

Nondestructive Sol–Gel Immobilization of Metal(salen) Catalysts in Silica Aerogels and Xerogels

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Nondestructive immobilization of cobalt and copper Schiff base complexes in silica aerogels and xerogels was achieved via the sol–gel method using a precursor *N,N*-ethylenebis(salicylideneaminato) (salen) ligand modified with pendant silyl ethoxy groups. Aerogels were obtained by semicontinuous extraction of the wet gels with supercritical CO₂ and xerogels by conventional drying. Cobalt and copper(salen) containing silica gels were characterized by FTIR, UV–vis, and XPS spectroscopy, laser ablation-ICP-MS, and EPR studies. Aero- and xerogel incorporated salen compounds exhibited similar spectroscopic properties to cobalt/copper(salen) precursors and known metal(salen) compounds. BET measurements confirmed the importance of supercritical CO₂ drying in maintaining the mesoporous structure of the aerogel. Laser ablation-ICP-MS and EPR studies of the aerogels showed that a uniform distribution of the isolated metal(salen) complex was achieved via molecular mixing using the sol–gel method. Stability of these materials was demonstrated by thermogravimetric analyses in air and leaching studies conducted under typical liquid-phase oxidation conditions. XPS analyses showed surface relative atomic concentrations in the modified gels to be similar before and following leaching studies.

Introduction

The development of environment-friendly technologies has prompted much research in heterogeneous catalysis and in particular the heterogenization of known active homogeneous catalysts for oxidation.¹ In theory, the heterogenization approach constitutes a convenient marriage of the engineering advantages of heterogeneous catalysts, such as ruggedness and ease of recovery, with advantageous features of homogeneous catalysts including well-defined structures that can be correlated with reactivity.²

Recently, our group has succinctly demonstrated the useful phenomenon of site isolation in hybrid silica aerogels prepared via the sol–gel method.³ In the two-step acid–base-catalyzed sol–gel process silylethoxy-modified ruthenium phosphine catalysts and tetraethoxy-

silane (TEOS) were hydrolyzed and co-condensed stepwise, forming a silica network with covalently bonded isolated active sites (Scheme 1). Characterization by solid-state ³¹P and ²⁹Si NMR, TEM, and EXAFS confirmed the isolation of the active ruthenium centers in these gels. The ruthenium phosphine catalysts thus prepared exhibited excellent selectivities (100%) in the synthesis of *N,N*-dimethylformamide and higher alkyl formamides from carbon dioxide and the appropriate amine.^{4–6} Given the degree of success achieved with the ruthenium phosphine aerogels⁶ and our current interests in oxidation, we decided to extend this work to the immobilization of known active homogeneous oxidation catalysts. Employing a similar strategy, in the case of *N,N*-ethylenebis(salicylideneaminato) (salen)-based systems (Scheme 1), our goal has been to prepare isolated active sites in a silica matrix, thereby avoiding deacti-

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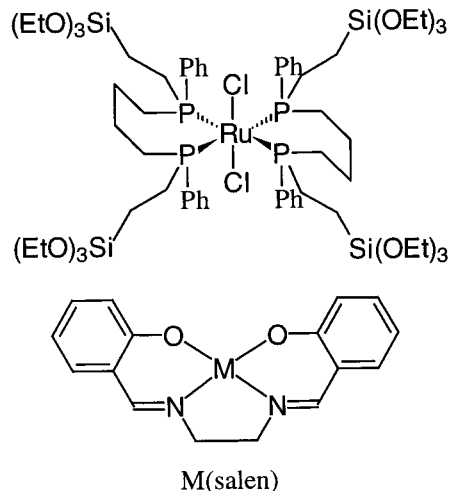
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Scheme 1. Silyl Ether Modified Ruthenium Phosphine Catalysts Immobilized via the Sol–Gel Method and Metal Coordinated *N,N*-Ethylenebis(salicylidenaminate) (M(salen)) Utilized in Catalytic Oxidations



vation by irreversible dimerization and/or oxidative degradation of the salen complexes which has been observed previously in the case of the homogeneous analogues.⁷

Site isolation is not a new concept in oxidation catalysis. In recent years encapsulation of salen complexes in porous materials, typified by zeolites, has been extensively studied in an attempt to prepare isolated catalytically active centers.^{8,9} In this instance the catalyst is retained via pore size restrictions providing the so-called “ship-in-a-bottle” materials.¹⁰ This class of material has been extended to include chiral metal(salen) complexes with applications in asymmetric catalysis.^{11–13} A disadvantage of this approach, however, is that preparation of encapsulated complexes via the cation-exchange method involves ligand chelation of the zeolite exchanged metal ion. Chelation may not be complete, and the residual zeolite coordinated metal ions can afterward be responsible for catalytic activity. In an alternative approach, organic polymers such as styrene have been employed, less successfully, however, as supports for salen catalysts in olefin epoxidation.¹⁴ The sol–gel method employing functionalized organometallic complexes has the advantage that the active species is covalently bound to the support, placing no restrictions on pore size. In addition, sol–gel chemistry with an appropriate precursor choice provides the unique possibility to control molecular scale mixing and consequently important catalytic properties of the resultant gel that depend on this.¹⁵

One of the bonuses of the immobilization approach has been the observation of often-unexpected properties for the supported homogeneous catalysts. In the case of immobilized ruthenium phosphine catalysts for *N,N*-diethylformamide synthesis, the activity of the heterogenized systems was significantly higher than the corresponding homogeneous catalysts, a feature which has been attributed to site isolation.^{6,16} Significant differences in behavior have also been described for salen,¹⁷ phthalocyanine,¹⁸ and porphyrin¹⁹ complexes encapsulated in porous materials.

In the present work details of the preparation and characterization of silica aero- and xerogels with covalently bonded metal(salen) complexes are presented. To our knowledge, this is the first report detailing the nondestructive immobilization of salen-ligated metals via the sol–gel procedure using a silyloxy-modified salen precursor.²⁰ Preparation of metal(salen) incorporated aerogels via the sol–gel process provides a novel approach to immobilization of these catalysts simultaneously allowing precise engineering of the silica gel framework.²¹ Our goal in preparing these materials has been to engineer systems with potential for catalytic oxidation of organic substrates.¹ Therefore, special attention has been paid to characterization, thermal stability, and also leaching studies of these materials.

Experimental Section

Materials and Procedures. All solvents, tetraethoxysilane (>99%, GC), salicylaldehyde (>99%, GC), aminopropyltriethoxysilane (ca. 99%, GC), cupric acetate monohydrate, and cobaltous acetate tetrahydrate were supplied by Fluka and used without further purification.

FTIR spectra were recorded on KBr pellets using a Perkin-Elmer series 2000 NIR FT Raman instrument. Diffuse reflectance UV–vis spectra were measured on a Perkin-Elmer UV–vis spectrometer Lambda 16 as barium sulfate plates in the range 700–200 nm. Elemental analyses (C, H, N) were performed in-house. Metal content of the gels was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Continuous wave EPR spectra were recorded on a Bruker ESP300 spectrometer (microwave frequency 9.43 GHz), equipped with a liquid helium cryostat from Oxford Inc. A microwave power of 20 mW, a modulation amplitude of 0.5 mT, and a modulation frequency of 100 kHz were used. The spectra were recorded in the temperature range 10–300 K. For LA-ICP-MS investigations aerogel samples pressed as pellets were, without any additional sample preparation, ablated using a 193 nm laser beam. The resulting aerosol was transported into an inductively coupled plasma where the sample was atomized and ionized. Ions were separated using a quadrupole mass filter and detected with a dynode detector. Details of the principles of LA and the equipment used for the direct analysis of the aerogels can be found elsewhere.²² The specific surface areas (S_{BET}) and specific desorption pore volumes (PV) were determined by nitrogen physisorption at

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–196 °C using a Micrometrics ASAP 2000 instrument. Thermogravimetric analyses were carried out on a Netzsch STA 409 thermoanalyzer connected via a heated (ca. 200 °C) stainless steel capillary to a Balzers quadrupole mass spectrometer QMG 420. Gas flow rates were controlled by Brooks's model 5850E mass flow controllers based on a thermal mass flow sensing technique. The studies were carried out in an oxygen atmosphere (20 vol %, balance He) with a heating rate of 10 °C/min. Oxidation studies were carried out in a 100 mL conical flask, with magnetic agitation under an oxygen atmosphere (1 bar). Quantitative analysis of product mixtures was carried out using a HP 5890A/HP 5972 GC/MS system fitted with a HP 50+ column (50% Ph/Me siloxane, 30 m, 0.25 μ m) using dodecane as internal standard. XPS measurements were performed on a Leybold Heraeus LHS11 apparatus using Mg K α radiation (240 W) incident at 45°. Photoelectrons were collected normal to the sample surface, analyzed by a concentric hemispherical analyzer (EA 11), and detected with a multichannel detector. The probed spot size was roughly 1 mm in diameter as estimated from measuring small Au samples on a Cu disk. The spectrometer energy scale was calibrated using the Au $f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ lines at 84.2, 367.9, and 932.4 eV. Thin sample films were pressed on a steel holder for analysis. Slight sample charging was compensated using the C 1s line at 284.8 eV as an internal standard. X-ray satellites were subtracted before analyzing the spectra. Quantification was performed using the sensitivity factors according to Wagner.²³

Preparation of Cobalt and Copper(salen) Precursors.

Cobalt and copper(salen) precursors were prepared according to the following procedure. Typically a dark reaction solution formed on addition of the appropriate metal (cobaltous and cupric) acetate hydrate (6.00 mmol) in acetonitrile (25 mL) to a yellow solution of aminopropyltriethoxysilane (2.66 g, 12.02 mmol) and salicylaldehyde (1.47 g, 12.04 mmol) in acetonitrile (40 mL). The solutions were stirred at room temperature for 24 h. Subsequent concentration of the reaction solutions led to precipitation of the metal(salen) precursor as a dark-green (cobalt)/brown (copper) powder. The solid products were removed by filtration, washed with chloroform, and dried in vacuo at 100 °C for 24 h.

Preparation of Cobalt and Copper(salen) Xerogels.

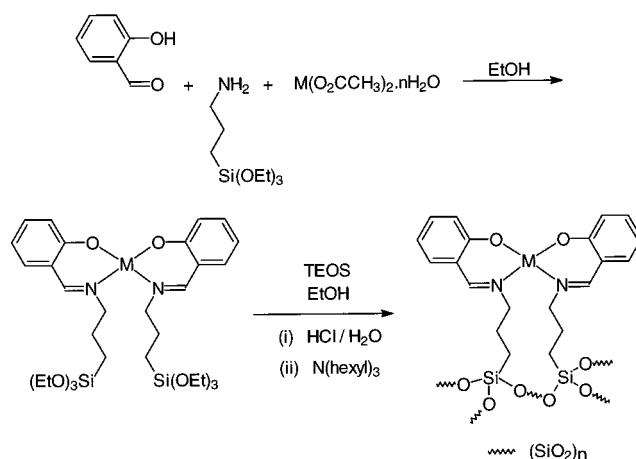
The procedure for the preparation of cobalt and copper xerogels is similar up to the point where base is added to catalyze co-condensation of the metal(salen) precursor/TEOS hydrolyzed sol. Typically the appropriate metal (cobaltous and cupric) acetate hydrate (6.00 mmol) in ethanol (25 mL) was added to a solution of aminopropyltriethoxysilane (2.66 g, 12.02 mmol) and salicylaldehyde (1.47 g, 12.04 mmol) in ethanol (50 mL). TEOS (31.26 g, 150 mmol) was added slowly and the solution stirred for 1 h. Dropwise addition of dilute HCl (14.4 mL, 1 M HCl) to the solution was noticeably exothermic. The solution was then stirred at room temperature for a further 2 days.

A solution of trihexylamine (THA) (3.89 g, 14.4 mmol) in ethanol (60 mL) was prepared and used in the base-catalyzed co-condensation. In the case of the cobalt co-condensation, addition of 18 mL of THA/ethanolic solution was required to give gelation in just 3 h. For copper(salen) co-condensation, the entire amount of base was added (i.e., 3.89 g in 60 mL of ethanol), and gelation was observed after 6 h. The gels were aged for 14 days and then removed by filtration, washed with copious amounts of ethanol and a chloroform/10% pyridine solution, and dried in vacuo at 100 °C for 24 h providing the xerogels.

Preparation of Cobalt and Copper(salen) Aerogels.

Cobalt and copper(salen) aerogel preparations are identical to that for the xerogels up to the point where ethanol is removed from the porous gel. In the case of aerogel preparations, aging of the gels was also carried out for 14 days. The resulting wet gels were then dried by semicontinuous extraction of ethanol with supercritical CO₂ at 42 °C affording aerogels. This

Scheme 2. In-Situ Preparation and Immobilization via the Sol–Gel Process of Silyl Ether Modified Salen Catalysts in a Silica Gel (M = Co, Cu)



procedure has been described in detail elsewhere.²⁴ The aerogels thus obtained were further extracted with ethanol (Soxhlet) for 4 days and finally dried in vacuo at 100 °C for 24 h.

Results

Gel Preparations. Preparation of the modified Schiff base complexes and immobilization via the sol–gel method in a silica matrix is depicted in Scheme 2. A solution of the silylethoxy-modified salen complex prepared in situ in ethanol with TEOS (matrix formation) is first subjected to acid-catalyzed hydrolysis, followed in a second step by base-catalyzed condensation. Typically gel formation was observed in 3–24 h following addition of base with gelation occurring more rapidly for the cobalt(salen) precursor. Conventional filtration, washing, and drying of the wet gels gave xerogels. Removal of ethanol via semicontinuous extraction with supercritical CO₂ afforded aerogels. Aerogels were further extracted (Soxhlet) for 4 days, to remove organic residues from the gel pores, giving light brown/green solids. Isolation of the metal(salen) precursors was accompanied by partial condensation of the silylethoxy groups, probably due to the presence of small amounts of water in the solvent. The insolubility of these materials prevented their use as gel precursors. Therefore, in the preparation of gels the precursors were prepared in situ, and gels were obtained by the sol–gel procedure as described above. An unusual feature of the sol–gel process in the case of cobalt(salen) gel preparation was the Schiff base self-catalysis, in the absence of added base, of condensation after 24 h. In the preparation of base-modified silica aerogels, Hüsing et al. described a similar contribution to the sol–gel process in the preparation of aminopropyl-modified silica aerogels.²⁵ Attempted preparation of a manganese(salen)-modified aerogel was hindered by formation of a precipitate at the hydrolysis step of the sol–gel procedure.

Hydrolysis of the silylethoxy-modified salen ligand under conditions used in the sol–gel procedure de-

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Table 1. Textural Properties and Spectroscopic Characteristics of the Metal(salen) Precursors and Metal(salen) Modified Gels

	λ (nm)		ν (cm ⁻¹)		textural properties			
	copper	cobalt	copper	cobalt	copper		cobalt	
					S_{BET}^a	PV ^b	S_{BET}^a	PV ^b
precursor	374	400	1622	1621				
xerogel	362	396	1625	1620	490	0.30	490	0.20
aerogel	364	395	1625	1621	550	1.40	620	1.35

^a S_{BET} : BET surface area [m²/g]. ^b PV: average specific pore volume between 1.7 and 300 nm [cm³/g].

scribed above led to a reverse Schiff base reaction. Formation of salicylaldehyde was confirmed by GC-MS analysis of the reaction solution, and under aqueous acidic conditions this is not unexpected.²⁶ Salicylaldehyde was not, however, detected during the preparation of the metal(salen) incorporated xero- and aerogels, suggesting that complexation stabilized the ligand against this reverse reaction. Another interesting feature of the sol-gel process of the free ligand is the formation of a bright-yellow precipitate on addition of trihexylamine to an acid-free hydrolyzed solution of TEOS and the modified salen ligand in the absence of any metal. The insolubility of this solid suggests that it is a polymer, probably formed by condensation of the silyloxy groups with the hydroxy group of the salicylaldehyde ring.

Spectroscopic Characterization. Infrared and UV-vis spectroscopic data for cobalt/copper precursors and gels are collected in Table 1. Bands characteristic of the salen imine functionality are found in the range 1650–1590 cm⁻¹ for the precursors and silica-incorporated compounds.²⁷ For comparison purposes, $\nu_{(\text{C}=\text{N})}$ for the free half/ligand in carbon tetrachloride appears at 1633 cm⁻¹. Complexation of the free ligand gives the expected decrease in $\nu_{(\text{C}=\text{N})}$ value.²⁰ A sharp band at 1330–1355 cm⁻¹ in the cobalt and copper(salen) precursors attributable to the C–O vibration is not visible in the spectra of the gels due to a very intense and broad SiO₂ band (1380–1000 cm⁻¹). Absorptions corresponding to d–d transitions in the electronic spectra of cobalt^{28–30} and copper(salen)^{17,27,31} precursors (Table 1) are similar to related metal(salen) compounds described in the literature. Intense n– π^* and π^* – π^* ligand charge-transfer bands in the range 300–220 nm are present in all cases. The characteristic $\nu_{(\text{C}=\text{N})}$ vibration and the spectroscopic similarity of the metal(salen) precursors to other metal(salen) complexes, in combination, confirm that the modified-salen ligand also coordinates via an N₂O₂ donor arrangement. The small changes in the IR spectra in the $\nu_{(\text{C}=\text{N})}$ region and in the UV-vis spectra on progressing from precursor to metal(salen)-modified aero- and xerogels are also consistent with only small changes in metal–ligand geometry upon incorporation,

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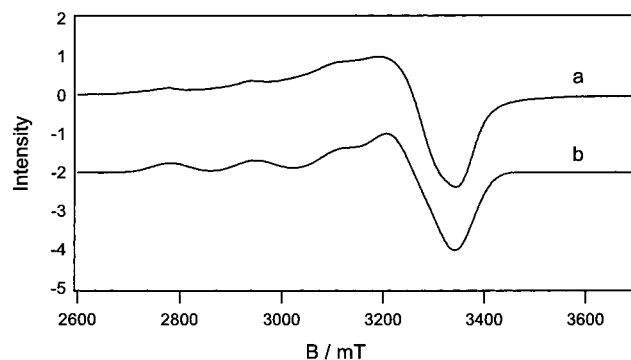


Figure 1. X-band EPR spectrum of copper(salen) aerogel taken at room temperature: (a) experimental spectrum and (b) simulation using the parameters given in the text.

and a similar metal coordination is very probable in the gels.

Chemical analyses (C, H, N) of the isolated gel precursors confirm that partial condensation of the silyloxy groups has occurred, providing a possible explanation for the insolubility of these materials. Residual organics in the xero- and aerogels from the sol-gel procedure significantly distort the elemental analyses, and the values allow only a rough determination of the amount of complex incorporated into the gel matrix. It is not surprising therefore that metal contents as determined by ICP-AES are lower than theoretical values in all cases. However, the values measured show that a high catalyst loading is attained in both cobalt (2.67 wt % Co) and copper(salen) (2.83 wt % Cu) aerogels.

EPR Studies. The cobalt(salen) aerogel is essentially EPR silent in the temperature range –263 to 27 °C, showing only a weak intensity signal from an unidentified organic radical. EPR signals characteristic for cobalt(2+)salen and the oxygenated cobalt(2+)(salen)-O₂ complex were also absent.^{32,33} Consequently, either the cobalt(2+) has been oxidized to cobalt(3+), which is EPR silent, or a diamagnetic bridged (salen)Co(2+)–O–O–Co(2+)(salen) complex is formed. It is known that in solution cobalt(2+)(salen) tends to form bridged-dioxygen complexes.³⁴ However, it has also been reported that in protic solvents (e.g., ethanol) cobalt(2+)(salen) and related Schiff base complexes are readily oxidized in air to the corresponding cobalt(3+)(salen) ethoxides.³⁵ The absence of any EPR signal here, therefore, strongly indicates that all cobalt has been oxidized to cobalt(3+). This observation is not totally unexpected given that the aerogel preparation is carried out in ethanol in air over a long period of time.

In the case of the copper(salen) aerogel, even at room temperature, an EPR spectrum typical of copper(2+) complex is observed (Figure 1a). The EPR spectrum can be simulated with the parameters $g_{\parallel} = 2.232 \pm 0.001$, $g_{\perp} = 2.074 \pm 0.001$, $A_{\parallel}(^{63}\text{Cu}) = 515 \pm 5$ MHz, and $A_{\perp}(^{63}\text{Cu}) = 40 \pm 20$ MHz (Figure 1b), which differ from the ones found for copper(2+)(salen) and nickel(2+)-

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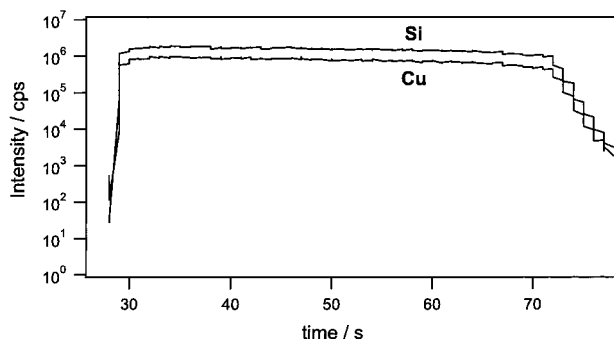


Figure 2. An example of a transient signal for the copper(salen) aerogel ablation using an ArF 193 nm excimer laser ablation system (40 μm crater diameter, 10 Hz) is shown. The rising signal at 28 s indicates the start of ablation, and at 74 s the laser was switched off.

(salen).³⁶ The EPR parameters of copper Schiff base complexes are found to depend both on the matrix and on the substitution at the nitrogens which explains the observed discrepancy.³⁷ Interestingly, the observed g_{\parallel} and A_{\parallel} (⁶³Cu) values agree more with a trans than a cis-planar N_2O_2 configuration of copper(salen) in the aerogel.³⁷ The observed EPR line width is very large (>220 MHz). This is most likely due to the high local concentration of copper (2.8 wt %) which is known to cause line broadening.³⁸ At half-field, no signal was observed, indicating that direct $\text{Cu}(2+) - \text{Cu}(2+)$ interactions do not exist, eliminating any possibility of metal-metal bonding interactions in the silica gel.

Homogeneity of Gels by Laser Ablation-ICP-MS.

In our previous studies of ruthenium phosphine incorporated aerogels EXAFS was used to confirm a uniform distribution and site isolation of the active species in the silica aerogel matrix.⁴⁻⁶ In the cobalt and copper(salen) aerogels metal concentrations have been determined, after sample digestion, using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The metal concentrations in the aerogels, however, do not provide any information regarding the distribution of the metal in the bulk sample. To investigate this feature, silicon/metal ratios (Si/Co and Si/Cu) for cobalt and copper(salen) aerogels were determined by laser ablation-ICP-MS (LA-ICP-MS) at 10 different locations on each sample with craters of 40 μm diameter. LA-ICP-MS is well established as a direct solid sampling technique for the determination of major, minor, and trace elements in minerals.³⁹ The results confirm a uniform distribution of these elements (Si/Cu = 3% RSD, Si/Co = 4% RSD, relative standard deviation). The transient signal for the ablation of the copper(salen) aerogel to a depth of 40 μm , shown in Figure 2, demonstrates clearly the uniformity of the elemental ratios in the sample. The weight percent ratio of silica to copper determined as 12 fits well with that determined by ICP-AES and is also in good agreement with the theoretical value (11.94). In addition, the absolute concentration of copper determined using NIST610 glass

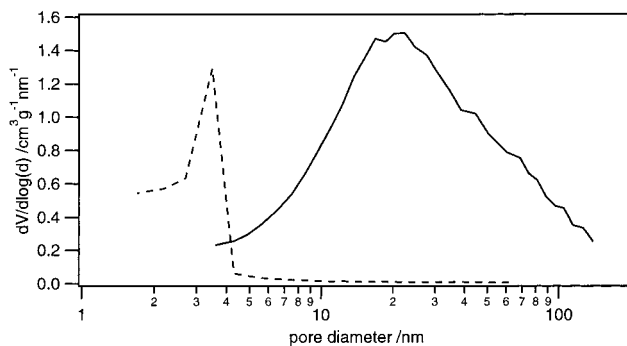


Figure 3. Pore size distribution for copper(salen) xerogel (dashed line) and aerogel (full line).

as external calibration standard validates the determination by ICP-AES (2.8 wt % Cu by ICP-AES and 3.1 wt % Cu by LA-ICP-MS).

Textural Properties. Textural properties of the aero- and xerogels were investigated by nitrogen physisorption. The cobalt and copper xerogels display a "type I" like isotherm⁴⁰ which is characteristic for adsorbents with small pores. On the other hand, the aerogels show "type IV" isotherms characteristic of solids with relatively large pores. This difference between pore size distribution in xero- and aerogels is depicted for the copper(salen) xero- and aerogel in Figure 3. There is a clear shift in the pore size distribution to smaller pores in the case of the copper xerogel due to the collapse of mesopores by capillary forces during thermal drying. This structural deformation could be avoided by exchange and extraction of the solvent with supercritical CO_2 , as with the copper aerogel. The cumulative pore volume for pores in the range 1.7–300 nm diameter for the different gels are shown in Table 1. Clearly the drying method provides an important tool in controlling the pore size distribution, with both aerogels possessing a 5–7 times higher pore volume than the mainly microporous analogues. The importance of this feature has been demonstrated with incorporated bidentate ruthenium phosphine complexes where the mesoporous hybrid gel exhibited a more than 8-fold higher activity in the synthesis of *N,N*-diethylformamide compared with the analogous xerogel material.⁶

Thermal Stability. Thermal stabilities of precursors and aerogels were determined by monitoring several variables including mass change, evolution of ethanol and ethyl acetate (products of TEOS decomposition), and formation of CO_2 resulting from the decomposition/combustion of the incorporated metal(salen) complex as a function of temperature under oxidizing conditions. The results for the precursors and aerogels are presented in Figures 4 and 5, respectively.

Significant differences are apparent between the decomposition of the cobalt and copper(salen) precursors (Figure 4). Decomposition of the copper precursor begins at higher temperatures and proceeds in one distinct stage with a maximum at ca. 290 $^{\circ}\text{C}$. On the other hand, decomposition of the cobalt precursor starts much earlier and proceeds through two stages. The first of these starts at ca. 130 $^{\circ}\text{C}$, as detected by the beginning

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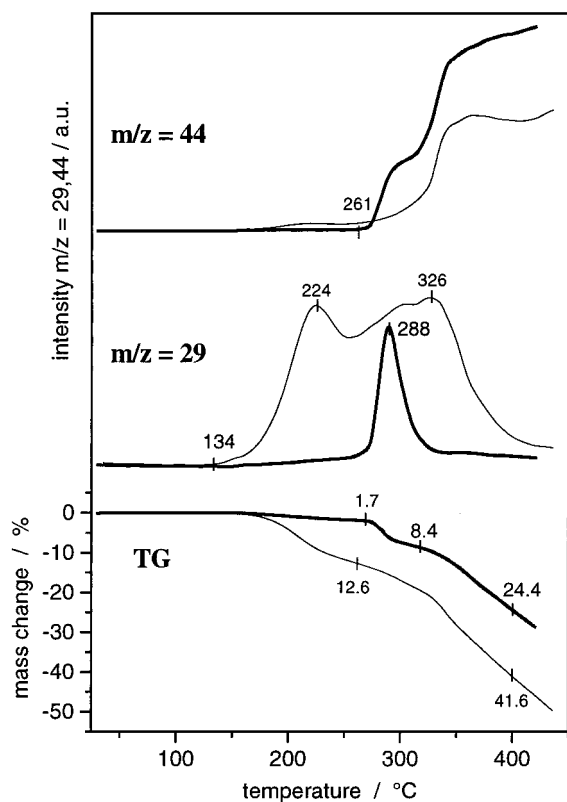


Figure 4. Thermal decomposition of copper (bold) and cobalt(salen) precursors in oxygen (20 vol %, balance He) monitored by thermogravimetry (TG) and mass spectrometry. The signal $m/z = 29$ indicates the formation of both ethanol and ethyl acetate, and the signal $m/z = 44$ indicates the formation of carbon dioxide.

of the mass loss and the course of the $m/z = 29$ mass spectrometric signal resulting from the formation of ethanol and ethyl acetate. The maximum of the second stage is centered at ca. 325 °C. At temperatures greater than ca. 260 °C the gaseous products of decomposition react with oxygen in the carrier gas forming carbon dioxide. The mass loss at 400 °C corresponds to 41.6 and 24.4 wt % for the cobalt and copper(salen) precursors, respectively.

Three phenomena can be observed during decomposition of the aerogels: first, evolution of ethanol and ethyl acetate from the aerogel matrix, second, decomposition, and finally oxidation of the metal(salen) complex (Figure 5). An interesting feature of these studies is that differences observed during the course of decomposition of the cobalt and copper(salen) precursors are also visible during thermal treatment of the respective aerogels.

The cobalt aerogel contains considerably greater amounts of ethoxide/ethanol in the matrix. The evolution of ethanol and ethyl acetate was monitored by the characteristic mass spectrometric signals $m/z = 31$ (ethanol) and $m/z = 43$ (ethyl acetate) and was additionally confirmed by FTIR analysis of the evolved gases in a TA-FTIR system (data not presented). Quantification of FTIR signals enabled the determination of the amount of evolved ethanol in the temperature range 25–150 °C to be 1.3 and 0.2 wt % from the cobalt and copper(salen) aerogels, respectively. The amount of ethyl acetate evolved from the matrix was also greater for the cobalt aerogel, and only traces of ethyl acetate could be

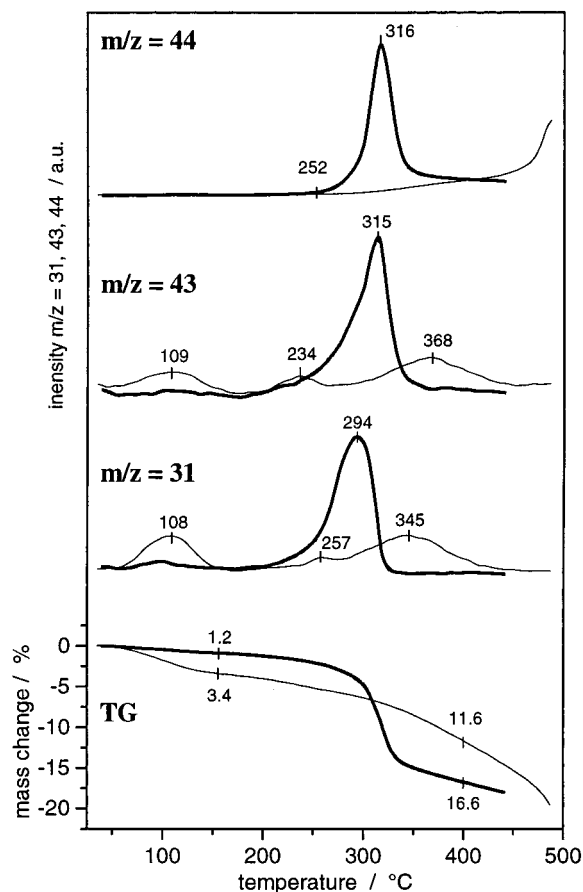


Figure 5. Thermal decomposition of copper (bold) and cobalt(salen) modified aerogels in oxygen (20 vol %, balance He) monitored by thermogravimetry (TG) and mass spectrometry. The evolution of ethanol, ethyl acetate, and CO_2 are represented by the mass spectrometric signals $m/z = 31$, 43, and 44, respectively.

detected for the copper aerogel. The weight loss at 150 °C due to the evolution of water, ethanol, and ethyl acetate amounts to 3.4 and 1.2 wt % for cobalt and copper(salen) aerogels, respectively. Previously we investigated the degree of condensation of the silica matrix in ruthenium phosphine modified aerogels via ^{29}Si CP-MAS NMR.^{4–6} In the NMR spectra of cobalt/copper aerogels, the presence of paramagnetic centers leads to severe signal broadening. For example, in the solid-state ^{29}Si CP-MAS NMR of the cobalt(salen) aerogel a very broad resonance centered at –109 ppm was found. This broad resonance was composed of three to four unresolved signals, indicating the presence of silicon centers of varying degrees of condensation. This is in agreement with thermal analysis which shows that in the cobalt aerogel cross-linkage is lower with large amounts of ethanol/ethyl acetate generated up to 150 °C on thermal treatment.

The cobalt(salen) aerogel decomposes in two steps as confirmed by the presence of two peaks with MS signals characteristic for ethanol (257 and 345 °C) and ethyl acetate (234 and 368 °C). The decomposition of copper(salen) occurs in one step with maxima at ca. 295 °C for ethanol and 315 °C for the ethyl acetate. The decomposition of the copper(salen) ligand occurs much faster as shown by the higher intensities of MS signals and considerably larger mass loss at 400 °C. The mass losses resulting from the ligand decomposition amount

Table 2. Results of Ethylbenzene Oxidation with Cobalt(salen) Aerogel (0.60 g, 2.7 wt % Cobalt), Ethylbenzene (40 g, 377 mmol), and Dodecane (1 mL) as Internal Standard at 130 °C

entry	catalyst	time (h)	ethylbenzene % conversion	rate conv (mol L ⁻¹ h ⁻¹)	acetophenone % selectivity	methylphenylmethanol % selectivity
1	+	1.5	6.4	0.35	71.9	28.1
2	+	2.5	8.3	0.27	72.3	27.7
3	+	24	70.4	0.24	75.2	8.0
4	+	48	89.9	0.15	77.0	4.2
5	+	72	99.9	0.11	78.7	2.3
6	none	6	5.0	0.07	68.2	24.0

to 8.2 wt % for cobalt and 15.4 wt % for copper. Faster decomposition of the copper(salen) aerogel is additionally confirmed by the course of carbon dioxide formation from the oxidation of the evolved organic molecules. The evolution of CO₂ is much more significant for the copper(salen) aerogel, with the maximum centered at ca. 315 °C. The onset of CO₂ formation is observed for both aerogels at ca. 250 °C.

Lower thermal stabilities of the copper(salen) precursor and aerogel relative to the cobalt analogues are reflected in the stabilities of unmodified cobalt and copper(salen) compounds.^{41,42} The introduction of a ring substituent such as the pendant propylsilylethoxy group also influences the thermal stability of this class of compound. In cobalt(salen), for example, 3-methoxy ring substitution leads to a slight decrease in thermal stability.⁴³

Leaching Tests and Preliminary Oxidation Studies. In the search for truly heterogeneous catalysts the question of leaching of the metal and/or ligand from the support is always highly debatable.⁴⁴ For instance, in studies of cobalt(salen) encapsulated in zeolite Y, leaching of cobalt(salen) from the outer layers was confirmed by XPS, even after much preliminary solvent extraction of this material.⁴⁵ Typical conditions used for catalytic liquid-phase oxidations include polar solvents with organic/inorganic bases as additives. The cobalt and copper(salen) aerogels stirred in DMSO, DMF, and ethylbenzene at 110 °C under an oxygen atmosphere for up to 24 h in the presence of pyridine and potassium *tert*-butoxide were recovered unchanged from suspension. As described below, XPS confirms the similarity of the surface composition of the starting and recovered materials (see Table 3). On the basis of these experiments it appears that the aerogel incorporated metal(salen) complexes are stable under relatively harsh reaction conditions.

Details of the cobalt(salen) aerogel catalyzed oxidation of ethylbenzene to acetophenone (Scheme 3) are collected in Table 2. Increased activity of the cobalt(salen) aerogel catalyzed oxidation (entries 1, 2) over the background oxidation (entry 6) is evident even at short reaction times and becomes more significant as the reaction proceeds. Although the oxidation reaction is slow, good selectivity to acetophenone is achieved at quantitative conversion of ethylbenzene (entry 5). The rate of conversion decreases with time probably due to

Table 3. Quantification of Surface Concentration from XPS^a

	M %	Si %	N %	O %	C %	Cl %	energy (eV) ^c
copper precursor	1.0	1.8	2.4	7.5	28.9	0.0	934.7
cobalt precursor	1.0	2.4	2.0	8.8	25.7	0.0	769.5 ^d
copper xerogel	0.3	25.0	1.5	54.6	17.7	0.8	933.4 ^e
cobalt xerogel	1.1	27.4	1.8	49.9	19.2	0.6	769.4
cobalt aerogel	1.0	23.3	1.6	55.2	18.3	0.6	769.1
cobalt aerogel ^b	1.0	22.8	1.7	59.3	17.1	0.0	769.3
copper aerogel	0.8	26.3	2.0	54.5	16.3	0.2	933.4 ^e
copper aerogel ^b	0.7	23.1	1.8	53.4	21.1	0.0	933.2

^a 1s of C, N, and O, 2p of Cl and Si, 2p_{3/2} of Cu, and LMM Auger line of Co were used for quantification. ^b After leaching tests. ^c Binding energy of Cu 3p_{3/2} and kinetic energy of Co LMM auger line, respectively. ^d Cobalt 2p_{3/2} at 781.2 eV. ^e Shifts from initially 934.7 to 933.4 eV due to reduction.

competitive adsorption of reactant and product at the catalytically active sites. Quantitative conversion is a significant feature of this work since in previously investigated heterogenized systems for ethylbenzene oxidation a drastic reduction in activity was observed after 50% conversion.²⁰ Minor amounts of other oxidation products including benzoic acid and benzyl benzoate have been detected during reaction. In the present study, ethylbenzene oxidation was conducted without any added solvent under oxygen (1 bar) at 130 °C. Continuous azeotropic distillation with a Dean–Stark apparatus was used to remove water, produced as the reaction progressed, from the system. This removal of water proved essential in avoiding catalyst deactivation. Similarly, in the oxidation of ethylbenzene with an immobilized chromium(salen) catalyst, deactivation was observed within 1 h when water was not removed from the system.²⁰ As described above, the cobalt(salen) aerogel catalyst was recovered from the reaction mixture unchanged as determined by XPS. In addition, filtration of the cobalt(salen) aerogel from the hot ethylbenzene oxidation reaction mixtures followed by ICP-AES of the reaction solution showed that cobalt leaching into solution amounted to <0.1 wt % cobalt. Catalyst recycling tests and efforts to maximize reaction conditions are currently in progress.

XPS of the Gel Surfaces. In general, the elemental surface concentrations as determined by XPS correspond well with the atomic ratios for precursors MC₃₂H₅₂N₂O₈Si₂ (M = Co or Cu) and aerogels MC₂₀H₂₂N₂O₅₂Si₂₇ (M = Co or Cu) based on complete metal(salen) integration. Table 3 shows the relative surface atomic concentrations of the elements M (Co, Cu), C, O, N, Si, and Cl for the materials investigated. The binding energy of the Cu 3p_{3/2} photoelectron and the kinetic energy of the Co LMM auger electron are also included.

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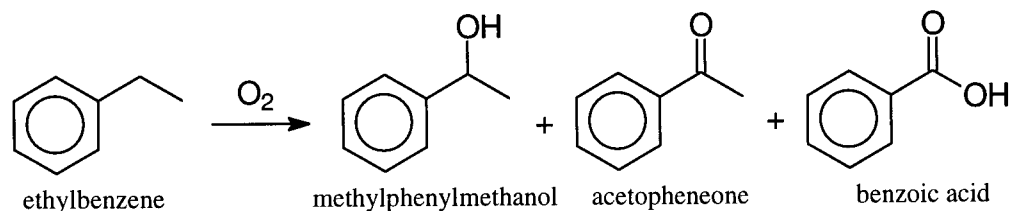
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Scheme 3. Oxidation of Ethylbenzene to Acetophenone; Benzoic Acid is an Overoxidation Product



For the cobalt(salen) precursor and gels the N/Co ratio is close to the nominal value of 2. The very similar surface composition of the aerogel before and after leaching tests demonstrates good stability against dissolution of metal/ligand from the gel surface. Satellite lines and the doublet separation of the $2p_{1/2}$ and $2p_{3/2}$ spin-orbit levels often provide valuable information concerning the oxidation state and electronic structure of cobalt.⁴⁶ Unfortunately, the 2p lines overlap with strong O (KVV) auger lines and could therefore not be used for analysis in the case of the gels. The $2p_{1/2}$ and $2p_{3/2}$ separation of 15.3 eV, for the cobalt(salen) precursor, is identical to the value reported for $\text{Co(salen)} \cdot \frac{1}{2}\text{H}_2\text{O}$.³⁸ The presence of satellite lines in the $2p_{1/2}$ and 3p spectra is furthermore indicative of a high-spin cobalt(2+) center in the precursor.⁴⁶

For copper complexes the N/Cu ratio is again close to the expected value of 2 for the copper(salen) precursor and aerogel, whereas it is smaller for the xerogel. The spectrum of the precursor showed characteristic shake-up satellites at 5.2 (weak) and 9.8 eV (strong) to higher energy from the main copper 2p lines. Such satellites are characteristic for copper(2+), whereas copper(1+) compounds do not exhibit these features.⁴⁷ The intensity and position of the satellites are characteristic for the coordination of the copper(2+) ion with shake-up lines at similar energy being reported for copper(acac)₂ (acac = acetylacetonate) for example.⁴⁷ These lines are associated with ligand-to-metal charge-transfer transitions.⁴⁸ The satellite energies correspond to wavelengths at 238 and 127 nm, with the former correlating well with an intense transition observed around 244–240 nm in the UV spectrum of the copper(salen) precursor and gels. Importantly, the presence of the shake-up lines in the gels provides strong evidence for a similar coordination mode for copper in the precursor and gels. Interestingly, for the gels the satellites were only observed during the first scans and disappeared afterward. This is due to photoreduction of copper(2+) to copper(1+) taking place in the spectrometer.⁴⁷ In parallel, the position of the copper $2p_{3/2}$ line shifted from initially 934.7 to 933.4 eV, confirming reduction.⁴⁷ Small amounts of chloride detected in cobalt aero- and xerogel materials were removed by stirring in dimethyl sulfoxide at elevated temperatures. The likely source of chloride is an insoluble ammonium chloride formed by reaction of hydrochloric acid with trihexylamine used during the sol-gel procedure.

Discussion

Although sol-gel immobilization of the modified salen ligand is not possible, cobalt and copper coordination of the ligand provides stability against acid-catalyzed reverse Schiff base reaction under the sol-gel conditions, thereby allowing nondestructive immobilization of the metal(salen) precursor. The preparation of silica aerogel incorporated metal(salen) systems via the sol-gel method is facilitated by a judicious choice of precursors with relatively similar reactivities regarding sol-gel chemistry. In addition, the ease of preparation of the metal(salen) gels depends on the stability of the respective metal(salen) precursors during the sol-gel procedure.

In *N,N*-ethylenebis(salicylideneaminato) complexes the presence of the ethylene bridge between the two halves of the salen moiety leads to conformational stability imposing a *cis*- N_2O_2 bonding geometry at the metal center. In the metal(salen) aerogels conformational restrictions are imposed by the pendant silyloxy groups upon incorporation in the silica gel. EPR studies of the copper(salen) aerogel show that a *trans*- N_2O_2 geometry is likely at the metal center in the modified gels. This arrangement probably originates in solutions of the metal(salen) precursors where the sterically more favorable *trans*-geometry would be expected to prevail.

Combined EPR and laser-ablation ICP-MS studies confirm that our approach affords a homogeneous distribution of the isolated metal(salen) complex in the silica aerogel matrix. In addition to stereochemical information, EPR confirms the absence of any metal-metal bonding interactions which may prove invaluable in avoiding catalyst deactivation as a result of dimerization. Application of the LA-ICP-MS method to aerogel incorporated metal(salen) complexes simultaneously provides valuable information regarding the elemental ratio distributions in the silica matrix, thereby confirming homogeneity, and also absolute analyte concentrations. This solid sampling technique enables facile access to elemental concentrations compared with ICP-AES analysis where sample preparation involves time-consuming HF digestion of the modified silica aerogel.

The high thermal stability of the incorporated metal(salen) complexes under oxidizing conditions is a property that makes them particularly interesting candidates for heterogeneous oxidation catalysis. XPS of the aerogel surfaces before and after oxidation studies confirms the integrity of the immobilized metal/metal(salen) complexes against leaching. While difficult to treat separately, consequences of the immobilization and *cis*-stereochemical arrangement at the metal center for catalysis are currently under investigation. Preliminary data for ethylbenzene oxidation to acetophenone

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with the cobalt(salen) aerogel indicate the potential application of these metal(salen) modified gels in oxidation catalysis. In combination with oxygen/air as oxidant they constitute interesting examples of environment-friendly materials based on the heterogenization approach of known homogeneous systems.

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