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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.

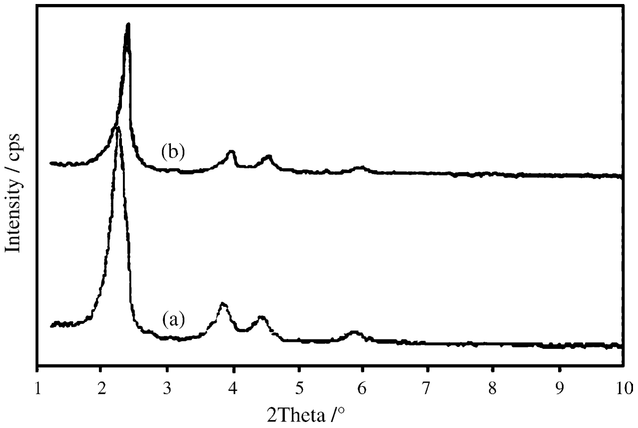

Fig. 1. XRD of: (a) calcined MCM-41 and (b) Vit-B_{12}/MCM-41.

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 ($m^2 g^{-1}$)	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