



Cobalt–acetato complexes immobilised on PYPA-organomodified silica: a case study of different ways of immobilisation

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Received 6 August 2003; received in revised form 6 August 2003; accepted 8 October 2003

Abstract

In this paper, we compare the properties and activities of immobilised forms of in situ formed cobalt–acetato complexes of pyridin-4-ylmethyl-(3-triethoxysilylanyl-propyl)-amine (PYPA) on organomodified hexagonal mesoporous silica (HMS) prepared via different routes, namely sol–gel synthesis, post-modification of sol–gel AMP-HMS, and grafting. All materials are able to act as host for cobalt–acetato complexes to different extents, and are able to catalyse the aerial oxidation of styrene. The support materials and catalysts were characterised by DRIFT, X-ray photoelectron spectroscopy (XPS), N₂ adsorption and elemental analysis, and compared with their homogeneous counterpart and a material obtained by grafting of a complex formed prior to immobilisation on the silica surface.

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Keywords: Supported catalysts; Cobalt; Oxidation; Silica

1. Introduction

The discovery of micelle templated silicas like MCM-41 [1], MCM-48 [2], or, more recently, SBA-15 [3] first reported in the early 1990's has led to a whole new class of materials with high thermal and mechanical stability [4]. These materials can easily be modified and functionalised by incorporation of organic groups in the silica structure via various methods, notably through the use of substituted trialkoxysilanes Si(OR)₃R' in the sol–gel synthesis, and grafting of these on the pre-formed silica by reaction with surface silanol, and, mainly, siloxane groups [5]. Due to van der Waals interaction between the micelle and the organic group R' the organic group is incorporated mainly inside the pores of the hexagonal mesoporous silica (HMS) when the sol–gel route is chosen, whereas, due to better accessibility, functionalisation occurs mainly on the external surface of the silica pores when the modification is achieved via the grafting method [6]. Materials synthesised via the sol–gel route are considered to possess isolated organic groups inside the pores, whereas materials obtained via grafting can be described as an inorganic support with a partial organic

monolayer, where the structure of the underlying inorganic support is maintained [7]. Fig. 1 compares the different structures obtained by grafting and the sol–gel methodology.

A wide range of organic groups has been incorporated in the silica structure [6], which can be subsequently modified by normal organic chemistry [8]. The hybrid organic–inorganic materials obtained are not only interesting as materials in their own right, but they also have potential application in catalysis when catalytically active species are incorporated, e.g. amines [9–11], imines [12], acids [13] or peracids [14], or as resin scavengers [15]. Besides their use as catalysts, organomodified silicas can also be used to immobilise catalytically active compounds, for example cobalt acetate [16], cobalt–acetato complexes [17,18], chromium complexes [19], copper triflate [20], or palladium compounds [21].

Metal leaching is the biggest problem that must be overcome for truly heterogeneous catalysis using supported metallic species, especially in oxidations, as the reaction typically proceeds via a radical chain mechanism and the catalyst is attacked itself. Also changes in the oxidation state of the immobilised metal can cause destabilisation of the immobilised state. The most promising way to overcome this drawback is the search for a support material that provides the most stable environment for the metal centre, and therefore minimises, or in the best case prevents, leaching of the

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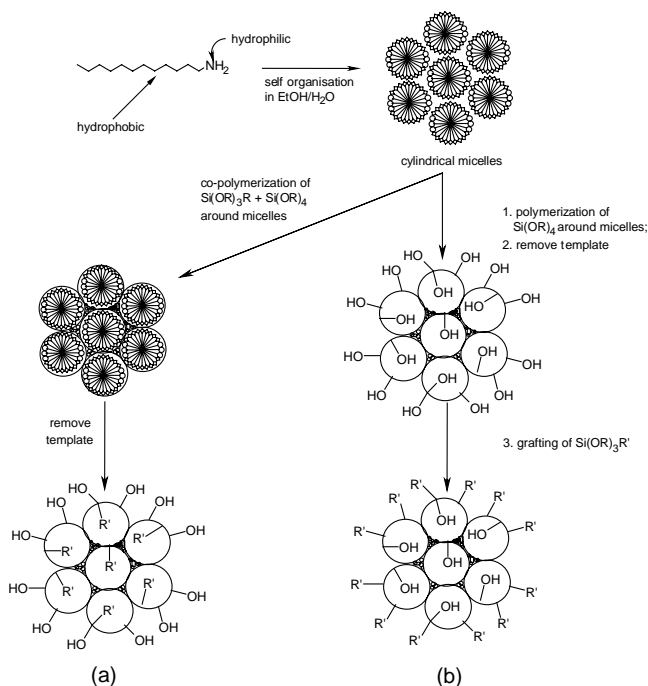


Fig. 1. Comparison of organomodified HMS prepared via (a) sol-gel synthesis (b) grafting.

metal from the support. In this paper, we compare the properties of pyridin-4-ylmethyl-(3-triethoxysilanyl-propyl)-amine (PYPA) modified HMS materials prepared via (a) incorporation of PYPA in the sol-gel synthesis of the silica; (b) grafting of PYPA on the silica surface; and (c) preparation of PYPA on the silica surface by condensation of pyridine-4-carbaldehyde with aminopropyl-HMS. Furthermore, the ability of these materials to provide a stable environment for cobalt-acetato complexes and their catalytic activity are investigated.

2. Experimental

All chemicals were purchased from Lancaster Chemicals unless stated differently.

2.1. Preparation of PYPA

Ten millimoles 3-aminopropyl-triethoxysilane (2.36 ml) and 11 mmol pyridine-4-carbaldehyde (1.05 ml) (Aldrich) are dissolved in 40 ml CH_2Cl_2 and refluxed for 16 h using an inverse Dean-Stark trap to remove condensation water from the reaction mixture. The solvent is removed, and the resulting yellow oil is used without further purification.

2.2. Preparation of sol-gel PYPA-HMS

To a mixture of 26.5 ml ethanol and 23.5 ml water 2.26 g dodecylamine are added and the mixture stirred until a clear

solution is obtained. Then 5 mmol TEOS are added, and after 2 min further 25 mmol TEOS and 10 mmol $\text{Si}(\text{OR})_3\text{R}'$ are added simultaneously. The mixture becomes cloudy and is stirred for 18 h. After filtration, washing with ethanol and drying at 105°C , the template is removed by 16 h of sohxlet extraction with ethanol. The HMS is filtered off, washed with ethanol and water, and dried at 105°C .

2.3. Grafting of PYPA on HMS

Two grams of HMS, which has been activated by refluxing in 2 M HCl for 5 h and dried at 105°C over night, are suspended in 50 ml dry toluene. A total of 10 mmol of PYPA are added, and the mixture refluxed for 16 h. The resulting yellow solid is filtered off, washed extensively with ethanol, and dried over night at 105°C .

2.4. Preparation of condensed PYPA-HMS

A total of 10 mmol pyridine-4-aldehyde are added to a suspension of 2 g AMP-HMS in 40 ml CH_2Cl_2 , and the mixture refluxed for 16 h using an inverse Dean-Stark trap to remove condensation water. The resulting bright yellow solid is filtered off and extensively washed with ethanol, and dried at 105°C .

2.5. Formation of cobalt-acetato complex on the surface

To a suspension of 1 g organomodified HMS in 40 ml water 10 ml of a 0.1 mol/dm^3 cobalt acetate solution are added. Aqueous NaOH is added until a colour change from pink to blue is observed. After 5 min, 1 ml 30% H_2O_2 is added, which results in a colour change from blue to olive green. The mixture is heated to boil for 3 min, the solid filtered off and extensively washed with water and ethanol. The resulting olive green to pale green solid is dried at 105°C over night.

2.6. Test reaction conditions

Catalyst (0.1 g), tetradecane (0.5 ml) (internal standard) and 1,4-dioxane (40 ml) are charged to a three-necked flask fitted with septum and condenser and heated to 90°C using an oil bath. Then, 2.86 ml (25 mmol) styrene are added, and an airflow of 15 ml min^{-1} is bubbled through the solution. The reaction is followed via GC and products are identified by GC-MS.

2.7. Instrumental

IR spectra were recorded using a BRUKER EQUINOX 55 FT-IR with DRIFT setup. Thermal analysis was performed using a POLYMER LABORATORIES STA 625. Porosimetry experiments for the calculation of BET surface areas and BJH Pore Volumes were carried out using a COULTER SA3100 surface analyzer. X-ray photoelectron spectroscopy (XPS)

spectra were obtained using a KRATOS AXIS HSi in normal emission mode using Mg K α radiation and a 20 eV energy pass filter. The obtained spectra were fitted with CASAXPS[®] 2.134 software, using a SHIRLEY-type background and mixed Gaussian/Lorentzian line shape with 30% Lorentzian character. GC samples were analysed using a VARIAN3800 Gas Chromatograph fitted with a 30 m DB5 column. Elemental analysis was obtained as an external service from the University of Manchester; samples were weighed using a METTLER MT 5 microbalance and analysed using a CARBO ERBA 1106 elemental analyzer.

3. Results and discussion

3.1. Elemental analysis

The values obtained from the CHN analysis, and cobalt loadings (measured by atomic absorption spectroscopy), are listed in Table 1.

As can be seen, the values obtained for the support materials and the cobalt-loaded catalysts are very similar. The distinct loss of nitrogen and carbon during the loading step of the preparation, which is most obvious for the grafted material, is caused by hydrolysis of PYPA. The similar C/N ratios in this case indicate that the Si–C bond in PYPA, and not the C=N bond, is attacked. Another possibility is the loss of the whole PYPA group and therefore hydrolysis of a Si–O–Si bond. Nitrogen loadings are similar in all cases, between 3.3 and 4.4%.

3.2. DRIFT analysis

Fig. 2 shows the DRIFT spectra of the different support materials and their precursors. As DRIFT is a surface technique and the support materials are expected to exhibit significant differences in their structure (see Fig. 1), quantitative analysis is not possible in this system. Nevertheless, the DRIFT spectra obtained give information about the degree of incorporation. The spectrum of sol–gel and condensed PYPA-HMS show peaks attributable to unreacted amino groups on the surface; this was confirmed by ¹³C-MAS-NMR. In the case of sol–gel PYPA-HMS, this

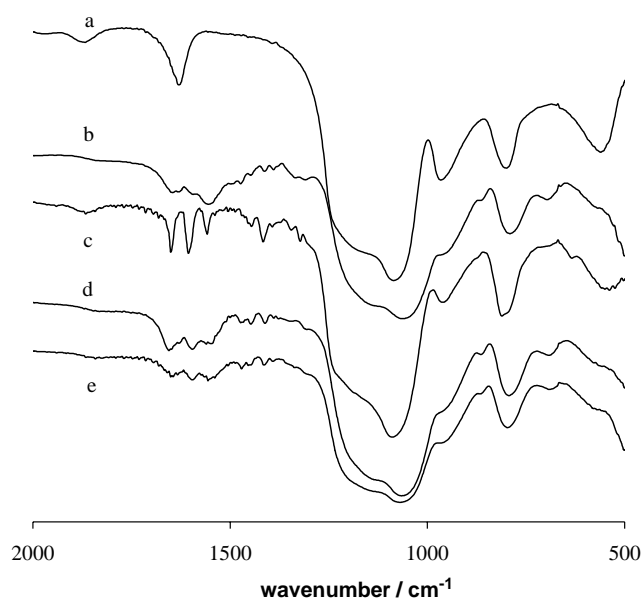


Fig. 2. DRIFT spectra of support materials: (a) activated HMS; (b) aminopropyl-HMS; (c) grafted PYPA-HMS; (d) condensed PYPA-HMS; and (e) sol–gel PYPA-HMS.

Table 2
C=N_{py} ring vibration absorption bands

Preparation method	C=N _{py} absorption bands (cm ⁻¹)		
	Support material	After loading with cobalt	After reaction with styrene
Sol–gel	1596	1593	1592
Condensed	1597	1595	1594
Grafted	1606	1606	1597
Pure complex	–	1597	–
Pre-formed	–	1597	1593

is caused by hydrolysis of the imine bond under the basic aqueous reaction conditions applied in the sol–gel synthesis. In the case of condensed PYPA-HMS, the presence of amino groups indicates incomplete reaction of the AMPS.

The spectra show the expected peaks for the imine function at 1645–1659 cm⁻¹ and peaks corresponding to C=N_{py} ring vibrations at 1593–1606 cm⁻¹. Characteristic absorption bands are listed in Table 2. After chemisorption of

Table 1
Elemental composition measured by elemental analysis, and cobalt loading (a) before and (b) after reaction

	C (%)	N (%)	H (%)	C/N ratio	Co (mmol/g) ^a	Co (mmol/g) ^b
Homogeneous complex	39.8	6.0	3.8	7.7	–	–
Sol–gel support	10.6	3.3	2.7	3.7	–	–
Sol–gel support + Co	9.9	3.2	2.7	3.7	0.15	0.12
Grafted support	15.7	3.6	1.7	5.1	–	–
Grafted support + Co	8.0	1.9	1.3	5.0	0.95	0.90
Amps	12.0	4.2	3.0	3.4	–	–
Condensed support	12.9	4.4	2.7	3.4	–	–
Condensed support + Co	12.3	4.3	2.7	3.3	0.15	0.21
Pre-formed complex	17.7	4.9	3.1	4.2	0.41	0.51

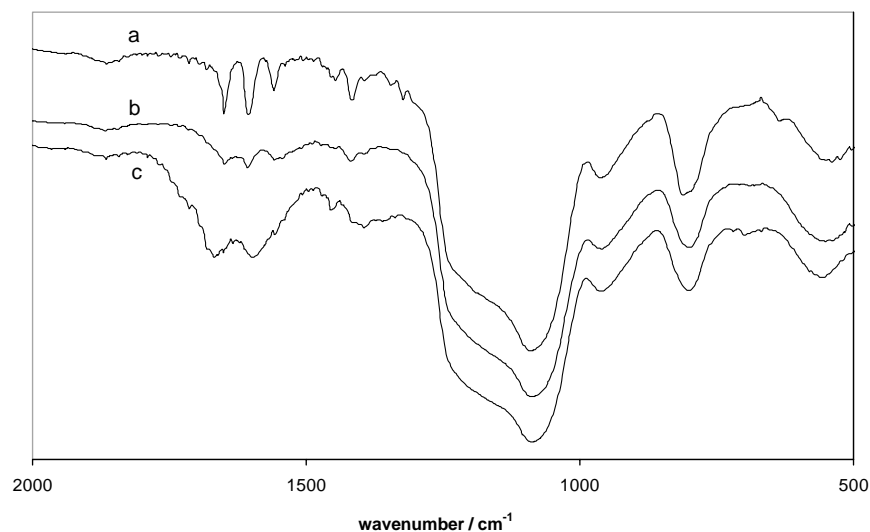


Fig. 3. DRIFT spectra of grafted support (a), after loading with cobalt (b), and after reaction with styrene (c).

cobalt the $C=N_{py}$ ring vibration bands are shifted to lower frequencies by $2\text{--}3\text{ cm}^{-1}$, indicating the weakening of the $C=N_{py}$ bonds by co-ordination to cobalt. No shift is observed for the grafted PYPA-HMS, indicating that, because of the high loading with PYPA, not all pyridine groups have bonding interaction with cobalt. In the cases of the pre-formed complex and the pure complex, the $C=N_{py}$ absorption is observed at 1597 cm^{-1} , which is $2\text{--}4\text{ cm}^{-1}$ higher than in those cases where the ligand was immobilised before loading with cobalt via a sol-gel process. This behaviour can be explained by interaction—and therefore weakening of the $C=N_{py}$ bond—of the pyridine with the silica support. This is also believed to be the reason for the observed differences in the energy of the $C=N_{py}$ between the sol-gel, condensed and grafted PYPA-HMS (1596 , 1597 and 1606 cm^{-1} , respectively), as in these cases, the pyridine is closer to the silica surface (see Fig. 1).

After use in styrene oxidation reactions the absorption bands are broad, and the band caused by the imine group

could not be resolved due to physisorbed compounds. The $C=N_{py}$ absorption maxima do not shift significantly except for grafted PYPA-HMS, suggesting that no change in the metal-ligand interaction occurs. The $C=N_{py}$ band of grafted PYPA-HMS shifts from 1606 to 1597 cm^{-1} after reaction with styrene, which is very close to the values observed for the low-loaded compounds sol-gel and condensed PYPA-HMS and identical with the peak position found for the pre-formed complex, suggesting that only those ligands which have bonding interaction with cobalt remain attached to the support, and the remainder is lost or oxidised under the radical reaction conditions. Fig. 3 shows the DRIFT spectra of the grafted support material, after loading with cobalt, and after the styrene oxidation.

3.3. Surface analysis by N_2 absorption

Although no direct correlation between the surface area or the porosity and the catalytic activity of the support is

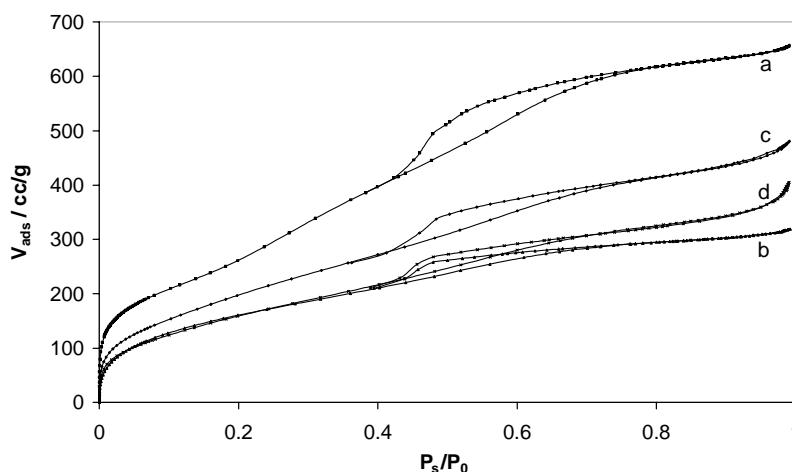


Fig. 4. N_2 adsorption/desorption isotherms of (a) activated HMS (b) after grafting of PYPA (c) after loading with cobalt (d) after reaction in styrene.

observed, N₂ absorption experiments can still give valuable information about the structure of the support materials and the ready-made catalysts before and after use. The results clearly show the differences in the structure of the materials under investigation.

Fig. 4 shows the N₂ absorption isotherms of activated HMS, after grafting of PYPA, following loading with cobalt, and after use in the oxidation of styrene.

The shapes of the isotherms are very similar, indicating that the porous structure has been maintained throughout the preparation and after use as catalyst in the aerial oxidation of styrene. All isotherms are of type IV after IUPAC classification. The pore size distribution is narrow and shows that the majority of the pores have a diameter between 3.48 and 3.82 nm. The BET surface area drops from 957 m²/g for the activated silica to 614 m²/g after grafting of PYPA; following the same trend, the total pore volume decreases from 1.00 to 0.49 cm³/g. Interestingly, the surface area increases after the loading procedure to 753 m²/g, indicating that the imine bond or the silicon–oxygen bond of PYPA has partly been hydrolysed. After use in the oxidation of styrene, the surface area decreases to 607 m²/g, which is very close to the value for the material after grafting. This may be explained by reaction of the amine function, which has been formed by hydrolysis of PYPA in the loading step of the preparation, with a reactive product or intermediate like styrene oxide, or physisorption of organics, restoring the initial coverage of the surface. This assumption is backed by DRIFT experiments on the catalyst after reaction, which show a broad peak around 1655 cm⁻¹ caused by aromatic compounds. The results of the adsorption experiments are listed in Table 3.

As can be seen in Table 3, the structural differences caused by the different preparation methods used are obvious. Only the material obtained via the grafting method shows the

Table 3
Porosimetry data

	Grafted	Sol-gel	Condensed	Pre-formed complex
Total pore volume (cm ³ /g)				
Support	0.49	0.03	0.02	1.00
After loading	0.53	0.04	0.02	0.02
After reaction	0.59	0.05	0.04	0.03
BET surface area (m ² /g)				
Support	614	12	3	956
After loading	753	31	4	5
After reaction	607	20	13	14

expected porous structure of HMS, whereas in the other cases the structure collapsed. The pore area distribution in this case is narrow, whereas it is broad in the other cases. Fig. 5 compares the desorption pore size distribution of the materials after loading with metal.

The pore area distribution shows that the structure of the materials obtained from the sol-gel and the condensation process, which is based on AMP-HMS with a similar structure to non-modified HMS, do not show the expected regular HMS structure, but are more amorphous. This is not surprising for the sol-gel material, as it has been reported that a regular HMS structure can only be obtained when the ratio of organosilane to TEOS is kept lower than 1:4 [22]. Nevertheless, the material is able to act as host for cobalt in a complexing manner to a certain extent, as shown by AAS/elemental analysis, as this is not directly dependent on the porosity, but more on the accessibility of the ligand function on the silica surface, which is limited for the sol-gel and condensed support materials.

Surprisingly, the structures of the materials obtained via condensation of the surface amino groups with pyridine-

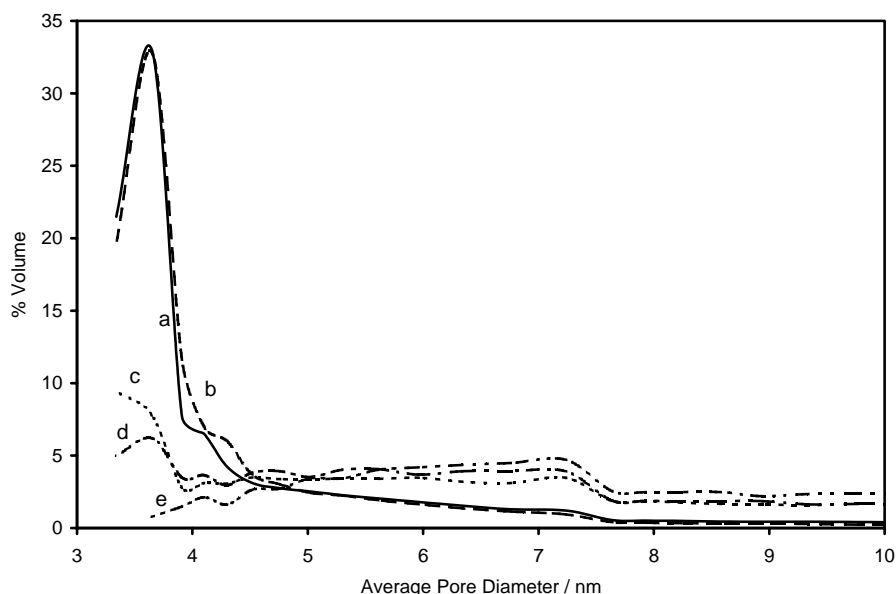


Fig. 5. Pore area distribution of (a) grafted PYPA-HMS; (b) non-modified HMS; (c) sol-gel PYPA-HMS; (d) pre-formed complex; and (e) condensed PYPA-HMS after loading with cobalt.

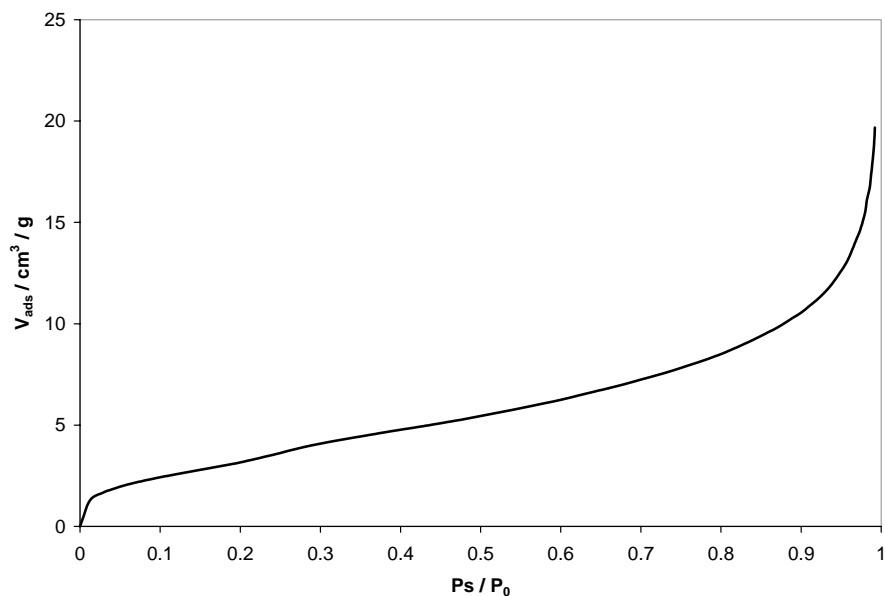


Fig. 6. N_2 adsorption/desorption isotherm of sol-gel PYPA-HMS.

4-carbaldehyde and by grafting of the pre-formed complex on non-modified HMS are not of the HMS-type expected, but also show a broad pore area distribution. This may be explained by hydrolysis under the basic reactions conditions applied in the preparation of the compounds, which can lead to re-organisation of the silica. Additionally, in the case of the pre-formed complex this behaviour can be explained by the filling of the pores with the grafted complex; therefore the porosity of the material is reduced. This can also be assumed for the condensed material. The differences in the structural features are obvious regarding the isotherms of these materials, which can be seen in Fig. 6 for the sol-gel material before loading with cobalt, showing a shape similar to type II isotherms, which are typical for microporous materials. The pore volume and pore area distributions suggest a mixture of micro- and mesopores.

3.4. Catalytic activity

All catalysts were tested for their activity as catalysts in the aerial oxidation of styrene. All catalysts exhibit the same selectivity towards oxidation products (32% for styrene oxide, the remaining being oxidative coupling and over-oxidation products like benzoic acid), consistent with the species on the surface being similar and the reaction proceeding via the same pathway. Reaction rates are very similar for each system, and are not linked to the metal loading. Significant differences were observed in the induction period, as can be seen by Fig. 7, which shows the conversion of styrene with time.

The homogeneous complex is the only catalyst which does not show an induction period. In all other cases, induction periods between 1 and 3 h are observed. Although

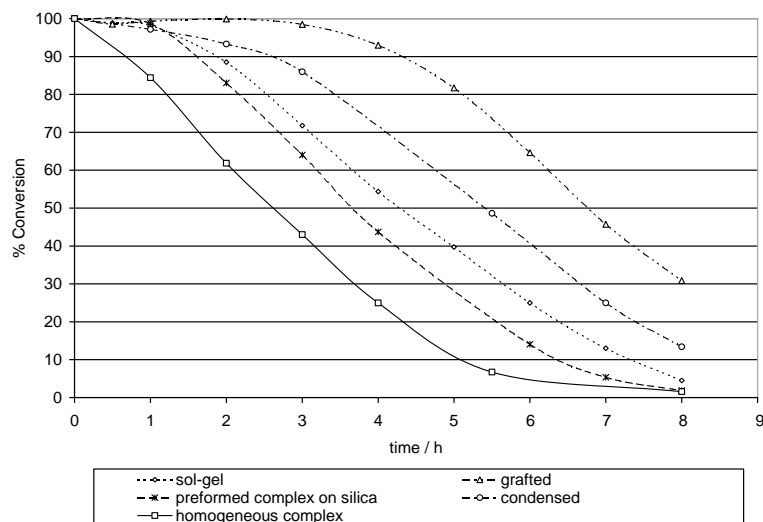


Fig. 7. Catalytic activity of supported complexes in comparison to its homogenous counterpart.

the reasons for induction periods, which are often observed in heterogeneous catalysis, are not fully understood, it can be argued that reactions between the active species and the support material occur, delaying any reaction with the substrate. This theory is backed by the different induction periods observed, which increase with increasing PYPA concentration on the surface. Accordingly, the neat complex shows no induction period, and the induction period rises from 1 h for the pre-formed complex and the low-loaded materials (sol–gel and condensed) up to 3 h for the grafted version of the catalyst, where the highest amount of accessible PYPA is present.

3.5. XPS analysis

X-ray photoelectron spectroscopy is a powerful surface technique that is used to investigate the electronic properties of the species on the surface. As the electronic environment, e.g. oxidation state and/or spin multiplicity, of a certain metal influences the binding energy of the core electrons of the metal, XPS yields detailed information about the metal species on the surface. Fig. 8 shows the XPS spectra obtained for the pure complex, the material prepared via grafting of PYPA and following chemisorption of cobalt acetate, and the supported pre-formed catalyst.

Briggs and Seah [24] proposed that the intensity ratio and the energy difference between the two signals obtained for electrons ejected from the p1/2 and p3/2 levels [25] can be used as a means to investigate the spin multiplicity and therefore the electronic properties of the cobalt compounds. Furthermore, the peak position is directly related to the electron density, and therefore the oxidation state of the species under investigation can be determined.

Best fits of the data were obtained using a SHIRLEY-type background and a mixed Gaussian/Lorentzian line shape. In most cases, better fits were yielded assuming the presence of two different cobalt species on the surface, which can either be caused by the presence of a multinuclear complex with cobalt in different environments/oxidation states, or chemisorption of the metal by different functionalities on the silica surface (e.g. by the pyridine or imino function, free amino functions, or both). An example of a related multinuclear complex is $\text{Co}_4\text{O}_4\text{Py}_4\text{OAc}_4$, which crystallises in a cubic core structure, as proposed by Das [23]. Due to the low concentration of cobalt on the surface the spectra obtained are noisy, and therefore peak positions and areas should be regarded with caution. Nevertheless, differences in the spectra are obvious and can give information about the influence of the support material on the metal environment on the surface. Binding energies before and after reaction with styrene are listed in Table 4, values for the energy of the spin-orbit coupling can be seen in Table 5.

The data suggests a mixture of Co(III) and Co(II) on the surface for the grafted and sol–gel materials and only Co(II) in the case of catalyst prepared via condensation with the surface amino groups. The pure complex and the material

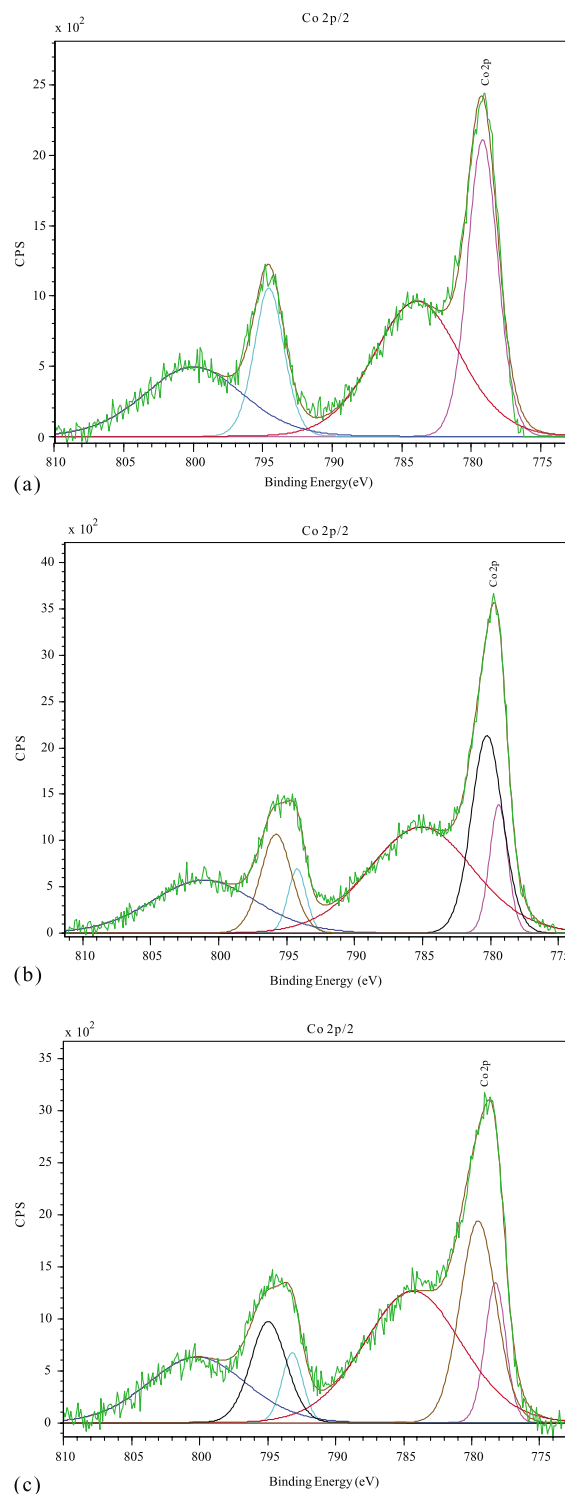


Fig. 8. Selected XPS spectra: (a) pure complex; (b) pre-formed; and (c) grafted.

prepared via grafting of the pre-formed complex exhibit the highest binding energies; thus it can be assumed that the supported metal species are stabilised by transfer of electron density from the support to the metal. This effect is strongest in the grafted material, therefore it can be assumed that the

Table 4
Binding energies of Co 2p electrons

	Co 2p 1/2 (eV)	Co 2p 3/2 (eV)	Co 2p 1/2 (eV)	Co 2p 3/2 (eV)
Pre-formed complex	779.4	794.2	780.3	795.8
After reaction in styrene	778.8	794.5	780.5	796.0
Sol-gel supported	778.5	793.5	781.2	795.9
After reaction in styrene	778.8	794.0	781.0	796.0
Condensation supported	778.8	794.1	781.0	796.2
After reaction in styrene	779.2	794.9	–	–
Pure complex	779.2	794.6	–	–
Grafted supported	778.3	793.2	779.5	794.9
After reaction in styrene	778.5	794.3	780.2	796.1

Table 5
Spin-orbit coupling of cobalt 2p electrons

	ΔE_1 (eV)	ΔE_2 (eV)
Pre-formed complex	14.8	15.5
After reaction in styrene	15.7	15.5
Sol-gel supported	15.0	14.8
After reaction in styrene	15.2	15.0
Condensation supported	15.3	15.2
After reaction in styrene	15.7	–
Pure complex	15.4	–
Grafted supported	14.9	15.4
After reaction in styrene	15.8	15.9

metal has interaction with more than one PYPA group on the surface, and weaker for the sol-gel and condensed catalysts, as these are thought to possess mainly isolated PYPA sites on the surface.

The pure complex contains only one species (Co(II)), whereas the catalyst prepared by grafting of the pre-formed complex, which is expected to be nearly identical to the neat complex, gives rise to signals for Co(III) and Co(II); thus indicating a stabilisation of Co(III) by the support material. The catalyst obtained via the grafting method exhibits a mixture of Co(II) and Co(III), whereas the materials obtained via sol-gel and condensation procedures only ex-

hibit spin-orbit coupling values typical for a single oxidation state of cobalt on the surface, Co(III) and Co(II), respectively. The changes after the materials were used to catalyse the aerial oxidation of styrene are interesting. Only in the case of the sol-gel supported cobalt complex are Co(III) species found to be still present on the surface, whereas in all other cases only Co(II) is present. This can be explained by degradation of the support materials, which is liable to attack by radicals formed under reaction conditions. The degradation of PYPA groups is thought to occur less in the sol-gel materials, as the PYPA groups are inside the structure and protected against attack by the bulk silica surrounding them, and therefore they are less likely to be attacked due to accessibility/diffusion problems. Basically, the same effect was expected for the support material prepared via condensation of pyridine-4-carbaldehyde with surface amino groups, but in this case only the accessible amino groups have reacted in the preparation of the support material to form surface-bound PYPA. As these groups are accessible from solution, they also can also be attacked by the radical species present under reaction conditions. Therefore, the electronic state of the metal on the silica is not the same before and after reaction. This is illustrated in Fig. 9, which shows the XPS spectra of the grafted catalyst before and after reaction.

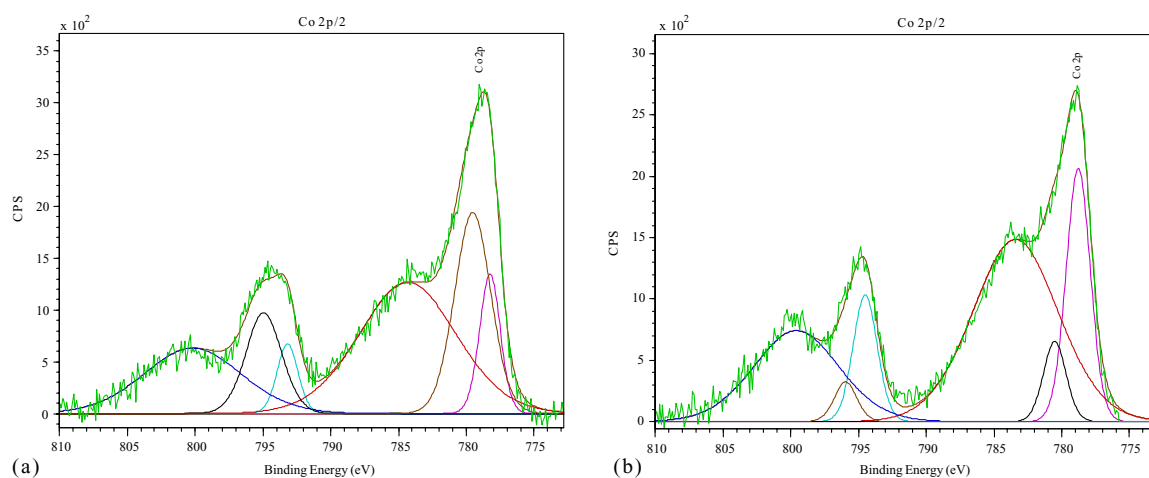


Fig. 9. XPS spectra of grafted catalyst before (left) and after reaction with styrene.

4. Conclusions

We were successful in immobilising cobalt–acetato complexes on PYPA-modified HMS-type materials. Incorporation of PYPA was achieved via different methods, namely grafting, sol–gel, and post-modification of AMP-HMS. The achieved cobalt loading is similar for the sol–gel and post-modified material around 0.1 mmol/g due to restricted accessibility of the ligand function, suggesting that only around 5% of the PYPA is accessible and therefore able to act in a complexing manner. In these cases, the immobilised cobalt species are in similar electronic states, as shown by XPS. In all cases, at least two different cobalt species are present, but only the grafted version of the catalyst exhibits cobalt in two different oxidation states. The immobilised species undergoes significant changes under reaction conditions, and some leaching is observed for the condensed and grafted version of the catalyst, which may be explained by removal of physisorbed compounds. Immobilisation occurs mainly via interaction with the aromatic nitrogen in this system, as shown by DRIFT analysis. No correlation between the porosity of the support and the catalytic activity in the aerial oxidation of styrene was found. Induction periods between 1 and 3 h were observed for all supported catalysts, which can be explained by reaction of the active species with surface-bound PYPA, delaying oxidation of the substrate. The theoretical advantage of having a high surface concentration of ligands in order to allow easy and stable immobilisation therefore proves to be a disadvantage for real applications as catalyst in this system.

References

- [1] J.S. Beck, et al., *Nature* 359 (1992) 710.
- [2] J.S. Beck, et al., *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] Q.S. Huo, et al., *Chem. Mater.* 8 (1996) 1147.
- [4] A. Galarneau, et al., *Catal. Today* 68 (2001) 191–200.
- [5] D. Brunel, *New. J. Chem.* 24 (2000) 807–813.
- [6] A. Stein, *Adv. Mater.* 12 (2000) 1403–1419.
- [7] A. Ulman, *Chem. Rev.* 96 (1996) 1533–1554.
- [8] J.H. Clark, D.J. Macquarrie, K. Wilson, *Stud. Surf. Sci. Catal.* 129 (2000) 251–264.
- [9] D.J. Macquarrie, D.B. Jackson, *Chem. Commun.* (1997) 1781.
- [10] J.E.G. Mdoe, J.H. Clark, D.J. Macquarrie, *Synlett* (1998) 625.
- [11] K.A. Utting, D.J. Macquarrie, *Appl. Catal. A Gen.* 232 (2002) 7–12.
- [12] K.A. Utting, D.J. Macquarrie, *New. J. Chem.* 24 (2000) 591–595.
- [13] K. Wilson, J.H. Clark, *Pre. Appl. Chem.* 72 (2000) 1313–1319.
- [14] A. Lambert, J.H. Clark, et al., *Synlett* 7 (2000) 1052–1054.
- [15] D.J. Macquarrie, H. Rousseau, *Synlett* (2003) 244.
- [16] A.J. Butterworth, *Chem. Commun.* (1996) 1859–1860.
- [17] B.K. Das, J.H. Clark, *Chem. Commun.* (2000) 605–606.
- [18] J. Rafelt, J.H. Clark, *Catal. Today* 57 (2000) 33–44.
- [19] I.C. Chisem, et al., *Chem. Commun.* (1998) 625.
- [20] A. Stiewe, et al., *NJC*, in press.
- [21] E.G. Mubofu, J.H. Clark, D.J. Macquarrie, *Stud. Surf. Sci. Catal.* 130 (2000) 2333.
- [22] D.J. Macquarrie, *Green Chem.* 1 (1999) 195.
- [23] Communication with B.K. Das, Guwahati University, India.
- [24] D. Briggs, M.P. Seah, *Practical Surface Analysis, Auger and X-Ray Photoelectron Spectroscopy*, vol. 1, second ed., Wiley, London, 1996, p. 129.
- [25] D. Briggs, V.A. Gibson, *Chem. Phys. Lett.* 25 (1974) 493.