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# Heterogenization of functionalized Cu(II) and VO(IV) Schiff base complexes by direct immobilization onto amino-modified SBA-15: Styrene oxidation catalysts with enhanced reactivity

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#### ABSTRACT

Two functionalized copper(II) and oxovanadium(IV) Schiff base complexes of type  $[M(N_2O_2), M=Cu, M_2O_2)]$ VO] bearing chloromethyl groups were respectively synthesized, directly anchored onto amino-modified SBA-15 materials and examined as catalysts for styrene oxidation. The purity of each ligand was confirmed by <sup>1</sup>H NMR, FT-IR and elemental analysis. XRD, N<sub>2</sub> adsorption/desorption and TEM results indicated that the mesoporous structure of SBA-15 remained intact throughout the grafting procedure. FT-IR, UV-vis spectroscopy plus TG-DTA data demonstrated the incorporation of copper(II) and oxovanadium(IV) complexes on amino-modified SBA-15. ICP-AES, SEM-EDX combined with XPS data further showed the different anchorage status of copper(II) and oxovanadium(IV) species on amino-modified SBA-15. The copper(II) Schiff base complex was anchored through the coordination of copper atom with the nitrogen atom of the amino group modified on the SBA-15 external surface. The oxovanadium(IV) Schiff base complex, however, was covalently anchored on SBA-15 via the condensation reaction of the chloromethyl group of the Schiff base with the amino group from the modified SBA-15 matrix. The catalytic properties of supported copper(II) and oxovanadium(IV) complexes in the oxidation of styrene with air or  $H_2O_2$  as oxidant were investigated and compared with the properties of their homogeneous analogues. It was found that both heterogeneous copper(II) and oxovanadium(IV) catalysts were more active than their homogeneous analogues and that the product selectivity varied in cases of different oxidants. The supported oxovanadium(IV) complex showed high yield of styrene oxide (56.0%) and good recoverability when using air as oxidant.

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#### 1. Introduction

The epoxidation of olefins is of great interest due to the importance of epoxides in the manufacture of both bulk and fine chemicals [1,2]. Recently, much attention has been focused on developing novel catalytic processes based on efficient catalysts with easy recoverability and inexpensive eco-friendly oxidants, for example  $H_2O_2$ ,  $O_2$  and air.

Various transition metal compounds (Cu, Fe, Co, V and Mn) have been reported as active catalysts for the epoxidation of olefins [3–7]. A few reports showed that some copper(II) and oxovanadium(IV) based catalytic systems were efficient for the oxidation of styrene when using  $H_2O_2$  as oxidant [8–12]. For example, Maurya et al. [12] reported that copper(II) and dioxovanadium(V) compounds encapsulated in zeolite-Y ([Cu(sal-ambmz)Cl]-Y and [VO<sub>2</sub>(sal-ambmz)Cl]-Y) exhibited high catalytic activity in the oxidation of styrene and hydroxylation of phenol. Recently, many chemical researchers pursue new oxidation processes using molecular oxygen or naturally cheap air as the oxidant. Several successful examples of the catalytic epoxidation of styrene by molecular oxygen over cobalt(II)-containing molecular sieve catalysts (CoO<sub>x</sub>/SiO<sub>2</sub>, CoO<sub>x</sub>/NaX, Co/TS-1 and Co–ZSM-5) have been reported [13–15]. As far as we know, the catalytic performances of copper(II) and oxovandiun(IV) Schiff base complexes have not been evaluated in aerobic selective oxidations. Copper hydroxyphosphate (Cu<sub>2</sub>(OH)PO<sub>4</sub>) is one copper based catalyst used for aerobic epoxidation of styrene, with a low conversion of styrene (30.2%) and poor selectivity to styrene oxide (16.9%) [16].

Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts in a wide range of oxidation reactions [17–20]. Many strategies have been adopted to heterogenize the homogeneous catalysts to increase catalyst

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stability and allow for catalyst recycling and product separation. Conventionally, the Schiff base complexes are immobilized on polymeric organic materials such as resins, or polystyrene [21], then supported on inert porous solid such as alumina [22] and silica or encapsulated in the pores of zeolite-Y [23]. There are certain disadvantages with polymeric supports due to their vulnerability to some chemicals and solvents. Encapsulation of metal complexes in porous materials typified by zeolites leads to size restriction and severe leaching of catalysts. Mesoporous silica materials have been widely used as useful and versatile solid supports to construct various hybrid materials in catalysis, enzyme immobilization and drug delivery due to their large tunable pore dimensions, high surface areas and great diversity in surface functionalization [24,25]. Therefore, covalent anchoring of the Schiff base complexes onto a functionalized siliceous mesoporous material with large pore diameters seems to be promising. The mesoporous SBA-15 materials are more versatile than other mesoporous supports because of their larger pore diameter permitting easy diffusion of bulky reactants and products during the liquid-phase oxidation of styrene.

Herein, we report the immobilization of functionalized Cu(II) and VO(IV) Schiff base complexes bearing chloromethyl groups onto amino-modified SBA-15 materials and their catalytic properties in styrene oxidation. The catalytic performances of both heterogeneous copper(II) and oxovanadium(IV) catalysts were compared to those of their homogeneous analogues and the oxidation performances using air and H<sub>2</sub>O<sub>2</sub> as oxidizing agent were also compared.

#### 2. Experimental

#### 2.1. Materials

The following chemicals were commercially available and were used as received: 3-aminopropyltriethoxysilane (Aldrich), Pluronic P123 ( $EO_{20}PO_{70}EO_{20}$ ) (Aldrich), salicylaldehyde (99%), tetraethyl orthosilicate Si( $OC_2H_5$ )<sub>4</sub> (99%), styrene (98%). 30% H<sub>2</sub>O<sub>2</sub>, VOSO<sub>4</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub> and all organic solvents are A.R. grade. Toluene was dried by Na/diphenylketone ketyl and distilled under N<sub>2</sub> atmosphere. All air or moisture-sensitive compounds were transferred using a standard vacuum line and the Schlenk technique.

#### 2.2. Synthetic procedures (Scheme 1)

#### 2.2.1. Synthesis of amino-functionalized SBA-15

The mesoporous support SBA-15 (1.0 g), prepared by a literature method [26], was activated by heating at 120 °C for 2 h. After cooling, the activated SBA-15 was added to the 3-aminopropyltriethoxysilane (1.6 mmol in 20 ml of dry toluene) under N<sub>2</sub> atmosphere and the mixture was stirred at room temperature for 24 h. The resulting solid was filtered, washed, Soxhlet-extracted with CH<sub>2</sub>Cl<sub>2</sub> for 24 h and dried under vacuum. Found for APS–SBA-15: C, 5.37; H, 1.41; N, 1.39%. FT-IR (KBr pellets, cm<sup>-1</sup>): 1510 (NH<sub>2</sub>), 1000–1130 (Si–O–Si), 960 (Si–OH), 687 (N–H).

#### 2.2.2. Synthesis of 5-chloromethyl-2-hydroxybenzaldehyde

5-Chloromethyl-2-hydroxybenzaldehyde was synthesized from salicylaldehyde by the classical chloromethylation method. In a typical synthesis, 17.5 g (160 mmol) of salicylaldehyde was treated with 24 ml of 38% aqueous formaldehyde and 1.2 g of ZnCl<sub>2</sub> in 100 ml of con. HCl. The mixture was stirred at room temperature under N<sub>2</sub> atmosphere for 24 h. The resulting white solid was filtered and repeatedly extracted with diethyl ether. The combined organic phases were washed with saturated aqueous NaHCO<sub>3</sub> and water and then dried over MgSO<sub>4</sub>. The viscous oil was obtained by distillation and then subjected to crystallization in petroleum ether. The extract furnished 5-chloromethyl-2-hydroxybenzaldehyde as white-colored needles (9.0 g, 32.0% yield). Found: C, 57.57; H, 4.12%. Calc. for  $C_8H_7O_2Cl$ : C, 56.30; H, 4.10%. FT-IR (KBr pellets, cm<sup>-1</sup>): 3240 (OH), 2925, 2873 (Aliph-H), 1659 (C=O), 1260 (CH<sub>2</sub>Cl), 772 (C-Cl) (Supplementary Fig. S1). UV-vis,  $\lambda$  (nm): 224, 257, 332. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS,  $\delta$  ppm): 11.07 (1H, s, OH), 9.90 (1H, s, CHO), 7.59 (1H, s, Ar–H), 7.26–7.19 (1H, d, Ar–H), 7.02–6.08 (1H, d, Ar–H), 4.59 (1H, s, CH<sub>2</sub>Cl) (Supplementary Fig. S2).

#### 2.2.3. Synthesis of

#### *N*,*N*'-bis(5-chloromethyl-salicylidene)ethylenediamine (CM–SalenH<sub>2</sub>) and its metal complexes

3.41 g (20.0 mmol) of 5-chloromethyl-2-hydroxybenzaldehyde was dissolved in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>. A solution of ethylene diamine (0.67 ml, 10 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was then added. The resulting solution was stirred at room temperature for 24 h. After the solvent was removed under vacuum, the product was obtained as bright yellow crystals. Found: C, 58.50; H, 5.10; N, 7.86%. Cal. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 59.20; H, 4.90; N, 7.70%. FT-IR (KBr pellets, cm<sup>-1</sup>): 3423 (OH), 2929, 2887 (Aliph-H), 1647 (C=N), 1262 (CH<sub>2</sub>Cl), 769 (C–Cl). UV–vis,  $\lambda$  (nm): 252, 340, 381. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, TMS,  $\delta$  ppm): 11.12 (2H, s, OH), 7.83–6.98 (6H, m, Ar–H), 8.40, 8.44 (2H, s, CH=N), 4.44 (4H, s, CH<sub>2</sub>Cl), 3.48–3.38, 3.19–3.10 (4H, t, N–CH<sub>2</sub>–CH<sub>2</sub>–N) (Supplementary Fig. S3).

To prepare the metal complexes of CM–SalenH<sub>2</sub>, we dissolved 0.367 g of CM–SalenH<sub>2</sub> (1 mmol) and 1 mmol of Cu(CH<sub>3</sub>COO)<sub>2</sub> or VOSO<sub>4</sub> in 20 ml THF under N<sub>2</sub> atmosphere and we stirred the mixture at room temperature for 24 h. The solvent was removed by filtration, and the resulting solid was washed with copious tetrahydrofuran and dried in vacuum. Found for Cu–CM–Salen: C, 50.50; H, 3.82; N, 6.32; Cu, 13.50%. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>Cu: C, 50.61; H, 3.75; N, 6.56; Cu, 14.88%. FT-IR (KBr pellets, cm<sup>-1</sup>): 3423 (OH), 2929, 2887 (Aliph-H), 1621 (C=N), 767 (C–Cl), 526 (Cu–O), 470 (Cu–N). UV–vis,  $\lambda$  (nm): 240, 345, 389, 572. Found for VO–CM–Salen: C, 49.92; H, 3.63; N, 6.42; V, 11.50%. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub>V: C, 50.20; H, 3.72; N, 6.51; V, 11.84%. FT-IR (KBr pellets, cm<sup>-1</sup>): 3423 (OH), 2929, 2887 (Aliph-H), 1631 (C=N), 769 (C–Cl), 976 (V=O), 534 (V–O), 456 (V–N). UV–vis,  $\lambda$  (nm): 263, 323, 379, 554.

## 2.2.4. Immobilization of Cu–CM–Salen and VO–CM–Salen on amino-functionalized mesoporous SBA-15

Metal Schiff base complexes were anchored onto SBA-15 matrix based on the nucleophilic reaction between the chloromethyl modified metal complexes and the aminopropyl-functionalized SBA-15. A known amount of Cu–CM–Salen (0.33 g, 0.8 mmol) or VO–CM–Salen (0.32 g, 0.8 mmol) was added to a suspension of the amino-functionalized SBA-15 (1.0 g) in dry toluene and stirred at reflux temperature for 24 h. The resulting samples were filtered off, Soxhlet-extracted with CH<sub>2</sub>Cl<sub>2</sub> to remove untethered species and dried in vacuum. Cu–Salen–SBA, FT-IR (KBr pellets, cm<sup>-1</sup>): 3413 (OH), 3236 (N–H), 2926 (Aliph–H), 1636 (C=N), 1087, 808, 468 (Si–O–Si). UV–vis,  $\lambda$  (nm): 265, 349, 380, 576. VO–Salen–SBA, FT-IR (KBr pellets, cm<sup>-1</sup>): 3407 (OH), 3220 (N–H), 2931 (Aliph–H), 1629 (C=N), 1086, 804, 464 (Si–O–Si). UV–vis,  $\lambda$  (nm): 243, 325, 389.

#### 2.3. Characterization

Powder XRD was collected with a Rigaku X-ray diffractometer with nickel filtered CuK $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The samples were scanned in the range 2 $\theta$  = 0.4–5.0° and in steps of 2°/min. N<sub>2</sub> adsorption/desorption isotherms were recorded at 196 °C with a Micromeritics ASAP 2020. Before measurements, the samples were outgassed at 120 °C for 12 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore size distributions were measured using Barrett–Joyner–Halenda (BJH) analyses from the desorption branch of the isotherms. The infrared spectra (IR) of samples were recorded in KBr disks using a NICO-LET impact 410 spectrometer. UV-vis spectra were recorded on a PerkinElmer UV-vis spectrophotometer Lambda 20 using barium sulfate as the standard in the range 200-800 nm. TG-DTA was carried out on Shimadzu DTG-60 instrument. X-ray photoelectron spectra (XPS) were recorded on a VG ESCA LAB MK-II X-ray electron spectrometer using AlK $\alpha$  radiation (1486.6 eV, 10.1 kV). The spectra were referenced with respect to the C1 s line at 284.7 eV. The measurement error of the spectra was  $\pm 0.2 \text{ eV}$ . <sup>1</sup>H NMR experiments were carried out in sealed NMR tubes on a Varian Mercury-300 NMR spectrometer. Microanalyses for C, H, N were performed at the PerkinElmer 2400. Metal content was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a PerkinElmer emission spectrometer. The chemical microanalyses by EDX were performed on a JSM-6301F scanning microscope FEI with an EDX detector. Samples were coated with gold using a sputter coater. Transmission electron microscopy (TEM) results were recorded on a JEOL JEM 2010 operated at 200 kV.

#### 2.4. Catalytic reactions

All catalysts were dried overnight before they were subjected to epoxidation reactions. Typically, a 100 ml two-necked flask supplied with a magnetic stirrer and a backflow condenser was kept in a constant temperature oil bath. Ten mmol styrene, 50 mg of catalyst (5 mg for the homogeneous catalyst) were suspended in 10 ml of CH<sub>3</sub>CN. The reaction was started by adding 3.06 ml of 30%  $H_2O_2$  (3 equiv.) or 2.28 ml of isobutvraldehvde (2.5 equiv.), combined with bubbling air (80 ml/min) as oxidant at the reaction temperature. After the reaction was finished, the catalyst was filtered, washed with CH<sub>3</sub>CN, dried at 100 °C overnight and reused directly without further purification. The liquid organic products were quantified by using a gas chromatography (Shimadzu, GC-8A) equipped with a flame detector and an HP-5 capillary column. The products were identified by GC–MS, and calibration of GC peak areas of products was carried out with quantitative authentic samples.

#### 3. Results and discussion

#### 3.1. Structural integrity studies

The powder XRD patterns for SBA-15, Cu-Salen-SBA and VO-Salen-SBA are depicted in Fig. 1. The SBA-15 sample showed three peaks, indexed as the (100), (110) and (200) diffraction peaks, associated with the typical two-dimensional hexagonal symmetry of the SBA-15 material (Fig. 1a) [27]. For the hybrid materials, the relative intensities of the prominent diffraction peak (100) decreased after the introduction of bulky organometallic groups. The intensity reduction may be mainly due to contrast matching between the silicate framework and organic moieties which are located inside the channels of SBA-15 [28]. TEM images provide a direct visualization of well-ordered hexagonal arrays of 1D mesoporous channels particularly along the direction of the pore axis or in the direction perpendicular to the pore axis (Fig. 2). This result is in good agreement with the conclusion drawn from the XRD patterns and confirms that characteristic pore dimensions and channel structures of the support materials remain intact after the introduction of metal complexes to the support SBA-15. The N<sub>2</sub> adsorption/desorption isotherms of SBA-15 and the hybrid materials shown in Fig. 3 further confirm that the channels of the SBA-15 support remain accessible. Obviously, the hybrid materials maintain the characteristics of type IV isotherms and show a uniform pore size distribution in the mesoporous region.



Fig. 1. XRD patterns of (a) SBA-15, (b) Cu-Salen-SBA and (c) VO-Salen-SBA.

As shown in Table 1, the pore diameter decreased from 6.35 nm for pure silica SBA-15 to 6.19 nm for Cu–Salen–SBA and to 5.18 nm for VO–Salen–SBA. This result is in good agreement with the conclusion drawn from the TEM studies. Compared to the pure silica SBA-15, a pronounced decrease of the BET surface area and the pore volume and an increase of the wall thickness occurred due to the introduction of copper(II) or oxovanadium(IV) complexes. Similar trend has also been observed previously [29].

#### 3.2. Spectroscopic characterization

Fig. 4 shows the FT-IR spectra of the pure ligand and unsupported complexes of copper(II) and oxovanadium(IV). The ligand CM–SalenH<sub>2</sub> exhibited a band at  $1647 \text{ cm}^{-1}$  due to azomethine v(C=N) stretch (Fig. 4a). This band registered a low frequency shift of ca. 16–26 cm<sup>-1</sup> in the spectra of unsupported copper (Fig. 4b) and oxovanadium (Fig. 4c) complexes, indicating the coordination of azomethine nitrogen to the metal ions [30,31]. The coordination of the phenolic oxygen could not be ascertained unequivocally due to the appearance of a strong band in the  $3400 \, \text{cm}^{-1}$  (not shown). In the lower frequency region, the bands appeared at 526 and 470 cm  $^{-1}$  due to  $\upsilon$ (Cu–O) and  $\upsilon$ (Cu–N) vibrations in the Cu-CM-Salen material [32]. Similarly, VO-CM-Salen presented bands at 976, 534 and 456 cm<sup>-1</sup> assigned to v(V=0), v(V=0) and v(V–N), respectively [8]. However, these bands became vague upon homogeneous complex anchorage due to the appearance of strong and broad bands at 1086, 807 and 402 cm<sup>-1</sup> assigned to SBA-15 framework [33]. Moreover, in the region of 1600–1300 cm<sup>-1</sup>, the spectra of hybrid materials showed some weak peaks, which could be due to the existence of organic ligands in the hybrid materials (Fig. 4d and e). The UV-vis spectra of the samples are shown

#### Table 1

Characteristics of support and catalysts, specific surface area,  $S_{BET}$  (m<sup>2</sup> g<sup>-1</sup>); pore volume,  $V_{BJH}$  (cm<sup>3</sup> g<sup>-1</sup>); pore diameter,  $D_{BJH}$  (nm); cell parameters,  $A_0$  (nm); interplanar spacing,  $D_{100}$  (nm); wall thickness, W (nm); C (M), initial concentration of metal species (mmol g<sup>-1</sup>).

Materials	C(M)	SBET	$V_{\rm BJH}$	$D_{\rm BJH}{}^{\rm a}$	Ao	D <sub>100</sub>	W <sup>b</sup>
SBA-15	_	892	1.01	6.35	11.87	10.28	5.52
APS-SBA-15	-	411	0.68	6.23	11.41	9.88	5.18
Cu-Salen-SBA	0.180	299	0.59	6.19	12.37	10.71	6.18
VO-Salen-SBA	0.312	276	0.50	5.18	11.67	10.01	6.49

<sup>a</sup> Calculated from the desorption branch.

<sup>b</sup>  $W = A_{\rm o} - D_{\rm BJH} \left( A_{\rm o} = \frac{2D_{100}}{\sqrt{3}} \right)$ .





Fig. 2. TEM images of (a, b) SBA-15, (c, d) Cu–Salen–SBA and (e, f) VO–Salen–SBA.

in Fig. 5. Intense  $n-\pi^*$ ,  $\pi-\pi^*$  ligand charge transfer bands in the range of 220–380 nm were present in all cases. The expected d–d transitions at 630 nm for Cu–Salen–SBA ( $t_g^{-6}e_g^{-3}$ ) as well as those at 560 nm for its homogeneous analogues indicate that copper(II) complexes have been incorporated onto the surface of SBA-15. A weak band usually appears in the ca. 600 nm region in oxovana-dium(IV) complexes [34].

#### 3.3. TG-DTA studies

Quantification of weight loss at various steps is possible because of nonoverlapping. TG–DTA analysis results of Cu–Salen–SBA are depicted in Fig. 6. The TG curve recorded under N<sub>2</sub> atmosphere showed a three-step weight loss at temperatures ranging from 30 to 800 °C. The weight loss below 250 °C was due to the physically adsorbed water and solvent inside the pores. The 20% weight loss at 250–450 °C was mainly related to the combustion of amine. Weight loss (6.0%) in the temperature range from 450 to 670 °C was probably attributed to the decomposition of Schiff base groups [35]. The loading of Schiff base ligand was 0.22 mmol/g based on 6.0%



Fig. 3. N<sub>2</sub> adsorption/desorption isotherms and pore size distribution profiles of (a) SBA-15, (b) APS-SBA-15, (c) Cu-Salen-SBA and (d) VO-Salen-SBA.



**Fig. 4.** FT-IR spectra of (a) CM–SalenH<sub>2</sub>, (b) Cu–CM–Salen, (c) VO–CM–Salen, (d) Cu–Salen–SBA and (e) VO–Salen–SBA.



**Fig. 5.** UV-vis spectra of (a) CM-SalenH<sub>2</sub>, (b) Cu-CM-Salen, (c) VO-CM-Salen and (d) Cu-Salen-SBA.



Fig. 6. TG and DTA curve of Cu-Salen-SBA.

of weight loss and the copper content was 0.180 mmol/g estimated by ICP-AES. The molar ratio of ligand to copper was approximately 1.2:1 and was close to the nominal value of 1:1, indicating that the homogeneous copper complexes remained intact after being introduced to the SBA-15 matrix. This result demonstrates that heterogenization of functionalized Cu(II) Schiff base complexes by direct immobilization ensures the purity of the metal complex present on the solid. The DTA curve corresponds with the TG result. The intense exothermal peak at 387 °C along with a shoulder peak at 429 °was observed. The higher temperature peaks of supported copper(II) complexes, in comparison with those of APS–SBA-15 (Supplementary Fig. S4), give another piece of evidence for the existence of copper complexes in hybrid materials. Similar results were obtained for VO–Salen–SBA (Supplementary Fig. S5).

#### 3.4. Anchorage status analysis

The anchorage status of supported copper(II) and oxovanadium(IV) complexes may closely relate to their catalytic behavior. In our study, the initial concentration of copper species in Cu-Salen-SBA was 0.180 mmol/g and the surface concentration was 0.100 mmol/g as estimated by XPS; such values suggest that some copper(II) complexes were located on the external surface of hexagonal pores. But for VO-Salen-SBA, the total concentration of vanadium was 0.312 mmol/g and its surface concentration was neglectable. These results indicate that most oxovanadium(IV) complexes were located in the mesoporous channels. The interior location may directly lead to the thicker walls and smaller pore diameters of oxovanadium(IV) complex anchored SBA-15 in comparison with those of copper (II) complex immobilized materials (Table 1). Furthermore, the amino groups were not completely depleted by chloromethyl in the Cu-Salen-SBA material. SEM-EDX results (Supplementary Fig. S6) confirm this fact, since the molar ratio of N/Cu was 14.4 (N/V = 13.8), which was much higher than the theoretical value of 4:1. Moreover, the molar ratio of Cu/Cl in Cu-Salen-SBA was 1:2.1, suggesting the possibility that the amino groups bound to the copper atoms instead of producing the nucleophilic substitution on the benzyl halide (Scheme 1). This probably leads to some extent of leaching of the copper(II) species to the solution during the progress of the reaction. The binding energy of Cu 2p<sub>1/2</sub> (933.8 eV) in unsupported copper complexes shifted to a lower value of 933.0 eV after immobilization. It can be speculated that the amino groups coordinated to copper and thus increased the electronic density around copper atoms (Supplementary Fig. S7). On the contrary, chlorine was not detected in the VO-Salen-SBA material by EDX analysis (Supplementary Fig. S8) and the binding energy of vanadium(IV) (V 2p3/2, 516.4 eV) was almost unchanged after immobilization. This result indicates that all the oxovanadium complexes were covalently anchored on SBA-15 matrix.

#### 3.5. Catalytic properties

The catalytic performances of various catalysts are shown in Table 2. When the oxidant air was used in combination with CH<sub>3</sub>CN as the solvent (Entries 1–10), all catalysts were active for the aerobic oxidation of styrene. The fresh VO–Salen–SBA catalyst showed high activity with 78.6% conversion of styrene after 8 h (TOF 63.0 h<sup>-1</sup>), while the fresh Cu–Salen–SBA catalyst showed low activity with 26.9% conversion after 8 h (TOF 37.4 h<sup>-1</sup>). Moreover, the catalytic performances of the recycled catalysts also differed significantly. The catalytic activity of Cu–Salen–SBA decreased rapidly after the first run. To test for leaching, we filtered the catalyst at the reaction temperature (80 °C) after 2 h (5.0% styrene conversion). At this time, half the volume was filtered and the resulting clear solution was allowed to react. The percentage of leaching was estimated by comparing the time–conversion plot of the twin reactions with and



Cu-Salen-SBA

Scheme 1. Schematic outlines of syntheses of (a) homogeneous metal complexes of copper(II) and oxovanadium(IV) and (b) anchored metal complexes.

without solid (not shown). It was found that after the hot filtration, the mother liquor reacted further at roughly the same rate as that observed when the Cu-Salen-SBA catalyst was not filtered, which indicates that the leaching of active species should be the main reason for the rapid deactivation of supported copper(II) catalysts. According to the literature [36,37] and to our experimental results, metal complexes heterogenized by a coordination bond are not stable during the process of preparation and can be easily leached into solutions. But VO-Salen-SBA could be successfully recycled for four times without significant decrease of activity or selectivity under test conditions. The absence of vanadium in the filtrate solution of subsequent runs and the inactivity of filtrate indicate that the supported vanadium catalyst is stable and that any leaching of active species into solution is insignificant. The ICP analysis also showed that the vanadium content for the used catalysts just decreased slightly (0.295 mmol/g of vanadium after 4 cycles) compared with the fresh one. These results suggest that the large majority of the catalysis is carried out by a truly heterogeneous vanadium catalyst.

For comparison, the catalytic properties of the homogeneous complexes were also examined under identical reaction conditions.

When VOSO<sub>4</sub> or VO-CM-Salen was used as catalyst, 42.9 or 69.0% conversion of styrene (Table 2, Entries 1 and 2) could be obtained after 8 h; such values were much lower than the results obtained when we used supported oxovanadium catalyst VO-Salen-SBA. Similarly, the fresh Cu-Salen-SBA showed higher activity than the homogeneous Cu(CH<sub>3</sub>COO)<sub>2</sub> and Cu–CM–Salen catalysts (Table 2, Entries 7–9). The same trend was also observed when using  $H_2O_2$  as oxidant for both copper(II) and oxovanadium(IV) catalysts (Table 2, Entries 11-13). These results suggest that the heterogenization of homogeneous metal complexes probably isolated the active species and prevented their dimerization. The enhanced activity of heterogeneous catalyst may also be due to the synergistic beneficial catalytic interaction between the metal complexes and the SBA-15 support. The synergistic effect was also observed in other catalytic systems. For example, González-Arellano et al. [38] reported that the heterogenized Rh(I) and Ir(I) metal complexes with chiral triaza donor ligands showed much higher activity than that observed under homogeneous conditions for the hydrogenation reactions.

The influence of the oxidants on the catalytic properties of copper(II) and oxovanadium(IV) catalysts was also investigated. With

2	8	0	

Table 2	
Catalytic activity and selectivity of various catalysts in the oxidation of styrene	2

Entry	Catalyst	Styrene conversion <sup>a</sup> (%)	$TOF^{b}(h^{-1})$	Selectivity <sup>c</sup>	Selectivity <sup>c</sup> (mol%)	
				So	Bza	Others
1	VOSO <sub>4</sub>	42.9	27.5	10.1	85.2	4.7
2	VO-CM-Salen	69.0	63.4	58.2	41.8	-
3	VO-Salen-SBA (1st)	78.6	63.0	71.2	28.3	0.5
4	VO-Salen-SBA (2nd)	82.3	_	62.5	30.5	7.0
5	VO-Salen-SBA (3rd)	69.6	_	55.4	42.6	2.0
6	VO-Salen-SBA (4th)	64.6	54.7	51.6	42.8	5.6
7	Cu(CH <sub>3</sub> COO) <sub>2</sub>	16.8	7.6	57.8	41.4	0.8
8	Cu-CM-Salen	22.5	27.7	59.5	40.4	0.1
9	Cu-Salen-SBA (1st)	26.9	37.4	48.0	26.6	25.4
10	Cu-Salen-SBA (2nd)	10.2	_	46.7	25.3	28.0
11	VOSO <sub>4</sub>	12.8	8.2	7.3	92.7	_
12	VO-CM-Salen	53.2	51.2	9.6	83.3	7.1
13	VO-Salen-SBA	84.1	67.4	11.9	83.3	4.8
14	Cu(CH <sub>3</sub> COO) <sub>2</sub>	9.0	4.0	88.9	11.1	-
15	Cu-CM-Salen	83.7	87.2	15.3	57.4	27.3
16	Cu-Salen-SBA	96.9	134.6	13.5	45.2	41.3

<sup>a</sup> Reaction conditions (Entries 1–10): styrene 1.14 ml (10 mmol), CH<sub>3</sub>CN 10 ml, flow of air 80 ml/min, isobutyraldehyde 25 mmol, temperature 80 °C and duration 8 h; Reaction conditions (Entries 11–16): styrene 1.14 ml (10 mmol), CH<sub>3</sub>CN 10 ml, 30% H<sub>2</sub>O<sub>2</sub> 30 mmol, temperature 80 °C and duration 8 h.

<sup>b</sup> TOF, h<sup>-1</sup>: (turnover frequency) moles of substrate converted per mole metal ion per hour.

<sup>c</sup> So, styrene oxide, Bza, benzaldehyde and others: including benzoic acid, phenylacetadehyde and 1-phenylethane-1,2-diol.

 $H_2O_2$  as the oxidant, benzaldehyde was dominant in all cases. According to the literature [39], the high yield of benzaldehyde is possibly due to further oxidation of styrene oxide by nucleophilic attack of H<sub>2</sub>O<sub>2</sub> on styrene oxide followed by cleavage of the intermediate hydroperoxistyrene. This result is in good agreement with H<sub>2</sub>O<sub>2</sub> oxidized styrene reactions catalyzed by polystyrene supported  $Cu(hpbmz)_2$  and  $VO(hpbmz)_2$  catalysts [8]. When air was used as the oxidant, the selectivity to styrene oxide was relatively higher than that of benzaldehyde except for VOSO<sub>4</sub> catalyst. This indicates that the product distribution depends on oxidants and is not related to metal species. We also found that the VO-Salen-SBA catalyzed reactions produced more styrene oxide (56.0% yield) than their homogeneous counterparts, which suggests that heterogenization results in elevated styrene oxide selectivity in aerobic oxidation of styrene. Cu-Salen-SBA, however, displayed lower yields of styrene oxide (12.9%) with air as oxidant and of benzaldehyde (43.8%) with  $H_2O_2$  as oxidant compared to its homogeneous analogues and VO-Salen-SBA. In this aspect, Cu-Salen-SBA is an inferior oxidation catalyst under all the conditions explored. The better selectivity of supported oxovanadium complexes can be attributed to the homogeneity of active sites covalently anchored on the internal surfaces of hexagonal pores, since unselective reactive sites (external surface sites) would disproportionately contribute to selectivity and would erode the selectivity of the catalyst, as demonstrated by Becker and Gagné [40].

#### 4. Conclusions

A series of new copper(II) and oxovandium(IV) complexes with salen ligands have been anchored on SBA-15 matrix and fully characterized by various techniques. It was found that copper(II) and oxovandium(IV) complexes were active catalysts for the oxidation of styrene. Heterogenization increased the activity of the homogeneous catalysts due to site-isolation and cooperative effects between the SBA-15 support and the metal complexes. The supported oxovandium catalyst showed high selectivity to styrene oxide with air as oxidant and better selectivity to benzaldehyde when using  $H_2O_2$  as oxidant. Moreover, the heterogenized oxovanadium catalyst was quite stable and could be recycled many times. The excellent performance of heterogenized oxovanadium catalyst can be attributed to the homogeneity of active species as well as its covalent bonding to the interior mesoporous channels.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.04.018.

#### References

- [1] G. Grigoropoulou, J.H. Clark, J.A. Elings, Green Chem. 5 (2003) 1-7.
- [2] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457-2474.
- [3] C. Bowers, P.K. Dutta, J. Catal. 122 (1990) 271-279.
- [4] P.-P. Knops-Gerrits, D.D. Vos, F. Thibaut-Starzk, P.A. Jacobs, Nature 369 (1994) 543-550.
- [5] D.D. Agrawal, R.P. Bhatnagar, R. Jain, S. Srivastava, J. Chem. Soc., Perkin Trans. 2 (1990) 989–992.
- [6] M.J. Sabater, A. Corma, A. Domenech, V. Fornés, H. Garcia, Chem. Commun. 1997 (1997) 1285–1286.
- [7] S. Koner, Chem. Commun. 998 (1998) 593-594.
- [8] M.R. Maurya, M. Kumar, U. Kumar, J. Mol. Catal. A: Chem. 273 (2007) 133-143.
- [9] M.R. Maurya, U. Kumar, P. Manikandan, Eur. J. Inorg. Chem. (2007) 2303–2314.
- [10] M.R. Maurya, A.K. Chandrakar, S. Chand, J. Mol. Catal. A: Chem. 274 (2007) 192–201.
- [11] M.R. Maurya, S. Sikarwar, M. Kumar, Catal. Commun. 8 (2007) 2017–2024.
- [12] M.R. Maurya, A.K. Chandrakar, S. Chand, J. Mol. Catal. A: Chem. 263 (2007) 227-237.
- [13] Q.H. Tang, Q.H. Zhang, H.L. Wu, Y. Wang, J. Catal. 230 (2005) 384–397.
- [14] M.L. Kantam, B.P.C. Rao, R.S. Reddy, N.S. Sekhar, B. Sreedhar, B.M. Choudary, J. Mol. Catal. A: Chem. 272 (2007) 1–5.
- [15] Q.H. Tang, Y. Wang, J. Liang, P. Wang, Q.H. Zhang, H.L. Wan, Chem. Commun. 4 (2004) 440-441.
- [16] X.J. Meng, K.F. Lin, X.Y. Yang, Z.H. Sun, D.Z. Jiang, F.S. Xiao, J. Catal. 218 (2003) 460–464.
- [17] L. Canali, D.C. Sherrington, Chem. Soc. Rev. 28 (1999) 85–93.
- [18] G.-J. Kim, J.-H. Shin, Catal. Lett. 63 (1999) 83-90.
- [19] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189-214.
- [20] K.J. O'Connor, S.J. Wey, C.J. Burrows, Tetrahedron Lett. 33 (1992) 1001-1004.
- [21] M.R. Maurya, A. Kumar, J. Mol. Catal. A: Chem. 250 (2006) 190-198.
- [22] M. Salavati-Niasari, A. Amiri, Appl. Catal. A: Gen. 290 (2005) 46-53.
- [23] S.P. Varkey, C. Ratnasamy, P. Ratnasamy, J. Mol. Catal. A: Chem. 135 (1998) 295–306.
- [24] R. Liu, Y. Zhang, P.Y. Feng, J. Am. Chem. Soc. 131 (2009) 15128-15129.
- [25] R. Liu, X. Zhao, T. Wu, P.Y. Feng, J. Am. Chem. Soc. 130 (2008) 14418-14419.
- [26] P. Sutra, D. Brunel, Chem. Commun. 21 (1996) 2485–2486.

- [27] N.K.K. Raj, S.S. Deshpande, R.H. Ingle, T. Raja, P. Manikandan, Catal. Lett. 98 (2004) 217–223.
- [28] M.J. Jia, A. Seifert, W.R. Thiel, Chem. Mater. 15 (2003) 2174–2180.
- [29] T. Joseph, M. Hartmann, S. Ernst, S.B. Halligudi, J. Mol. Catal. A: Chem. 207 (2004) 131–137.
- [30] G.G. Mohamed, Spectrochim. Acta Part A 64 (2006) 188-195.
- [31] E.F. Murphy, L. Schmid, T. Bürgi, M. Maciejewski, A. Baiker, Chem. Mater. 13 (2001) 1296–1304.
- [32] A. Kilic, E. Tas, B. Deveci, I. Yilmaz, Polyhedron 26 (2007) 4009–4018.
  [33] M.R. Maurya, A.K. Chandrakar, S. Chand, J. Mol. Catal. A: Chem. 270 (2007)
- 225-235.
- [34] N.F. Choudhary, P.B. Hitchcock, G.J. Leigh, Inorg. Chim. Acta 310 (2000) 10-20.
- [35] C. Jin, W.B. Fan, Y.J. Jia, B.B. Fan, J.H. Ma, R.F. Li, J. Mol. Catal. A: Chem. 249 (2006) 23–30.
- [36] A.R. Silva, M.M.A. Freitas, C. Freire, B. de Castro, J.L. Figueiredo, Langmuir 18 (2002) 8017-8024.
- [37] C. Baleizão, B. Gigante, M.J. Sabater, H. Garcia, A. Corma, Appl. Catal. A: Gen. 228 (2002) 279–288.
- [38] G. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, Inorg. Chim. Acta 357 (2004) 3071–3078.
- [39] M.R. Maurya, A.K. Chandrakar, S. Chand, J. Mol. Catal. A: Chem. 263 (2007) 227-237.
- [40] J.J. Becker, M.R. Gagné, Acc. Chem. Res. 37 (2004) 798-804.