward the formation of the corresponding epoxide. Furthermore, the optimized reaction time was investigated and it was found that during 8 h, about 90% of norbornene is converted successfully to norbornene epoxide (Table 3).

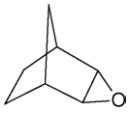
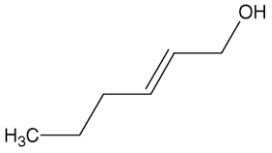
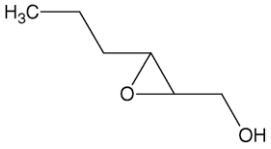
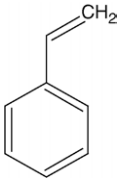
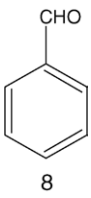
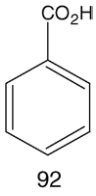
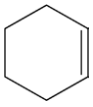
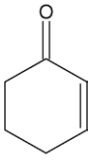
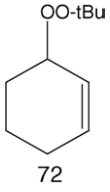
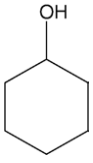
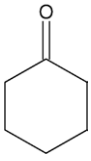
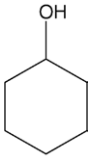
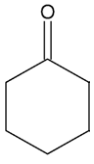
Table 4 presents the oxidation results of some organic substrates with TBHP in acetonitrile catalyzed by Vit-B_{12}/MCM-41. It should be emphasized that no changes in the oxidation

Table 3
Effect of solvent on norbornene epoxidation in the presence of Vit-B_{12}/MCM-41

Solvent	Conversion (%)	Epoxide selectivity (%)
Acetonetrile	90	100
Dichloromethane	45	100
Chloroform	90	100

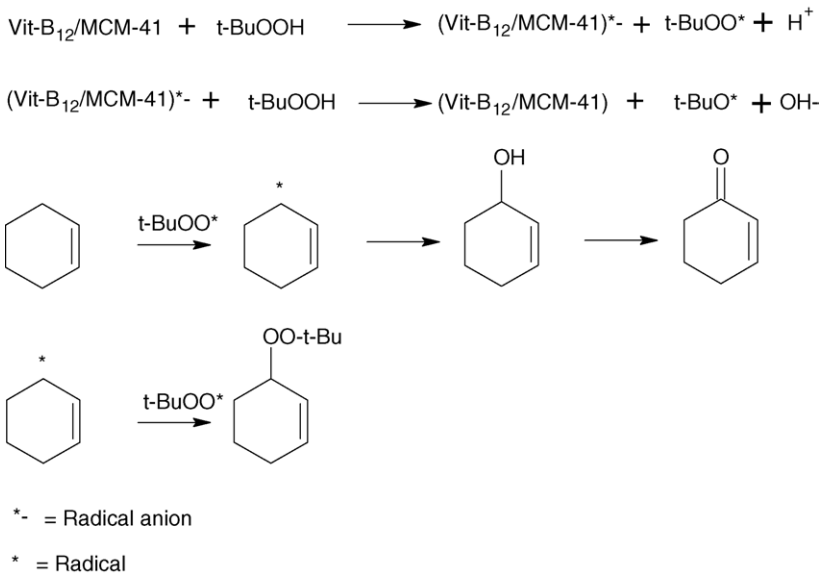
Reaction condition: Catalyst, 0.2 g; substrate, 20 mmol; TBHP, 24 mmol.

Table 4
Oxidation of organic substrates with TBHP in the presence of Vit-B_{12}/MCM-41[a]

Substrate	Conversion (%)	Product distribution (%)	TON
	90	 100	5960
	90		5960
	60	 8  92	3934
	70	 25  72	4768
	50		3311
	21	 32  68	1785

[a] Oxidation of norbornene in the presence of MCM-41 void of Vitamin B_{12} gives rise to 7% conversion to the corresponding epoxide. *Reaction conditions*: Catalyst, 0.2 g; substrate, 20 mmol; TBHP, 24 mmol; solvent—acetonitrile, 3 ml; temperature, 70 °C; time, 8 h plus trace amount of 2-cyclohexene-1-ol and unidentified products (totally 3%) TON is the mmol of product to mmol of Co content in Vit-B_{12}/MCM-41.

results were observed when the reactions were carried out under nitrogen atmosphere. Compared to the result obtained in the presence of MCM-41 void of Vit-B_{12}, which shows about 7% conversion of norbornene, the observation of 90% norbornene conversion catalyzed by Vit-B12/MCM-41 provides the key role of Vit-B_{12} catalyst immobilized within the mesopor. The formation of *t*-butylcyclohex-2-enyl peroxide in cyclohexene oxidation provides rather strong evidence for the involvement of *t*-BuOO radical as a reactive intermediate. Based on oxidation mechanism especially those studied by Iqbal and co-workers on versatile cobalt(II)–Schiff bases catalyzing the oxidation of organic substrates [6], Co(III)-superoxo and Co(IV)-oxo intermediates have been thought to be responsible for oxygen transfer to substrates. Since Vitamin B_{12} contains six ligands around the central cobalt cation, the formation of the active superoxo and oxo species is not possible unless the breakage of a bond to cobalt occurs prior to the approach and attachment of oxidant to the central cobalt cation. This is inferred from whatever happens to coenzyme B_{12} in catalytic conversion of 1,2-propanediol to propanal [30]. Due to the presence of a strong CN–Co bond in Vitamin B_{12} [30], an initial homolytic cleavage of any ligand to Co(III) and formation of Co(III)-superoxo and Co(IV)-oxo intermediates is not conceiveable. Therefore, an outer electron transfer from TBHP to corrin ring system of Vitamin B_{12} and formation of a radical anion (Vit-B_{12}/MCM-41)$^{*-}$ has probably been responsible for the generation of *t*-BuOO radical as the active intermediate to initiate the oxidation steps (Scheme 1). Therefore, one electron oxidation–reduction and homolytically



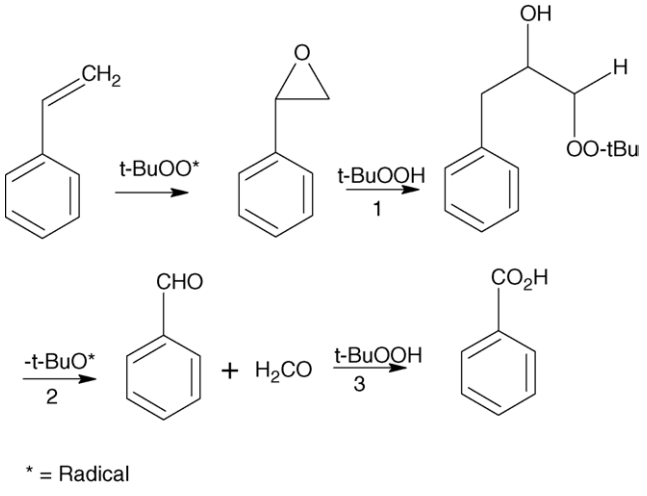
Scheme 1.

cleavage of TBHP and formation of *t*-BuOO• as the initiating oxidation process seems likely (Scheme 1). Since Collman and co-workers have reported that oxygen-radical trap Ph_2NH inhibits an oxidation [31], we used it to have insight into the reaction mechanism. Using an equimolar of trapping agent with TBHP completely suppressed cyclohexene oxidation based on the GC analysis of the products mixture, which showed that cyclohexene has left intact. Since 2-cyclohexene-1-one and not 2-cyclohexene-1-ol is obtained in cyclohexene oxidation, the former might have arisen from the oxidation of the latter as the initial oxidation product. This proposal finds support from cyclohexanol oxidation, which totally affords cyclohexanone with rather similar rate to cyclohexene (see Table 4). That epoxide is not obtained in the case of cyclohexene can be attributed to the presence of two oxidation sites in this substrate. Competition between addition of *t*-BuOO• either to double bond or hydrogen atom abstraction from allylic sites has led to the observed products distribution. Our previous results on cyclohexene oxidations and whatever found in this work clearly indicate the more tendency of the *t*-BuOO• toward allylic site oxidation under one electron reduction–oxidation conditions [32,33].

Whatever seems interesting is the formation of epoxide selectively from norbornene and *trans*-2-hexene-1-ol. That allylic oxidation products are not obtained from norbornene although allylic hydrogens are available can be explained by the fact that hydrogen atom abstraction by *t*-BuOO intermediate generates an unstable bridgehead radical [34]. Therefore, addition of *t*-BuOO• to double bond and subsequent elimination of *t*-BuO radical and formation of epoxide is the sole reaction path available to the system. As is seen, *trans*-2-hexene-1-ol undergoes the epoxidation while hydrogen atom abstraction route is possible. Based on our previous results from this molecule and formation of epoxide under different catalysis systems [32,33], we need more information in order to propose a plausible mechanism.

The formation of benzaldehyde and benzoic acid from styrene is explained according to our proposed mechanism depicted in Scheme 2. This proposal is suggested on the basis of the very recent work of Hulea et al. who studied the oxidation of styrene with H_2O_2 over Ti-containing molecular sieves [35]. They obtained a variety of oxidation products such as phenyl acetaldehyde, benzaldehyde, styrene oxide, 1-phenyl ethane-1,2-diol and benzoic acid with different distributions. By changing solvent and hydrophobicity surface of molecular sieves, they realized that the reaction can be directed toward the desired products [35]. Starting with styrene epoxide as starting material and obtaining the similar products under the reaction conditions, the implication of styrene epoxide as the preliminary product was uncovered [35]. On a less hydrophobic surface of Co-MCM-41, the TBHP molecule accedes easily and, as consequence, the reactions (1), (2) and (3) take place (Scheme 2). Also, the larger space offered by this catalyst allows the formation of bulky intermediates, which characterize these reactions.

Particularly significant in this study is the oxidation of cyclohexane, which is a topic of great interest [36]. The successful



Scheme 2.

conversion of cyclohexane to a mixture of 1:2 of the corresponding alcohol and ketone in about 21% total yield with a turnover of 1785 after 8 h at 343 K seems promising.

4. Conclusion

It was shown that the nanoreactors of MCM-41 is a suitable medium for immobilization of large molecules such as Vitamin B_{12}.The oxidation of some organic substrates with TBHP were successfully carried out under mild conditions in the presence of Vit-B_{12}/MCM-41 as catalyst. Products were obtained with fair to excellent turnover numbers. No desorption was detected during the course of reactions.

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