

Selective oxidation of benzyl alcohol catalyzed by Cr(salen) complexes immobilized on MCM-41

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Received 20 February 2007; received in revised form 13 June 2007; accepted 14 June 2007

Available online 19 June 2007

Abstract

A series of Cr(salen) complexes immobilized on MCM-41 via four typical linkers was prepared for the selective oxidation of benzyl alcohol (BzCH₂OH) to benzaldehyde (BzCOH). The results revealed that the complex-immobilized materials were effective catalysts and all exhibited much higher catalytic performance than their homogeneous analogue. Simultaneously, the catalytic performance of complex-immobilized materials was found to be closely related to the degree of flexibility of the linkers and the coordination abilities of terminal functional groups in linkers. The complex-immobilized via flexible aminopropyl linker displayed the highest catalytic performance, and the optimal BzCH₂OH conversion could reach 52.5% with 100% of the selectivity to BzCOH.

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Keywords: Heterogeneous; Cr(salen); Linker; Selective oxidation; Benzyl alcohol

1. Introduction

Catalytic liquid phase oxidation of benzyl alcohol (BzCH₂OH) to benzaldehyde (BzCOH) is a widely investigated reaction as it provides chlorine-free BzCOH required in perfumery and pharmaceutical industries [1], and many methods have been developed to accomplish this particular reaction. Among them, transition metal Schiff base complex-catalyzed oxidation in resemblance of enzymatic catalysis is eye-catching, especially for their more accessible synthesis conditions and versatile coordination structures, and various transition metal complexes have been reported [2–5]. However, such homogeneous complexes, on the one hand, suffer from the drawbacks of poor catalyst recovery and product separation [6]. Furthermore, another major drawback in homogenous system is the formation of μ -oxo dimers and other polymeric species which lead to irreversible catalyst deactivation. These problems could be avoided

in principle through isolating the homogeneous complexes by immobilization on supports [7–12]. Therefore, in recent years, much effort has been paid to immobilize the homogeneous catalysts onto solid supports in an attempt to tailor the catalysts for desired performance.

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 [13]. This immobilization strategy had a considerable advantage from the point of view of economy of synthetic steps and ensured the purity of homogeneous complex present on support [14], though it sometimes was thought to cause the problem of leaching [15]. Thus, many groups devoted to develop effective heterogeneous catalysts by coordinated bonding of homogeneous complexes to solids through different linkers. Zhou et al. reported the immobilization of Cr(III)-binaphthyl Schiff base complex onto MCM-41 through a flexible aminopropyl linker [13], and the resulting complex-immobilized materials showed high catalytic performance in the asymmetric epoxidation of alkenes while the leaching was only observed in very

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minor extend (2–3%). Recently, Agashe and co-workers also successfully immobilized Cu/Co(salen) onto MCM-41 and silica gel modified with aminopropyl linker, and found that the complex-immobilized on MCM-41 was more active in the liquid oxidation of olefins [7]. Li's group successively reported that the Mn(salen) complexes could be immobilized onto porous materials via phenolic groups and phenyl sulfonic groups [14,16], and the immobilization both resulted in high ee values and stability for epoxidation of olefins. Though these linkers had been proved to be successful in the immobilization of homogeneous complexes, to the best of our knowledge, the effect of linker flexibility and the coordination abilities of terminal functional groups in linkers on the catalytic performance of complex-immobilized materials was rarely dealt with, which was of significance for high effective heterogeneous catalyst design.

Here, we reported the efficient selective oxidation of BzCH₂OH with 30% H₂O₂ catalyzed by a series of Cr(salen) complexes immobilized on MCM-41 via four typical linkers. The catalytic performance of complex-immobilized materials was compared with that of their solution counterpart, and an in-depth study on the differences in their catalytic performance was carried out. Moreover, the roles of the nature of linkers, in terms of the flexibility and the coordination abilities of terminal functional groups, in the catalytic performance of complex-immobilized materials were also discussed in detail.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of MCM-41 modified with different organic groups (organo-modified MCM-41)

The synthetic procedures for MCM-41 had been previously described elsewhere as in ref. [17]. As reported previously in literatures [15,18], aniline, aminopropyl and mercaptopropyl functionalized MCM-41 (referred hereafter as NH₂Ph-MCM-41, NH₂-MCM-41 and SH-MCM-41, respectively) were prepared by refluxing the surfactant-free MCM-41 with appropriate amounts of alkoxysilane agents (anilinetriethoxysilane, aminopropyltriethoxysilane and mercaptopropyltriethoxysilane, respectively) in toluene. Following the procedures in literature [19], sulfonic group-modified MCM-41 (SO₃H-MCM-41) was prepared by the oxidation of SH-MCM-41 with a 6-fold excess of H₂O₂. Then, sulfonic groups were further converted into sodium sulfonate (SO₃Na-MCM-41) according to a similar report [14].

2.1.2. Preparation of the homogeneous chromium Schiff base complex of 3-[N,N'-bis(salicylideneamino)ethane] (Cr(salen))

The Schiff base ligand salen was prepared and purified according to the established procedures [20]. The homogeneous Cr(salen) complex was synthesized as in literature [7]. An equimolar amount of an ethanolic solution of CrCl₃·6H₂O (0.03 mol L⁻¹) was mixed with the ligand salen (0.03 mol L⁻¹ in ethanol). The mixture was then refluxed for 6 h. The solid

product was filtered, washed with cold ethanol, dried under vacuum (at 60 °C and 10⁻² Pa for 2 h) and recrystallized in chloroform.

2.1.3. Preparation of the heterogenized chromium(III) complexes

Since the chromium centre in homogeneous Cr(salen) complex was either five- or six-coordinate with a substitutionally labile water molecule, immobilization of the homogeneous complex onto MCM-41 could be readily achieved through coordination of chromium to terminal functional groups of the surface-bound linkers via simple addition or ligand substitution reactions [13]. Typically, to the suspension of freshly dried organo-modified MCM-41 (1 g) in 50 mL of dry toluene, the solution of the as-prepared homogeneous complex (3 g) in 50 mL of dry toluene was added. The mixture was vigorously stirred under reflux for 6 h. Then the resulting suspension was cooled and filtered through a Buchner funnel supplied with a fine-porous filter paper. The collected powder was washed overnight in a Soxhlet extractor using equivalent alcohol and acetonitrile as solvent to remove the homogeneous complexes adsorbed on the surface of support, and then the solid was dried in air at 80 °C for 10 h. By choosing in turn the different organo-modified MCM-41 (NH₂Ph-MCM-41, NH₂-MCM-41, SH-MCM-41 and SO₃Na-MCM-41), the corresponding complex-immobilized materials were obtained and denoted as Cr(salen)-NH₂Ph-MCM-41, Cr(salen)-NH₂-MCM-41, Cr(salen)-SH-MCM-41 and Cr(salen)-SO₃-MCM-41, respectively.

2.2. Characterization

Powder X-ray diffraction (XRD) experiments were performed at room temperature on a Rigaku D Max III VC instrument with Ni filtered Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$) at 40 kV and 30 mA. The specific surface area and average pore diameter were measured by N₂ adsorption–desorption method using a Micromeritics ASAP-2000 instrument (Norcross, GA). The samples were outgassed at 80 °C and 10⁻⁴ Pa overnight and then the adsorption–desorption isotherms were conducted by passing nitrogen into the samples, which were kept under liquid nitrogen temperature. Surface area was calculated by the BET method and the average pore diameter was calculated by the BJH method from the desorption isotherm. The contents of carbon, nitrogen and sulfur of all the samples were determined using a Vario EL analyzer. The chromium contents in the samples were measured by inductively coupled plasma (ICP) emission spectroscopy (Perkin-Elmer ICP OPTIMA-3000). FTIR spectra of all samples were recorded in KBr disks at room temperature on a Shimadzu (model 8201 PC) spectrophotometer. UV–vis absorption spectra were recorded on a Shimadzu (model 2501 PC) spectrophotometer (for solid samples, the optical grade BaSO₄ was used as reference). The solid state NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer with resonance frequencies of 75.5 and 59.6 MHz for ¹³C and ²⁹Si, respectively. The chemical shifts (ppm) were reported relative to the external standard of tetramethylsilane.

2.3. Catalytic test

The oxidation of BzCH₂OH was carried out in a 100 mL Teflon-lined and magnetically stirred autoclave. In a typical experiment, a mixture of 0.25 g heterogenized catalyst or 1 mol% of homogeneous complex (relative to H₂O₂) and 0.05 mol BzCH₂OH was stirred for about 10 min, and then 0.125 mol 30% H₂O₂ was introduced. The autoclave was heated to 50 °C within 5 min. After the reaction was run for the desired time, the products were filtered out of the catalyst and then were analyzed using a gas chromatograph with a capillary 30 m HP-5 column and an FID detector.

2.4. Adsorption test

Typically, 0.05 g complex-immobilized material was mixed separately with the solution A (8×10^{-8} mol BzCH₂OH in 15 mL *n*-hexane) and B (7.8×10^{-8} mol BzCOH in 15 mL *n*-hexane). After stirring at 50 °C for 4 h, the mixtures were filtered and the UV–vis absorptions of the filtrate solutions were recorded. The concentrations were determined on the basis of UV–vis spectra and comparison with standard solutions.

3. Results and discussion

3.1. Preparation process

All process variables were adjusted to achieve the successful preparation of the complex-immobilized materials. In order to minimize the presence of adventitious uncomplexed chromium ions on support which could act as non-selective catalytic sites [15,21], the preparation of solid catalysts was accomplished by anchoring a pre-formed, well-characterized Cr(salen) complex onto support. Moreover, during the preparation of the organo-modified MCM-41, the same amounts of alkoxy silane agents were deliberately introduced in the anchoring solution (moles MCM-41/moles alkoxy silane agent = 7) to obtain the similar amounts of linkers on the surface of MCM-41. Simultaneously, the structures of the obtained organo-modified MCM-41 were confirmed by elemental analysis, powder X-ray diffraction, N₂ adsorption–desorption technique, FTIR, ²⁹Si CP MAS NMR and ¹³C CP MAS NMR spectra before immobilization of homogeneous Cr(salen) complex (see [Supplementary information](#)). In addition, during the immobilization, the dosage of Cr(salen) was excessive to minimize the amounts of the undesired residual linkers on support.

3.2. Coordination structures of the complex-immobilized materials

All chromium complexes were characterized by elemental analysis, FTIR, UV–vis and ¹³C CP MAS NMR spectra. Owing to the paramagnetic nature of the complexes, NMR spectra of good quality were not observed. Chemical analysis revealed that the obtained values of Cr(salen) complex were quite comparable with the calculated values (see [Table 1](#)), indicating that the prepared homogeneous complex held the

Table 1
Components and textural structures of samples

Samples	Elemental analyses				Structural parameters				
	C (wt%)	N (wt%)	S (wt%)	Cr (wt%)	N/C ^a	S/C ^a	d _p (nm)	S _{BET} (m ² g ⁻¹)	Cr/S _{BET} (mol m ⁻²)
Cr(salen)	54.33 (54.31) ^b	7.91 (7.92) ^b	0	14.70 (14.71) ^b	2.00 (2.00) ^b	–	–	–	–
MCM-41	2.04	0.10	0	0	–	–	2.76	1050	–
Cr(salen)-NH ₂ -MCM-41	10.08	1.85	0	2.3	2.99 (3.00) ^b	–	2.25	680	6.51×10^{-7}
Cr(salen)-SH-MCM-41	9.66	1.19	1.34	2.2	2.01 (2.00) ^b	0.99 (1.00) ^b	2.16	654	6.45×10^{-7}
Cr(salen)-SO ₃ -MCM-41	9.21	1.13	1.29	2.1	2.00 (2.00) ^b	1.00 (1.00) ^b	2.08	622	6.49×10^{-7}
Cr(salen)-NH ₂ Ph-MCM-41	10.15	1.62	0	2.0	3.01 (3.00) ^b	–	2.00	585	6.57×10^{-7}

^a The molar ratio of N to Cr and N to S.

^b Value in parenthesis corresponds to the calculated results.

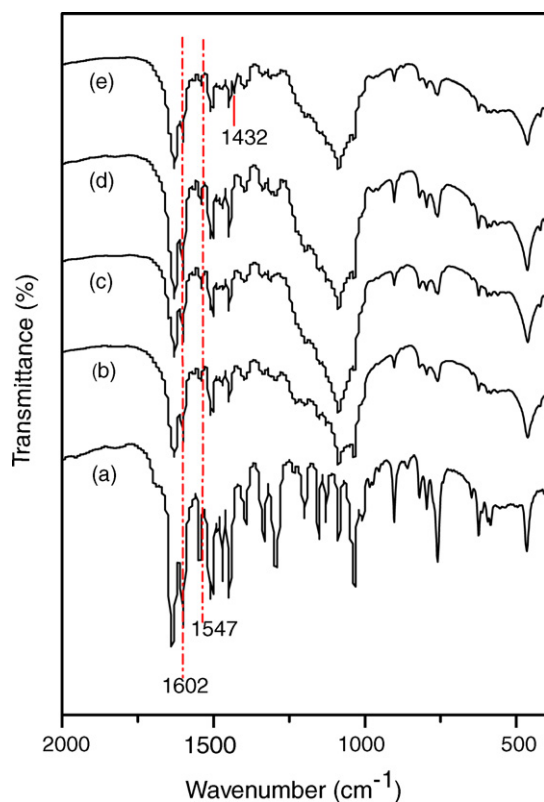


Fig. 1. FTIR spectra of (a) Cr(salen), (b) Cr(salen)-NH₂-MCM-41, (c) Cr(salen)-SH-MCM-41, (d) Cr(salen)-SO₃-MCM-41 and (e) Cr(salen)-NH₂Ph-MCM-41.

expected elemental composition. Simultaneously, the N/Cr and S/Cr molar ratios of all complex-immobilized materials were well consistent with the expected values, which suggested that the amounts of undesired residual linkers were negligible. Moreover, the densities of chromium complexes per surface area in all complex-immobilized materials were very similar, showing the almost identical dispersion degrees of active moieties present in complex-immobilized materials.

The FTIR spectrum of homogeneous Cr(salen) complex showed the characteristic bands at 1627, 1602, 1547, 1471, 1448, 1388, 1332 and 1287 cm⁻¹ (see Fig. 1), which fit well with the published data in literature [22]. The assignments of the representative bands for the successful preparation of Cr(salen) complex with a tetradentate ONNO functionality were the band at 1602 cm⁻¹ due to C=N stretching vibration of the imine groups and the typical band of metallosalen complex at about 1547 cm⁻¹ [23,24]. In the FTIR spectra of complex-immobilized materials, apart from the bands in the overlapping regions of silica backbone, the other bands of Cr(salen) complex were all clearly observed though there were some marginal shifts in the position of bands due to the immobilization. This indicated that the quadridentate coordination structure in homogeneous complex all survived from the immobilization in spite of the differences in linkers. Noticeably, an additional characteristic band of phenyl carbon to silicon ($\nu_{C-Si} = 1431 \text{ cm}^{-1}$) was also observed in the spectrum of Cr(salen)-NH₂Ph-MCM-41 [25]. However, for the FTIR spectra

of the other three complex-immobilized materials, no significant differences were found. And the characteristic bands due to the terminal functional groups were absent probably because they had been masked by the intensive bands of organometallic complex.

The UV-vis spectrum of the homogeneous complex displayed a peak at about 390 nm typical of the metal-ligand band and a broad peak at about 600 nm associated with d-d transition (see Fig. 2), which was similar to related metal (salen) compounds described in the literatures [26,27], and also indicated the successful preparation of Cr(salen) complex. The UV-vis spectra of all complex-immobilized materials were quite similar to the spectrum of homogeneous complex, further confirming that the complex-immobilized materials as depicted in Scheme 1 were all successfully prepared. Noticeably, the two characteristic bands both underwent different degrees of red shifts when the homogeneous complex was immobilized via different linkers. This suggested that the immobilization influenced the active complex to some extent; moreover, the degree of influence depended on the nature of linkers. A maximum shift of 16 nm was observed for the band at about 390 nm in the UV-vis spectra of Cr(salen)-NH₂Ph-MCM-41, indicating that the conformation of Cr(salen) complex tended to change when it was immobilized via aniline linker. Nevertheless, for Cr(salen)-NH₂-MCM-41, Cr(salen)-SH-MCM-41 and Cr(salen)-SO₃-MCM-41, the red shifts of the characteristic metal-ligand bands were marginal, so the influence originated from immobilization on the chemical conformations of their active complexes was negligible.

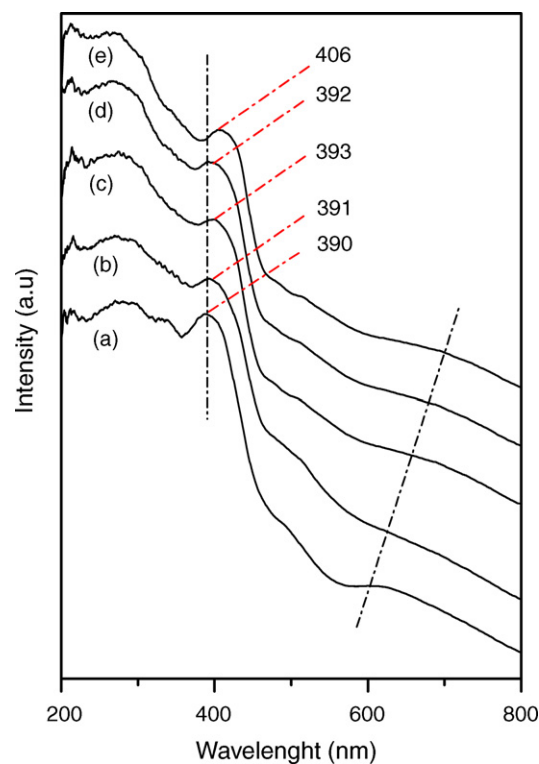
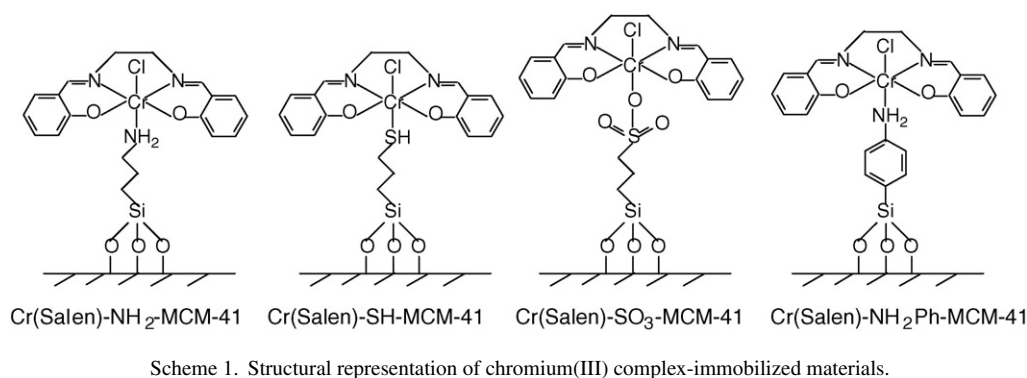


Fig. 2. UV-vis spectra of (a) Cr(salen), (b) Cr(salen)-NH₂-MCM-41, (c) Cr(salen)-SH-MCM-41, (d) Cr(salen)-SO₃-MCM-41 and (e) Cr(salen)-NH₂Ph-MCM-41.



3.3. Textural properties of the complex-immobilized materials

The mesostructures of complex-immobilized materials were confirmed by the powder X-ray diffraction and N₂ adsorption–desorption technique. The powder XRD patterns of complex-immobilized materials all showed one single peak around 2 θ angles of 2–3°, corresponding to the (100) plane of the hexagonal unit cell (see Fig. 3). The higher angle peaks associated with (110) and (200) reflections present in the parent sample no longer appeared, and an overall decrease in the intensity of (100) reflections was observed. This was due to the decrease in local order as previously mentioned by Lim and Stein [28]. Moreover, the (100) reflections of complex-immobilized materials showed clear shifts to higher 2 θ values compared to

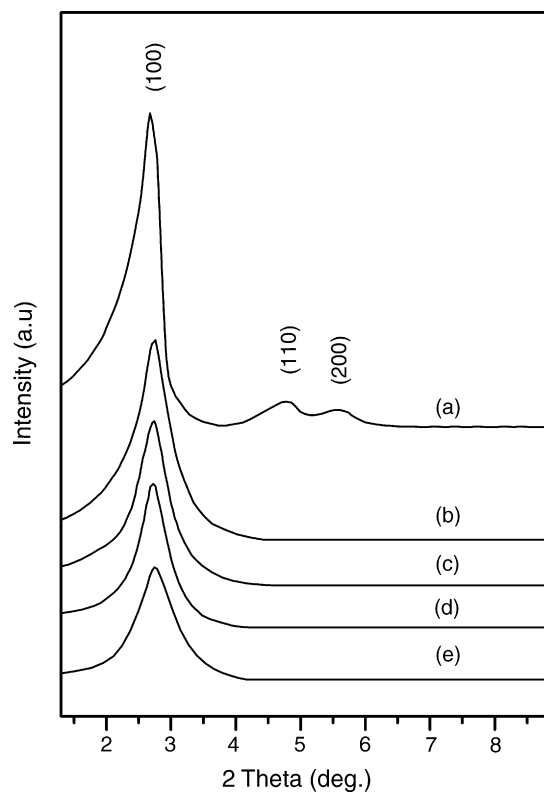


Fig. 3. XRD patterns of (a) MCM-41, (b) Cr(salen)-NH₂-MCM-41, (c) Cr(salen)-SH-MCM-41, (d) Cr(salen)-SO₃-MCM-41 and (e) Cr(salen)-NH₂Ph-MCM-41.

that of parent MCM-41, which could be attributed to the contraction of the unit cells of the grafted samples originated from the immobilization of the bulky organometallic groups inside the channels of MCM-41 [29–33].

The N₂ adsorption–desorption isotherms of complex-immobilized materials all displayed type IV isotherms according to the IUPAC [34], suggesting that the mesostructure of support remained after immobilization of Cr(salen) complex (see Fig. 4). However, a significant decrease in surface area and pore size of complex-immobilized materials was observed in comparison with that of parent MCM-41 (see Table 1), which might be due to the attaching of the organic moieties on the walls of support [35].

3.4. Catalytic performance

Without any organic solvent, phase transfer catalyst or additive, the obtained complex-immobilized materials and their homogeneous analogue were tested and compared in the selective oxidation of BzCH₂OH to BzCOH with 30% H₂O₂. Only three products BzCOH, benzoic acid and benzyl benzoate were detected. Other products, if any, present as minor constituents could not be detected by the gas chromatograph under the conditions used herein.

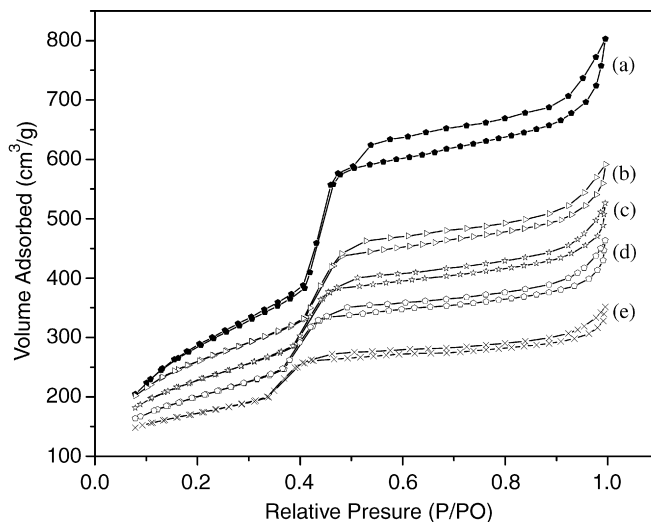


Fig. 4. Nitrogen adsorption–desorption isotherms of (a) MCM-41, (b) Cr(salen)-NH₂-MCM-41, (c) Cr(salen)-SH-MCM-41, (d) Cr(salen)-SO₃-MCM-41 and (e) Cr(salen)-NH₂Ph-MCM-41.

Table 2
Catalytic performance of the samples in BzCH₂OH oxidation

Entry	Catalysts	Conversion (mol%)	Selectivity (mol%)		
			BzCOH	Benzoic acid	Benzyl benzoate
1	Blank	3.0	100	0	0
2	Cr(salen)	11.3	65.5	22.7	11.8
3	Cr(salen)-NH ₂ -MCM-41	52.5	100	0	0
4	Cr(salen)-SH-MCM-41	41.4	93.3	3.9	2.8
5	Cr(salen)-SO ₃ -MCM-41	40.7	95.1	3.0	1.9
6	Cr(salen)-NH ₂ Ph-MCM-41	35.8	98.7	1.1	0.2

BzCH₂OH (0.05 mol), H₂O₂ (0.125 mol), heterogenized catalyst (0.25 g) or 1 mol% of homogeneous complex (relative to H₂O₂), 50 °C for 4 h.

Comparative results on the catalytic performance of Cr(salen) before and after being immobilized onto MCM-41 are listed in Table 2. It was found that no significant amount of BzCOH (<5%) was produced in the absence of catalyst. With Cr(salen) as catalyst, the BzCH₂OH conversion slightly increased to 11.3%, but the BzCOH selectivity was relatively low (65.5%) due to the simultaneous formation of benzoic acid (22.7%) and benzyl benzoate (11.8%). However, when the reaction was performed in the presence of the complex-immobilized materials, the catalytic performance, especially the selectivity to BzCOH, was significantly improved. The optimal BzCH₂OH conversion could reach 52.5 with 100% of the selectivity to BzCOH over Cr(salen)-NH₂-MCM-41. Such obviously enhanced catalytic performance could in part be attributed to the dispersion effect of support [7–12]. The isolated catalytic sites in complex-immobilized materials could prevent the formation of inactive μ -oxo dimers and other polymeric species. Thus, the complex-immobilized materials did not undergo rapid degradation as their corresponding homologous complex did, and then much higher catalytic performance was observed due to the immobilization.

Furthermore, considering that the oxidation reaction over complex-immobilized materials was carried out on support surface where the active sites were present, besides the dispersion effect originated from the large surface area, the support might also influence the surface reaction by modifying the local concentrations of reactants, reaction intermediates and products around active sites [7,36]. In the present investigation, this statement was further confirmed. Here, a series of adsorption tests was designed to investigate the local concentrations of the reactant (BzCH₂OH) and the product (BzCOH) around active sites in complex-immobilized materials, i.e. the amounts of BzCH₂OH and BzCOH molecules appearing around active sites by UV–vis spectroscopy. The UV–vis spectra of pure BzCH₂OH and BzCOH showed that one could trace the changes in their concentrations on the basis of absorptions at 258 and

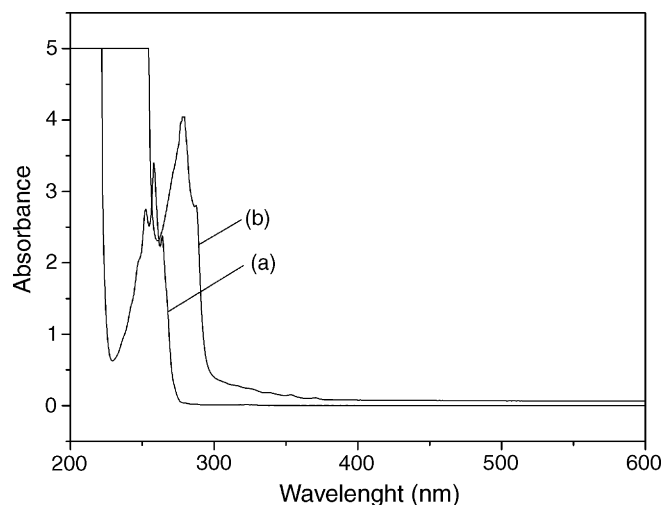


Fig. 5. UV–vis spectra of (a) BzCH₂OH and (b) BzCOH in *n*-hexane.

280 nm, respectively (see Fig. 5). And the adsorption capacities of all complex-immobilized materials for BzCH₂OH and BzCOH were compiled in Table 3. Interestingly, it was found that the adsorption capacities of complex-immobilized materials for BzCH₂OH were almost identical and were about 2.5 times that for BzCOH (see Table 3). This indicated that more BzCH₂OH molecules could appear around the active sites in complex-immobilized materials than BzCOH molecules under identical conditions. Since the two molecules had the comparable sizes, the significant difference in the probability of their appearing around active sites might be attributed to their different interaction with the support surface. In combination with the catalytic performance, some conclusions might be drawn. In homogeneous system, it was believed that the probability of BzCH₂OH and BzCOH molecules appearing around active sites was identical. Therefore, the freshly produced BzCOH tended

Table 3
Adsorption of BzCH₂OH and BzCOH with different complex-immobilized materials

Samples	Adsorption of BzCH ₂ OH (mol g ⁻¹)	BzCH ₂ OH in filtrate (mol L ⁻¹)	Adsorption of BzCOH (mol g ⁻¹)	BzCOH in filtrate (mol L ⁻¹)	BzCH ₂ OH/BzCOH ^a
Cr(salen)-NH ₂ -MCM-41	1.31 × 10 ⁻⁶	0.97 × 10 ⁻⁶	5.30 × 10 ⁻⁷	3.43 × 10 ⁻⁶	2.47
Cr(salen)-SH-MCM-41	1.33 × 10 ⁻⁶	0.90 × 10 ⁻⁶	5.27 × 10 ⁻⁷	3.44 × 10 ⁻⁶	2.52
Cr(salen)-SO ₃ -MCM-41	1.30 × 10 ⁻⁶	1.01 × 10 ⁻⁶	5.22 × 10 ⁻⁷	3.45 × 10 ⁻⁶	2.49
Cr(salen)-NH ₂ Ph-MCM-41	1.29 × 10 ⁻⁶	1.03 × 10 ⁻⁶	5.16 × 10 ⁻⁷	3.48 × 10 ⁻⁶	2.50

^a The molar ratios of the adsorption of BzCH₂OH to the adsorption of BzCOH with different samples.

to being further overoxidized to by-products. However, upon the homogeneous complex being immobilized on MCM-41, the probability of BzCOH appearing around active sites remarkably decreased, so the overoxidation of BzCOH was difficult to take place. This might afford the significant improvement in the selectivity to BzCOH over complex-immobilized materials than their homogeneous analogue. Simultaneously, the more BzCH₂OH molecules could accumulate around the active sites due to the introduction of support, which facilitated the oxidation and then led to much higher BzCH₂OH conversion. This also indicated that the diffusion limitation did not significantly influence the catalytic activities of the prepared complex-immobilized materials in the present catalytic oxidation system, which was different from other published reports [14,16]. Thus, it can be seen that the support exhibited a positive effect on the catalytic performance of complex-immobilized materials in BzCH₂OH oxidation.

The roles of linkers in the catalytic performance of complex-immobilized materials were also investigated in detail, and the comparisons with respect to their catalytic performance were represented in Fig. 6. It was found that the catalytic activities of all complex-immobilized materials increased with the prolonging of reaction time, whereas Cr(salen)-NH₂-MCM-41 always exhibited the highest BzCH₂OH conversion (see Fig. 6A). Moreover, the selectivity of 100% to BzCOH over Cr(salen)-NH₂-MCM-41 did not decrease until the BzCH₂OH conversion increased to 52.5% when the reaction run for 4 h (see Fig. 6B). In contrast, under the same conditions, in the presence of Cr(salen)-SH-MCM-41 and Cr(salen)-SO₃-MCM-41, the conversion was only 41.4 and 40.7% with a relatively lower BzCOH selectivity of 93.3 and 95.1%, respectively (see Fig. 6A and B). And the worst BzCH₂OH conversion of 35.8% and a moderate BzCOH selectivity of 98.7% were obtained with Cr(salen)-NH₂Ph-MCM-41 as catalyst.

Considering the similarity of dispersion degrees of active complexes in all complex-immobilized materials and the negligibility of the effect of the undesired residual linkers, which were confirmed by chemical analysis, the differences in the catalytic performance of complex-immobilized materials could be reasonably related to the nature of the linkers. For Cr(salen)-NH₂Ph-MCM-41 and Cr(salen)-NH₂-MCM-41, the terminal functional groups were both -NH₂ groups, however, much higher catalytic performance was obtained over Cr(salen)-NH₂-MCM-41. Such a significant difference could be attributed to their different linker flexibility. The UV-vis characterization indicated that the influences due to immobilization on active complexes via flexible linkers were relatively lesser, while the rigid aniline linker tended to denature the active groups by significantly changing their chemical conformations (see Fig. 2). Therefore, Cr(salen)-NH₂-MCM-41 which immobilized through flexible aminopropyl linker exhibited much higher catalytic performance than Cr(salen)-NH₂Ph-MCM-41 which immobilized through rigid aniline linker. Furthermore, the flexible aminopropyl linker in itself could allow the maximum conformational mobility of the active moieties [37], so the active complexes in Cr(salen)-NH₂-MCM-41 could relatively easily interact with the solvent and reactants similarly to homogeneous

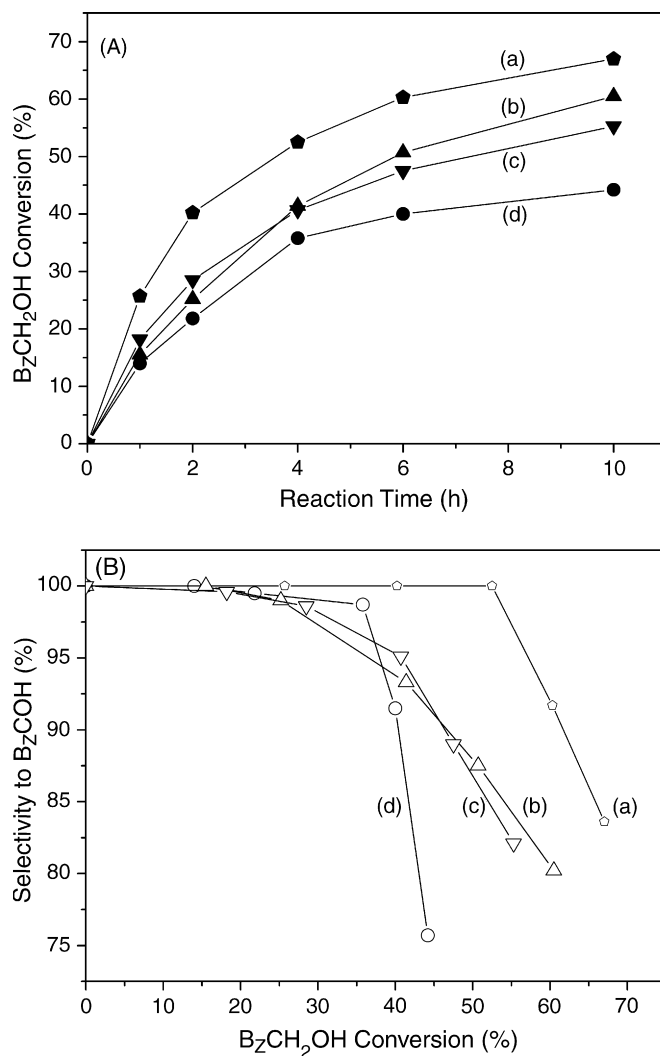


Fig. 6. The activity (A) and selectivity to BzCOH (B) in the oxidation of BzCH₂OH catalyzed by (a) Cr(salen)-NH₂-MCM-41, (b) Cr(salen)-SH-MCM-41, (c) Cr(salen)-SO₃-MCM-41 and (d) Cr(salen)-NH₂Ph-MCM-41.

catalyst. This might also account for the much higher catalytic performance of Cr(salen)-NH₂-MCM-41.

For Cr(salen)-NH₂-MCM-41, Cr(salen)-SH-MCM-41 and Cr(salen)-SO₃-MCM-41, they all immobilized via linkers with similar flexibility, and moreover, the influence due to the immobilization on the chemical conformations of their active complexes were negligible as depicted in UV-vis characterization. However, some significant differences in their catalytic performance were also detected. This could be associated with the different coordination abilities of the terminal functional groups in the three linkers to chromium. It was known that the stronger the coordination abilities of the terminal functional groups were, the more stable the resulting complex-immobilized materials would be. Therefore, the differences in the catalytic performance of the aforementioned three complex-immobilized materials could also be expected to depend on their different stabilities. In order to assess the stabilities of the complex-immobilized materials, an experiment to find out the extent of chromium leaching was carried out. The

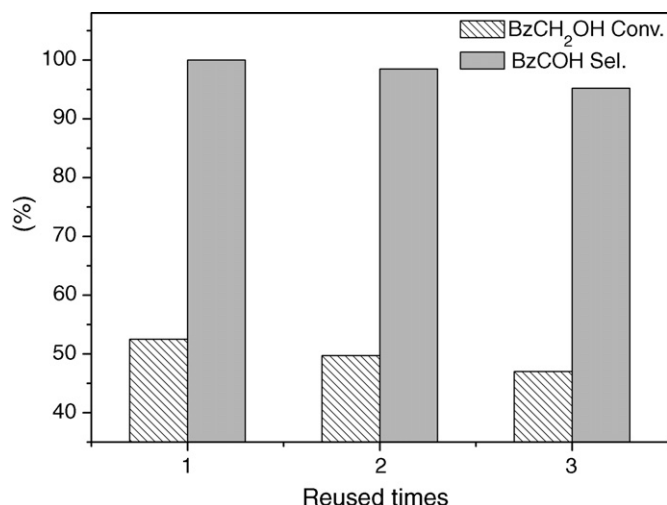


Fig. 7. Catalytic reusability of Cr(salen)-NH₂-MCM-41. Reaction conditions: BzCH₂OH (0.05 mol), H₂O₂ (0.125 mol), heterogenized catalyst (0.25 g), 50 °C for 4 h.

complex-immobilized materials were separated from the reaction mixtures by filtration after the oxidation reaction, and the filtrates were used for determination of chromium leaching by ICP emission spectroscopy. No chromium was detected in the filtrate of Cr(salen)-NH₂-MCM-41, while the chromium leaching from Cr(salen)-SH-MCM-41 and Cr(salen)-SO₃-MCM-41 was detectable at about 9 and 6%, respectively. Obviously, the relatively low catalytic performance of Cr(salen)-SH-MCM-41 and Cr(salen)-SO₃-MCM-41 suffered from their much low stabilities originated from the weak coordination abilities of their terminal –SH and –SO₃ functional groups. Consequently, the degree of flexibility of linkers and the coordination abilities of terminal functional groups in linkers both played important roles in the catalytic performance of complex-immobilized materials.

In addition, a further study on the catalytic reusability of Cr(salen)-NH₂-MCM-41, which was the most active catalyst in BzCH₂OH oxidation 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 solvent (water) to remove any physisorbed molecules, dried and reused in another two catalytic cycles. The catalyst was found to be still active after the third catalytic run, without much change in the catalytic performance (see Fig. 7). The nature of the recovered catalyst after reusing three times had been followed by FTIR spectrum and XRD pattern, and no significant change was observed. This indicated that the complex-immobilized materials with high catalytic performance and stability for the selective oxidation of BzCH₂OH was developed by coordinatively bonding the Cr(salen) complex on surface modified MCM-41.

4. Conclusions

Cr(salen) complex was successfully immobilized onto MCM-41 via aminopropyl, mercaptopropyl, sulfonicpropyl and aniline linkers, respectively. Owing to the abilities of support to highly disperse the active complexes and to control the local

concentrations of the reactant and product around active sites, the immobilization led to an enhanced catalytic performance in BzCH₂OH oxidation. Moreover, the catalytic performance of complex-immobilized materials decreased in the order: Cr(salen)-NH₂-MCM-41 > Cr(salen)-SH-MCM-41 > Cr(salen)-SO₃-MCM-41 > Cr(salen)-NH₂Ph-MCM-41. Such a difference could be attributed to their different linker flexibility and coordination abilities of terminal functional groups in linkers. The best BzCH₂OH conversion reached 52.5 with 100% of the selectivity to BzCOH over Cr(salen)-NH₂-MCM-41 under the conditions used, and this complex-immobilized material could be reused for several runs.

Acknowledgements

The authors acknowledge the financial supports from State Key Program for Development and Research of China (No. 2005CB221402) and National Science Technology Foundation of China (2006BAC2A08).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.06.012.

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