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Surface-modified Improvement in Catalytic Performance of Cr(salen) Complexes Immobilized on MCM-41 in Solvent-Free Selective Oxidation of Benzyl Alcohol

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Abstract A series of typical methyl regulators were used to finely modify the Cr(salen) complex immobilized on MCM-41. Such immobilized complexes were effective catalysts for solvent-free selective oxidation of benzyl alcohol (BzOH) with 30% hydrogen peroxide (H_2O_2), and they all exhibited much higher catalytic performance than their homogeneous analogue. Simultaneously, the introduction of methyl regulators was found to significantly improve the catalytic performance of immobilized complexes by modifying their surface properties. The optimal BzOH conversion reached 65.0% with 100% selectivity to benzaldehyde (BzH).

Keywords Immobilized Cr(salen) complex · Methyl regulator · Solvent-free · Selective oxidation · Benzyl alcohol

1 Introduction

Catalytic liquid phase oxidation of BzOH to BzH is a widely investigated reaction as it provides chlorine-free BzH required in perfumery and pharmaceutical industries [1], and many catalytic systems have been developed for this conversion. Among them, transition metal Schiff base complexes, especially the salen complexes containing flexible ethylenediamine backbone in resemblance of enzymatic catalysis are eye-catching due to the drastic change in the reactivity and special selectivity to a desired product [2, 3]. However, such homogeneous complexes suffered from the drawbacks of poor catalyst recovery and product separation [4]. Furthermore, the easy formation of μ-oxo dimers and other polymeric species in homogeneous systems also led to irreversible catalyst deactivation [3, 5–9]. Therefore, in the past decades, much effort has been paid to the binding of homogeneous complexes to various supports such as molecular sieves [7–9], ion exchange resins [10], polymeric membranes [11] and layered-double hydroxides [12].

In order to further improve the catalytic performance of heterogeneous catalysts, several groups devoted to finely modify their surface properties by introduction of methyl regulators [13–16]. Pérez-Pariente et al. introduced hydrophobic methyl groups to the surface of sulfonic acid founctionalized MCM-41 [15], and the resulting methyl-containing samples showed enhanced catalytic performance in the esterification of glycerol with lauric and oleic acids due to their improved hydrophobicity. Balwizão and coworkers also reported that the incorporation of methyl groups improved the catalytic performance of immobilized vanadyl Schiff base complex in the reaction of benzaldehyde with trimethylsilyl cyanide, which was attributed to the reduction in the amounts of free silanol groups on support surface [16]. These indicated that it was feasible to tailor the heterogeneous catalysts for desired performance through further finely modifying their surface properties by introduction of methyl regulators. Thus, an in-depth study on the effect of the methyl regulators on the catalytic

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performance of heterogeneous catalysts was very essential. In the present investigation, three typical methyl regulators were used to further modify the conventional Cr(salen) complex immobilized on MCM-41. The roles of hydrophobic methyl regulators in the catalytic performance of immobilized complexes were investigated in the solvent-free selective oxidation of BzOH with 30% H_2O_2.

2 Experimental

2.1 Catalyst Preparation

2.1.1 Preparation of MCM-41 and Aminopropyl Modified MCM-41 (APTES-MCM-41)

The synthetic procedures for MCM-41 had been previously described elsewhere as in the reference [17]. Following the procedures described in the literature [18], aminopropyl modified MCM-41 (referred hereafter as APTES-MCM-41) was prepared by refluxing the surfactant-free MCM-41 with aminopropyltriethoxysilane in toluene. Noticeably, the less amount of alkoxysilane agent was deliberately introduced in anchoring solution (moles MCM-41/moles aminopropyltriethoxysilane = 10) to reserve enough residual silanol groups for the following silylation with methyl regulators.

2.1.2 Preparation of Methyl-containing APTES-MCM-41 (APTES-MCM-41$(CH_3)_x$ (x = 1, 2, 3))

According to the literature [16], the as-prepared APTES-MCM-41 (3 g) was degassed at 50 °C under 10^{-2} Pa for 2 h. Then, an excess of methyltriethoxysilane (dimethyldiethoxysilane or trimethylethoxysilane) (0.03 mol) in dry toluene (100 mL) was added, and the suspension was stirred at reflux temperature under nitrogen flow for 24 h. The resulting solid was filtered, Soxhlet-extracted with dichloromethane for 24 h and dried in air (at 60 °C under 10^{-2} Pa for 3 h). Then, the corresponding methyl-containing APTES-MCM-41 were obtained and denoted as APTES-MCM-41$(CH_3)_1$ (APTES-MCM-41$(CH_3)_2$ or APTES-MCM-41$(CH_3)_3$).

2.1.3 Preparation of the Homogeneous Chromium Schiff Base Complex of 3-[N,N′- Bis(salicy1ideneamino) ethane] (Cr(salen))

The Schiff base ligand salen was prepared and purified according to the established procedures [19]. The homogeneous Cr(salen) complex was synthesized as in literature [3]. An equimolar amount of an ethanolic solution of $CrCl_3 \cdot 6H_2O$ (0.03 mol/L) was mixed with the ligand salen (0.03 mol/L 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.

2.1.4 Immobilization of Cr(salen) Over APTES-MCM-41 and APTES-MCM-41$(CH_3)_x$

Typically, to the suspension of freshly dried APTES-MCM-41 or APTES-MCM-41$(CH_3)_x$ (1 g) in 50 mL of dry toluene, the solution of the as-prepared Cr(salen) 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 neat complex 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 support (APTES-MCM-41 or APTES-MCM-41$(CH_3)_x$ (x = 1, 2, 3)), the immobilized complexes were obtained and denoted as Cr(salen)-MCM-41, Cr(salen)-MCM-41$(CH_3)_x$ (x = 1, 2, 3), respectively (see Scheme 1).

2.2 Catalyst Characterization

The contents of carbon and nitrogen of all samples were determined using a Vario EL analyzer. The chromium contents of complexes were measured by inductively coupled plasma (ICP) emission spectroscopy (PerkinElmer ICP OPTIMA-3,000).

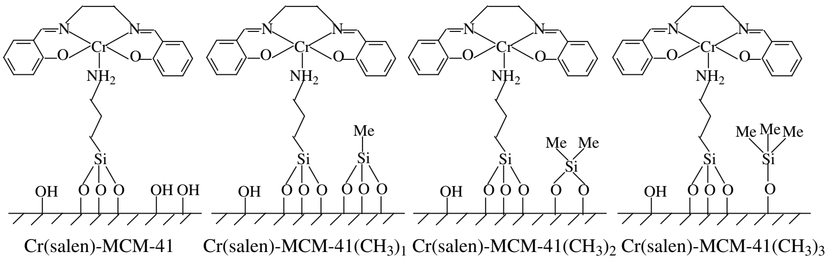
Powder X-ray diffraction (XRD) experiments were performed at room temperature on a Rigaku D Max III VC instrument with Ni filtered Cu Kα radiation (λ = 1.5404 Å) at 40 kV and 30 mA, in the 2θ range of 1~9° at a scan rate of 1°/min.

N_2 adsorption–desorption isotherms were obtained at liquid nitrogen temperature on a Micromeritics ASAP-2,000 instrument (Norcross, GA), using static adsorption procedures. Samples were outgassed at 80 °C and 10^{-4} Pa overnight prior to the measurement. Surface area (S_{BET}) was calculated by the BET method [20] and the average pore diameter (d_p) was calculated by the BJH method from the desorption isotherm [21].

Water adsorption isotherms were measured gravimetrically using a BELSORP 18 instrument (Bel Japan Inc.) at room temperature. Before the adsorption experiments, samples were pretreated at 110 °C for 6 h under vacuum.

FTIR spectra of samples for coordination structure characterization were recorded in KBr disks at room temperature on a Nicolet 470 FT spectrophotometer. And the

Scheme 1 Structural representation of the as-prepared immobilized chromium complexes



weight ratio of sample to KBr was 1/100. FTIR spectra of samples for calculating the amounts of silanol groups were recorded at room temperature under vacuum using a sealed greaseless quartz cell fitted with CaF_2 windows on a Nicolet 470 FT spectrophotometer. Self-supported wafers (~10 mg) were prepared by pressing the silicate powder at 1 Ton cm^{-2} for 3 min. The samples were outgassed at 100 °C under 10^{-2} Pa for 10 h before recording the FTIR spectra.

UV-vis absorption spectra of opaque powders for coordination structure characterization were recorded on a Shimadzu UV-vis spectrophotometer (model 2501 PC) with the optical grade BaSO4 as reference. UV-vis absorption spectra of transparent solutions for adsorption test were also recorded on this Shimadzu UV-vis spectrophotometer.

2.3 Catalytic Test

The oxidation of BzOH was carried out in a 100 mL Teflon-lined and magnetically stirred autoclave. First a mixture with 0.25 g heterogenised catalyst or 1 mol% of homogeneous complex (relative to H_2O_2) and 0.05 mol BzOH was stirred for about 10 min, then 0.125 mol 30% H_2O_2 was added. The autoclave was heated to 50 °C within 5 min. After the reaction run for 4 h, the catalyst was removed from the reaction mixture by centrifugal separation, and then the products were analyzed using a gas chromatograph with flame ionization detector, using a capillary 30 m HP-5 column and N_2 as carrier gas (Inj. temp. 250 °C, Dect. temp. 250 °C; Init. Temp. 40 °C, Init. time. 0 min, Rate. 10 °C/min, Final temp. 220 °C; Flow rate: 4 mL/min). H_2O_2 consumption was determined after the reactions by iodometric titration.

2.4 Adsorption Test

Typically, 0.05 g sample was mixed separately with the solution A (8×10^{-8} mol BzOH in 15 mL *n*-hexane) and B (7.8×10^{-8} mol BzH 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 Coordination Structures of Immobilized Complexes

Chemical analysis revealed that the obtained values of Cr(salen) were quite comparable with the calculated values (see Table 1), indicating that the as-prepared homogeneous complex held the expected elemental composition. The N/Cr molar ratios of all immobilized complexes were well consistent with the expected value of 3, which provided a supporting evidence for the successful immobilization of the homogeneous complex onto the support. Furthermore, the increasing carbon content from Cr(salen)-MCM-41 to Cr(salen)-MCM-41$(CH_3)_3$ was indicative of the successful introduction of the methyl regulators, and that the methyl content in immobilized complexes also increased gradually from Cr(salen)-MCM-41 to Cr(salen)-MCM-41$(CH_3)_3$.

Considering the similarity of Cr(salen)-MCM-41$(CH_3)_x$ ($x = 1, 2, 3$) in spectroscopic characterization, we chose Cr(salen)-MCM-41$(CH_3)_3$ as a typical sample for comparison with Cr(salen) and Cr(salen)-MCM-41. 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 representative bands for the successful preparation of Cr(salen) with a tetradentate ONNO functionality appeared at about 1602 cm^{-1} and 1547 cm^{-1}, which were attributed to the C=N stretching vibration of imine groups and the typical band of metallosalen complex, respectively [23, 24]. The FTIR spectra of immobilized complexes were similar to that of homogeneous Cr(salen) complex if the bands belonging to MCM-41 were excluded. This indicated that the quadridentate coordination structure of homogeneous complex remained intact in all immobilized complexes in spite of the incorporation of different methyl regulators.

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 transitions (see Fig. 2). This was similar to related metal salen compounds described in the literature [25, 26], indicating the successful preparation of Cr(salen) complexes. The UV-vis spectra of all immobilized complexes

Table 1 Composition and textural parameters of samples

Samples	Composition					Textural parameters	
	C (wt%)	N (wt%)	Cr (wt%)	C/N[a]	N/Cr[a]	S_{BET} (m^2/g)	d_p (nm)
Cr(salen)	54.33 (54.31)[b]	7.91 (7.92)[b]	14.7 (14.71)[b]	8.01 (8.00)[b]	2.00 (2.00)[b]	–	–
MCM-41	–	–	–	–	–	1030	2.76
Cr(salen)-MCM-41	5.71	1.05	1.3	6.34	2.99 (3.00)[b]	710	2.30
Cr(salen)-MCM-41(CH_3)$_1$	6.05	0.97	1.2	7.28	3.00 (3.00)[b]	659	2.18
Cr(salen)-MCM-41(CH_3)$_2$	6.82	0.98	1.2	8.12	3.02 (3.00)[b]	630	2.10
Cr(salen)-MCM-41(CH_3)$_3$	7.30	0.89	1.1	9.57	2.99 (3.00)[b]	595	2.06

[a] Molar ratio

[b] Value in parenthesis corresponds to the calculated results

were quite similar to the spectrum of neat complex, further confirming that the immobilized chromium Schiff base complexes as depicted in Scheme 1 were all successfully prepared.

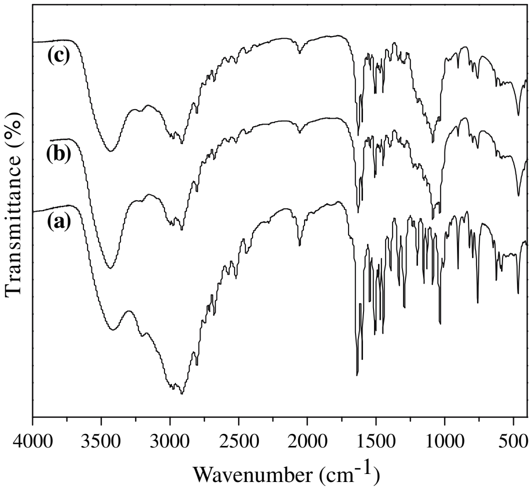


Fig. 1 FTIR spectra of (**a**) Cr(salen), (**b**) Cr(salen)-MCM-41, (**c**) Cr(salen)-MCM-41(CH_3)$_3$

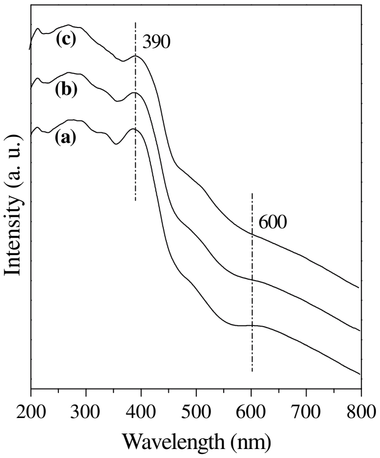


Fig. 2 UV-vis spectra of (**a**) Cr(salen), (**b**) Cr(salen)-MCM-41, (**c**) Cr(salen)-MCM-41(CH_3)$_3$

3.2 Structural and Textural Properties of Immobilized Complexes

The powder XRD patterns of immobilized complexes all showed one single peak around 2θ angles of 2–3°, corresponding to the (100) plane of the hexagonal unit cell (see Fig. 3). This indicated that the structural ordering of the MCM-41 channels remained after the immobilization of Cr(salen) complex. Nevertheless, 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) reflection was observed. These changes were due to the decrease in local order as previously mentioned by Lim et al. [27]. Simultaneously, the (100) reflections of immobilized complexes all showed clear shifts to higher 2θ value compared to that of parent MCM-41, which could be attributed to the contraction of

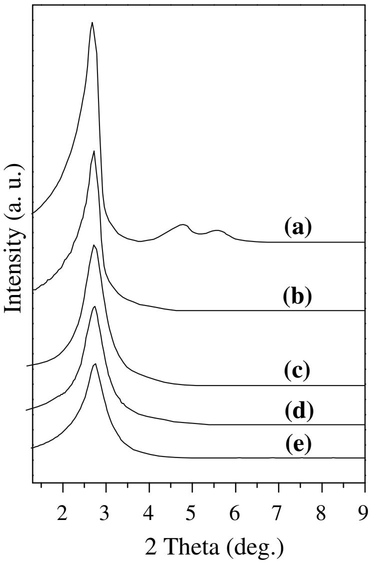


Fig. 3 XRD patterns of (**a**) MCM-41, (**b**) Cr(salen)-MCM-41, (**c**) Cr(salen)-MCM-41(CH_3)$_1$, (**d**) Cr(salen)-MCM-41(CH_3)$_2$, (**e**) Cr (salen)-MCM-41(CH_3)$_3$

the unit cells of the grafted samples originated from the immobilization of the bulky organometallic groups inside the channels of MCM-41 [28–30].

The N_2 adsorption–desorption isotherms of immobilized complexes all corresponded to the type IV class of the IUPAC classification (see Fig. 4), indicating the mesoporous character of the samples [31]. However, the immobilized complexes exhibited a significant decrease in surface area and pore size in comparison with their parent sample (see Table 1), which could be due to the attaching of the organic moieties on the walls of support [32].

3.3 Surface Properties of Immobilized Complexes

The densities of Cr(salen) complexes per surface area in all immobilized complexes were very similar (see Table 2), which indicated that almost identical dispersion degrees of active moieties were present in immobilized complexes. As expected, with the introduction of apolar methyl regulators, the amounts of polar residual silanol groups on support surface of immobilized complexes decreased, and then the surface polarity of immobilized complexes decreased too. Noticeably, for the methyl-containing immobilized complexes, the amounts of residual silanol groups on support surface were in the following order: Cr(salen)-MCM-41$(CH_3)_1$ < Cr(salen)-MCM-41$(CH_3)_2$ < Cr(salen)-MCM-41$(CH_3)_3$. Such an order could be attributed to the different anchorages of the three-methyl regulators on support surface, and was just consistent with the incremental tendency of methyl content in samples. Furthermore, the amount of water adsorbed in the immobilized complexes decreased as the samples became richer in methyl groups, indicating that the hydrophobic character of the surface increased with the loading of methyl groups.

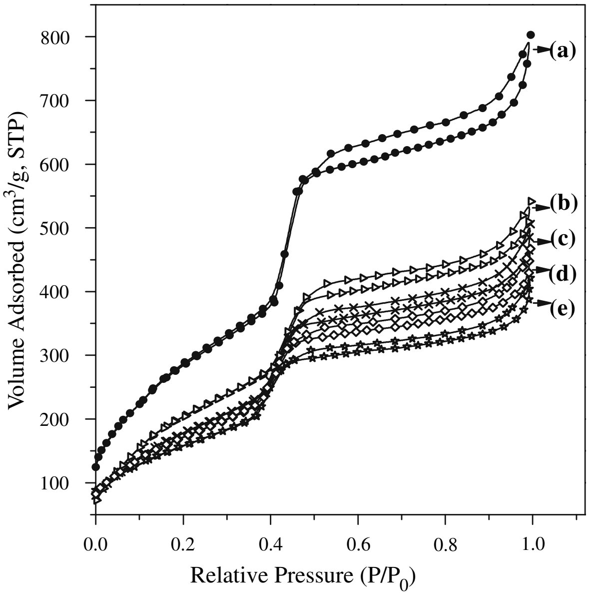


Fig. 4 Nitrogen adsorption–desorption isotherms of (**a**) MCM-41, (**b**) Cr(salen)-MCM-41, (**c**) Cr(salen)-MCM-41$(CH_3)_1$, (**d**) Cr(salen)-MCM-41$(CH_3)_2$, (**e**) Cr(salen)-MCM-41$(CH_3)_3$

3.4 Catalytic Performance

Without any organic solvent, phase transfer catalyst or additive, the so-obtained immobilized complexes and their homogeneous analogue were tested in the selective oxidation of BzOH to BzH with 30% H_2O_2. Only three products BzH, benzoic acid and benzyl benzoate were detected under the conditions used herein. The results in Table 3 revealed that no significant amount of BzH (<5%) was produced in the absence of catalyst. With Cr(salen) as catalytst, the BzOH conversion slightly increased to 12.2%, but the BzH selectivity was relatively low (65.4%). Noticeably, when the reaction was performed over immobilized Schiff base complexes, the catalytic performance was significantly improved. The optimal BzOH conversion reached 65.0% with 100% of the selectivity to BzH over Cr(salen)-MCM-41$(CH_3)_2$. Such obviously enhanced catalytic performance could be attributed to the dispersion effect of support [3, 5–9]. The isolated catalytic sites in immobilized complexes could prevent the formation of inactive μ-oxo dimers and other polymeric species. Thus, the immobilized complexes did not undergo rapid degradation as was observed in solution, and then exhibited much higher catalytic performance than their homologous analogue.

The comparisons with respect to the catalytic performance of immobilized complexes strongly indicated that the introduction of methyl regulators led to a significant improvement in catalytic activity, selectivity and H_2O_2 efficiency for this oxidation reaction (see Table 3). Moreover, with the rise of methyl content in the catalysts from Cr(salen)-MCM-41$(CH_3)_1$ to Cr(salen)-MCM-41$(CH_3)_3$, the BzOH conversion and H_2O_2 efficiency decreased gradually while the selectivity to BzH increased continually. Especially in the presence of Cr(salen)-MCM-41$(CH_3)_2$ and Cr(salen)-MCM-41$(CH_3)_3$, BzOH was oxidized to BzH exclusively without the formation of by-products.

Considering the similarity of dispersion degree of active Cr(salen) complexes in all immobilized catalysts (see Table 2), the differences in their catalytic performance could be related to their different textural properties and surface properties. The N_2 adsorption–desorption characterization showed that a significant decrease in surface area and pore size of methyl-containing immobilized complexes was observed in comparison with that of Cr(salen)-MCM-41 (see Table 1). This indicated that the introduction of methyl regulators could increase the steric hindrance. If

Table 2 Surface group densities of immobilized complexes

Samples	Densities of Cr(salen) ($\times 10^{-7}$ mol/m^2)	Residual silanol groups[a] per gram sample ($\times 10^{-3}$ mol/g)	Water adsorbed[b] per gram sample (g/g)
MCM-41	–	5.0	0.12
Cr(salen)-MCM-41	3.52	2.1	0.11
Cr(salen)-MCM-41$(CH_3)_1$	3.50	0.7	0.08
Cr(salen)-MCM-41$(CH_3)_2$	3.66	0.8	0.07
Cr(salen)-MCM-41$(CH_3)_3$	3.56	1.1	0.04

[a] Calculated from FTIR spectroscopy

[b] The saturation adsorption capacities of water for samples were obtained from the adsorption isotherms of water

Table 3 Catalytic performance of the obtained complexes in the selective oxidation of BzOH

Catalysts	BzOH Con.[a] (mol %)	Sel.[b] (mol %)			H_2O_2 efficiency[c] (mol %)
		BzH	Benzoic acid	Benzyl benzoate	
Blank	3.0	100	0	0	5.1
Cr(salen)	12.2	65.4	23.5	11.1	15.3
Cr(salen)-MCM-41	40.5	80.6	12.4	7.0	46.5
Cr(salen)-MCM-41$(CH_3)_1$	66.1	92.3	5.6	2.1	77.3
Cr(salen)-MCM-41$(CH_3)_2$	65.0	100	0	0	76.6
Cr(salen)-MCM-41$(CH_3)_3$	61.3	100	0	0	70.9

[a] Conversion = (moles of BzOH reacted/moles of BzOH in the feed) × 100

[b] Selectivity = (moles of BzOH converted to the products/moles of BzOH reacted) × 100

[c] Efficiency of H_2O_2 for BzOH oxidation = (moles of H_2O_2 converted to the products/moles of H_2O_2 consumed) × 100

this increased steric hindrance plays a decisive role in the present catalytic process, it would limit the accessibility of reactant (BzOH) to active sites and the expulsion of object product (BzH) freely out of pore, and then the methyl-containing immobilized complexes should exhibit lower catalytic performance than Cr(salen)-MCM-41. However, actually much higher BzOH conversion and BzH selectivity were both obtained over methyl-containing immobilized complexes than over Cr(salen)-MCM-41. Obviously, the increase in steric hindrance originated from the introduction of methyl regulators was not a primary factor in catalytic performance of immobilized complexes. This result could be due to the less molecule size of benzyl alcohol and benzaldehyde as compared with the pore size of immobilized complexes. Taking this into account, the significant differences in the catalytic performance of immobilized complexes could be reasonably attributed to their different surface properties due to the introduction of different methyl regulators.

Lv et al. reported that the silanol groups on support surface were involved in the decomposition reaction of H_2O_2 by exchanging with HO_2^- groups in H_2O_2, which facilitated the unproductive decomposition of H_2O_2 to O_2 [33]. This indicated that the amounts of residual silanol groups on support surface of immobilized complexes could influence the H_2O_2 efficiency. As mentioned above, the H_2O_2 efficiency and BzOH conversion showed almost identical profiles over the immobilized complexes, so the BzOH conversion might also relate to the amounts of residual silanol groups. In order to clearly understand their correlation, both H_2O_2 efficiency and BzOH conversion were plotted as a function of the amounts of residual silanol groups in Fig. 5. It was found that the H_2O_2 efficiency and BzOH conversion both increased with the decrease in the amounts of residual silanol groups. Thus, the much higher

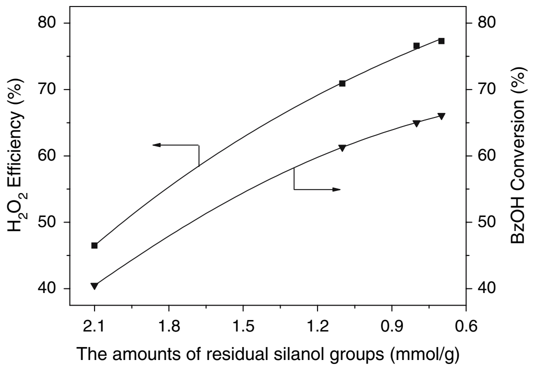


Fig. 5 The correlation between the H_2O_2 efficiency, BzOH conversion and the amounts of residual silanol groups

Table 4 Adsorption of BzOH and BzH with different immobilized complexes

Samples	Adsorption of BzOH ($\times 10^{-6}$ mol/g)	Adsorption of BzH ($\times 10^{-6}$ mol/g)
Cr(salen)-MCM-41	1.31	0.53
Cr(salen)-MCM-41$(CH_3)_1$	1.30	0.33
Cr(salen)-MCM-41$(CH_3)_2$	1.29	0.30
Cr(salen)-MCM-41$(CH_3)_3$	1.29	0.29

H_2O_2 efficiency and BzOH conversion over methyl-containing immobilized complexes than Cr(salen)-MCM-41 could be attributed to the decrease in the amounts of residual silanol groups on support surface due to the incorporation of methyl regulators. Similarly, the incremental tendency of the amounts of residual silanol groups in the catalysts from Cr(salen)-MCM-41$(CH_3)_1$ to Cr(salen)-MCM-41$(CH_3)_3$ could afford the gradually decreased H_2O_2 efficiency and BzOH conversion. Consequently, the methyl regulators played an important role in both H_2O_2 efficiency and BzOH conversion by modifying the amounts of residual silanol groups on support surface of immobilized catalysts.

The effect of methyl regulators on the BzH selectivity might also be attributed to their modification in the surface properties of immobilized complexes such as the increased hydrophobicity and the decreased polarity, which modified the amounts of BzOH and BzH molecules accessible to the active sites [13, 34]. In order to test this hypothesis, a series of adsorption tests were carried out. The amounts of BzOH and BzH molecules accessible to the active sites of immobilized complexes could be investigated by determining their adsorption capacities for BzOH and BzH, respectively [34]. The results in Table 4 revealed that upon the introduction of methyl regulators, the adsorption capacities of immobilized complexes for BzH decreased remarkably, while their adsorption capacities for BzOH varied slightly. This indicated that the introduction of methyl regulators suppressed mainly the accessibility of BzH molecules to the active sites of immobilized complexes. Thus, the probability of the freshly produced BzH being further overoxidized to by-products remarkably decreased in the presence of methyl-containing catalysts. This is why the much higher BzH selectivity was observed over the methyl-containing immobilized complexes than over Cr(salen)-MCM-41. Simultaneously, the adsorption capacities of methyl-containing immobilized complexes for BzH were found to decreased gradually from Cr(salen)-MCM-41 to Cr(salen)-MCM-41$(CH_3)_3$, so the selectivity to BzH over methyl-containing complexes continually increased as the catalysts became richer in methyl groups. As a result, the incorporation of methyl regulators into the immobilized complexes also influenced the BzH selectivity by inducing a significant decrease in the amounts of BzH molecules accessible to active sites.

4 Conclusions

A series of methyl-containing immobilized Cr(salen) complexes were successfully prepared and exhibited promising catalytic performance towards the selective oxidation of BzOH with 30% H_2O_2 in the absence of organic solvent. The introduction of methyl regulators decreased the amounts of residual silanol groups on support surface of immobilized complexes, which led to a remarkably enhanced H_2O_2 efficiency and BzOH conversion. Simultaneously, such a modification could also significantly improve the selectivity to BzH by inducing a decrease in the amounts of BzH molecules accessible to active sites. Under the optimum reaction conditions, the BzOH conversion could reach 65.0% with 100% of the selectivity to BzH.

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