A spectroscopic study of group IV transition-metal-incorporated direct templated mesoporous catalysts.
Part 2. A comparison of Ti-, Zr- and Hf-containing materials

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Ti, Zr and Hf ions have been incorporated into mesoporous silica using a novel one-pot procedure based on the true liquid crystal templating (TLCT) synthesis method. The nature of the metallic sites was assessed using diffuse reflectance UV-visible, photoluminescence and FT-IR spectroscopy. *In situ* adsorption of oxygen and ammonia probe molecules provided information on the accessibility of optically active species.

KEY WORDS: true liquid crystal templating; Ti, Zr and Hf incorporated into mesoporous silica; FT-IR; DR UV-vis; photoluminescence

1. Introduction

The importance of titanosilicates for several catalytic applications is paramount [1,2]. Some research has also been directed towards the incorporation of zirconium into mesoporous silica [3,4], but to our knowledge this is the first paper in which the possibility to incorporate hafnium ions into these materials is discussed. These materials should have catalytic properties linked with the acidic nature of Zr and Hf active sites [5,6].

In part 1, a spectroscopic study of Ti-incorporated active catalysts synthesized *via* a one-pot true liquid crystal templating (TLCT) route using two different Ti sources (Ti-acetylacetonate and titanocene dichloride) was reported [1,7]. It was found that the route involving the hydrophobic titanocene precursor produced a mesoporous siliceous material containing isolated tetrahedral Ti sites which were predominantly accessible to gaseous probe molecules. The use of water soluble Ti-acetylacetonate as the Ti source also led to the inclusion of tetrahedral titania sites in the mesoporous silica framework, but the accessibility of these sites to external gaseous probe molecules was more limited. Here we describe the extension of the metallocene route to the incorporation of Zr and Hf into mesoporous silica, and spectroscopic data for these materials is compared with the analogous Ti-incorporated material.

The idea behind studying Zr- and Hf-doped mesoporous frameworks by UV-vis spectroscopy was that ligand-to-metal charge transfer transitions could be expected to occur, as in the Ti-doped materials. Work has been published on the UV-vis spectroscopic properties of mixed Si–Zr oxides by Moon *et al.* [8], and on hafnium oxide by Schipper *et al.* [9]. The latter paper reported that bulk hafnium oxide had a strong absorption band at 220 nm in the UV-vis diffuse reflectance spectrum, but that excitation at this wavelength did not produce any luminescence. However, since the properties of bulk HfO_2 are likely to differ from those of the finely dispersed HfO_2 centers in our mesoporous products, further spectroscopic studies were justified.

2. Experimental

2.1. Synthesis

A hexagonal (type I) liquid crystal templating phase was used containing octaethylene glycol monododecylether, $C_{12}EO_8$ (Fluka), 10^{-2} M HCl, tetramethoxysilane (TMOS; Aldrich) and metallocene dichloride (Aldrich). The synthesis mixtures had the composition: 0.06 g metallocene/1.5 g $C_{12}EO_8$/1.5 ml 10^{-2} M HCl/3.165 ml TMOS. A purely siliceous product was also made (blank) as a comparison for the metal-doped materials. In all cases 3 ml methanol were used to aid dissolution of the various components in the initial synthesis gel. The gels were left to react overnight under light dynamic vacuum, at room temperature, to remove all the methanol hydrolysis product, as well as the added methanol. The optical textures of the products as seen by polarizing microscopy were all typical of hexagonal H_I lyotropic phases [1]. The Ti-, Zr- and Hf-doped products are denoted Ti[CP], Zr[CP] and Hf[CP], respectively.

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The amounts of metallocene used in the Ti[CP], Zr[CP] and Hf[CP] syntheses were at the upper limit of solubility in the synthesis gels. All as-synthesized products were calcined at 500 °C heating the samples controllably at 5 °C/min under nitrogen flow, and then after 1 h at 500 °C, switching the gas flow to oxygen. After a further 8 h at 500 °C, the samples were allowed to cool to room temperature at 5 °C/min.

The metal loadings in the calcined Ti[CP], Zr[CP] and Hf[CP] were determined by neutron activation analysis to be 0.62 wt% Ti, 1.1 wt% Zr and 1.53 wt% Hf.

2.2. Characterization

The calcined products were analyzed by diffuse reflectance (DR) UV-vis and UV-vis photoluminescence spectroscopy. The samples were all ground to a powder and placed in purpose-made quartz cells for spectroscopic analysis, which were attached to a vacuum-line and subjected to thermal treatments to remove all adsorbed water and organic impurities. The vacuum-line used for sample treatment reached pressures of 10^{-5} mbar by means of a diffusion pump. For oxidative treatments, a pressure of 100 Torr O_2 (0.133 bar) was used. The oxygen was introduced into the sample cell *via* the vacuum/Schlenk line and the quartz cell containing the sample was heated to 550 °C using a temperature-controlled mantle.

For DR UV-vis measurements a Perkin–Elmer (Lambda 19) spectrometer equipped with an integrating sphere attachment was used. The reflectance output from the instrument was converted using the Kubelka–Munk algorithm. The photoluminescence measurements were made using a Spex Fluorolog-2 (F212I) spectrometer.

For the FT-IR study, the powdered samples were compressed into thin disk-shaped pellets with a density of 2.5 mg/cm^2. The samples were mounted in a purpose-made quartz cell, which was attached to a vacuum-line similar to that used for the UV-vis *in situ* analyses. The samples were subjected to thermal treatments (oxidation at 550 °C) prior to the main series of measurements. The instrument used for the FT-IR measurements was a Bruker IFS88 spectrometer with a resolution of 4 cm^{-1}.

2.3. Catalytic experiments

Unlike Ti[CP], Zr[CP] and Hf[CP] were found to be catalytically inactive both in the epoxidation of 1-octene using *tert*-butylhydroperoxide as the source of oxygen, and in the peroxidative bromination of phenol red to tetrabromophenol blue. For experimental details of the catalytic tests, see part 1 [1,7].

3. Results and discussion

3.1. Synthesis

Due to the colourless nature of the Zr and Hf metallocene precursors, it was difficult to judge whether the organometallic compounds remained unhydrolyzed throughout the TLCT synthesis. The deep orange colour of the titanocene-doped as-synthesized material suggested that the titanocene complex was stable under the TLCT synthesis conditions [1], and the same behaviour can be assumed for the zirconocene and hafnocene synthesis mixtures. We postulate that the hydrophobic cyclopentadienyl complexes are soluble in the hydrocarbon cores of the polyoxyethylene (POE) surfactant micelles of the templating liquid crystal phase, where they are protected from hydrolysis reactions.

The as-synthesised products consisted of large (sometimes >1 cm^2) fragments of transparent material which remained virtually intact after calcination except for the formation of a few cracks. The symmetry of the products was confirmed to be 2D-hexagonal by polarizing microscopy and X-ray diffraction. Further structural characterization details for these TLCT materials were given in part 1 [1].

3.2. Characterization

Traces of organic material were still present in the calcined products, and produced high intensity absorbance and luminescence signals. The organic residues were due to the incomplete combustion of the organic template, and perhaps also of the cyclopentadienyl ligands decomposition products of the metallocene complexes. Lengthy oxidation of the precalcined materials at 550 °C *in situ* within the quartz cells used for spectroscopic analysis, was not completely successful in removing all organic impurities even after 30 h oxidation. This behaviour, which has not yet been rationalized, was peculiar to these mesoporous samples prepared using the TLCT process, and was not previously observed for Ti-doped MCM-41 [7,10–12]. However, a comparative study of the electronic spectra (both in diffuse reflectance and in photoluminescence) of the various materials enabled us to distinguish the spectroscopic features of organic residues from those of the transition metal ions in the mesoporous frameworks. This study was particularly instructive from the point of view of interpretation of electronic spectra for such complex systems.

3.2.1. Diffuse reflectance UV-vis spectroscopy

No previous spectroscopic study of similar zirconium- and hafnium-doped silicates was found in the literature, so our interpretation of the spectra for Zr[CP] and Hf[CP] relies on comparison with data obtained for Ti[CP] [1] and the blank.

The diffuse UV reflectance spectra for our metallocene-doped samples re-oxidized at 550 °C under static oxygen conditions are plotted in figure 1. The spectrum for Ti[CP] had an intense maximum absorbance centred at 220 nm, characteristic of isolated tetrahedral Ti(IV) sites within the mesoporous structure [1]. There was also a shoulder at 250 nm and two further much less intense absorption bands at 330 and 460 nm, which occurred with progressively higher intensities in the Zr- and Hf[CP] spectra. Interestingly, the "blank" sample, re-oxidized for only 8 h at 550 °C

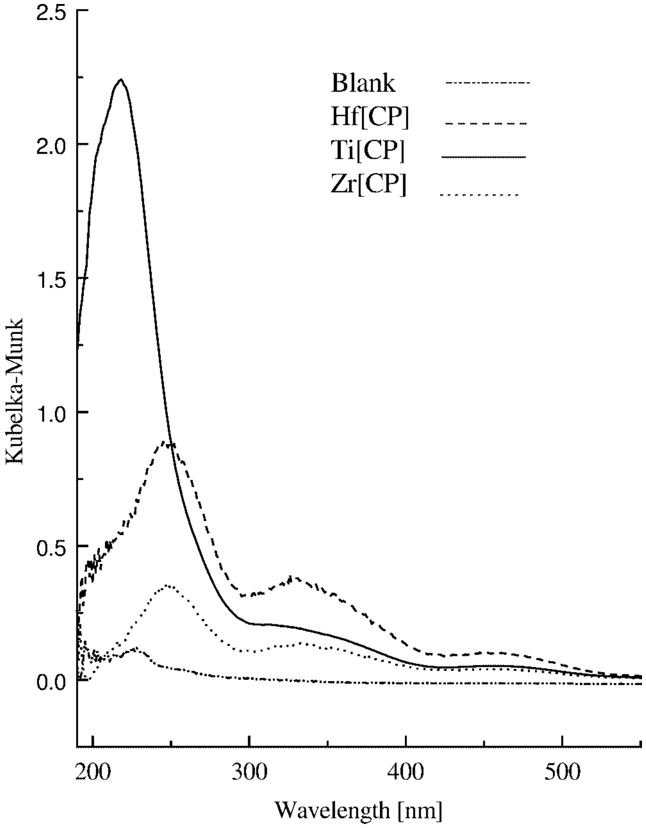

Figure 1. Diffuse reflectance UV-vis spectra for the blank, Ti [CP], Hf[CP] and Zr[CP] samples, calcined for 30 h.

(spectrum not shown for sake of brevity), also showed a weak absorption band at 245 nm. This band after a long oxidation (30 h) was removed and therefore it was assigned to organic impurities (pure siliceous materials do not present electronic transitions in this spectral region) [13].

Zr[CP] and Hf[CP] had their main absorption bands centered at 250 nm, only slightly displaced with respect to the absorption of the blank oxidised for 8 h. Additionally, the absorption bands at 330–340 and 460 nm were observed for all three Ti-, Zr- and Hf-doped materials even after a very prolonged oxidation (30 h). It is therefore likely that the absorption bands observed for the Zr[CP] and Hf[CP] samples, including the band at 250 nm, were caused by organic decomposition species common to all three samples, *i.e.*, cyclopentadienyl ligand decomposition products. There is no conclusive evidence from our spectra suggesting absorption bands were associated with Zr and Hf electronic transitions.

Electronic transitions in pure semiconductor oxides depend on the dimensions of the particles. This particle size effect, for example, was found for TiO_2 [14] and ZnO_2 [15] where the electronic transitions of the band gap shift to lower wavelengths by decreasing the dimension of the oxide particles (or clusters). For supported metal oxides this effect is very important, as the metal loading influences the dimension of the metal oxide particles (clusters), and it was found for both zirconium–silicon binary oxides [8] and titanium oxides dispersed on silica [16]. In the case of metal ions dispersed on oxides, oxygen to metal ion charge transfers (LMCT) occur at wavelengths lower than the band gaps of pure or mixed oxides. Whilst TiO_2 bulk, for example, has a signal at 330 nm, isolated Ti(IV) ions embedded in zeolitic matrix or dispersed on silica surfaces have signals at 200–250 nm [12,17].

Our DR UV-vis spectroscopic results for Zr ions dispersed within silica (Zr[CP]) agree with the data published by Moon *et al.* [8], who produced a series of spectra for decreasing Zr content in a mixed zirconium–silicon oxide. The trend seen from these published spectra was towards an absorption peak situated below 200 nm for low Zr contents (lowest content used was 3.9 wt% Zr). As in our sample the Zr content is much lower (1.1 wt%), the electronic transitions of the Zr ions should occur at wavelengths lower than 200 nm (which is a region not observable with our instruments).

An electronic transition at very low wavelengths can be also predicted for Hf[CP] mesoporous material, as an electronic transition for bulk HfO_2 was found at 220 nm [9].

In conclusion, we suggest that DR UV-vis cannot be used to distinguish whether small clusters of zirconium and hafnium oxides rather than isolated Zr and Hf ions are present on silicas.

3.2.2. Photoluminescence spectroscopy

The UV-vis photoluminescence spectra for Zr[CP] and Hf[CP] excited at 250 nm were very different from those obtained for the Ti-doped mesoporous material (figure 2(A)). For Ti[CP] the photoemission spectrum was characterized by two main emission maxima at $\sim$435 and 480 nm [1]. The intensity of the photoemission was a great deal lower for Zr[CP] and Hf[CP] than for the Ti[CP], and in both cases contained a main peak at 610 nm. This maximum at 610 nm was more intense for Hf[CP] than for Zr[CP], but appeared to stem from a similar electronic transition. For all three Ti[CP], Zr[CP] and Hf[CP] materials the 610 nm emission band was also obtained by exciting at 380 nm (see figure 2(B)). In these emission spectra, other bands heavily overlapping the main maxima were present in the 400–500 nm range, but these were also present in the spectra for the blank and for the empty quartz cell (maxima at around 420 nm).

The results suggest that the emission at 610 nm was linked to the presence of cyclopentadienyl ligand degradation products from the original Ti, Zr and Hf organometallic complexes.

The effect of O_2 adsorption on the Zr[CP] and Hf[CP] samples was to extinguish the photoemission signal at 610 nm entirely (spectra not shown). The signal at 420 nm was not affected by addition of O_2 suggesting that the lower signal was due to impurities in the quartz cell. This assignment was confirmed by the fact that on cooling Zr[CP] and Hf[CP] to 77 K the photoemission bands at 610 nm were intensified further with respect to the peak at 420 nm. Overall, the oxygen adsorption measurements showed that the species emitting at 610 nm were completely accessible to external gas molecules. It can therefore be assumed that

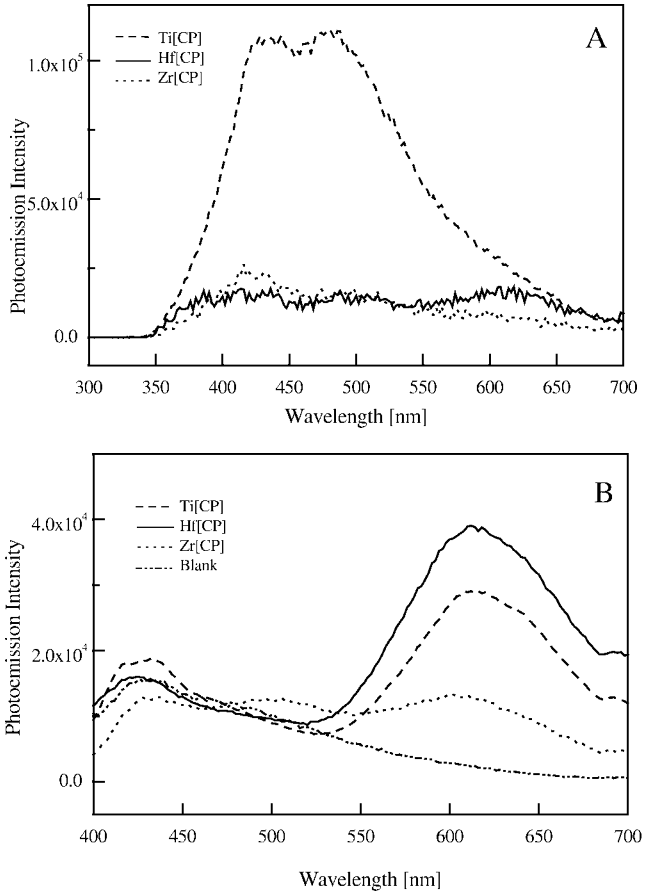

Figure 2. Photoluminescence spectra taken at 298 K, using exciting wavelength of 250 nm (A) and 380 nm (B) for the blank, Ti[CP], Hf[CP] and Zr[CP] samples.

the species were located within the mesopores of the silica, and as previously suggested consisted of organic degradation products rather than transition metal species. Nevertheless, it is puzzling that such organic products cannot be burned off even after a prolonged oxidation at 550 °C (30 h).

We conclude from our UV-vis spectroscopic study of Zr[CP] and Hf[CP] that the transition metal species were optically inactive in the UV spectral region examined, and that no information on the metal active centers could be derived from the spectra.

3.2.3. Fourier transform infrared spectroscopy

A comparative FT-IR study of calcined Ti[CP], Zr[CP] and Hf[CP] materials is now presented. The full interpretation of the FT-IR spectra obtained for Ti[CP] and the blank was given in part 1 of this work [1], and many parallels can be made with the spectra obtained for Zr[CP] and Hf[CP].

All samples were re-oxidised for 3 h and excluded from air prior to the FT-IR measurements. The sharp absorption band at 3740–3745 cm^{-1} due to the O–H stretching vibration of free hydroxyl groups (figure 3) was considerably more intense for the blank sample than for the Ti-, Zr- and Hf-incorporated samples suggesting that a proportion of the surface silanol groups were utilised for bonds to the transition metal sites. The O–H stretching band was also considerably broadened for the metal-incorporated samples, and slightly displaced, with respect to the blank showing that several different O–H groups were present in addition to free Si–OH groups. The diverse chemical nature of the silanols leading to band broadening for the Ti, Zr and Hf samples may have been due to additional H-bonding between hydroxide groups, or to interactions with neighbouring transition metal Lewis centres, increasing the hydroxide group acidity.

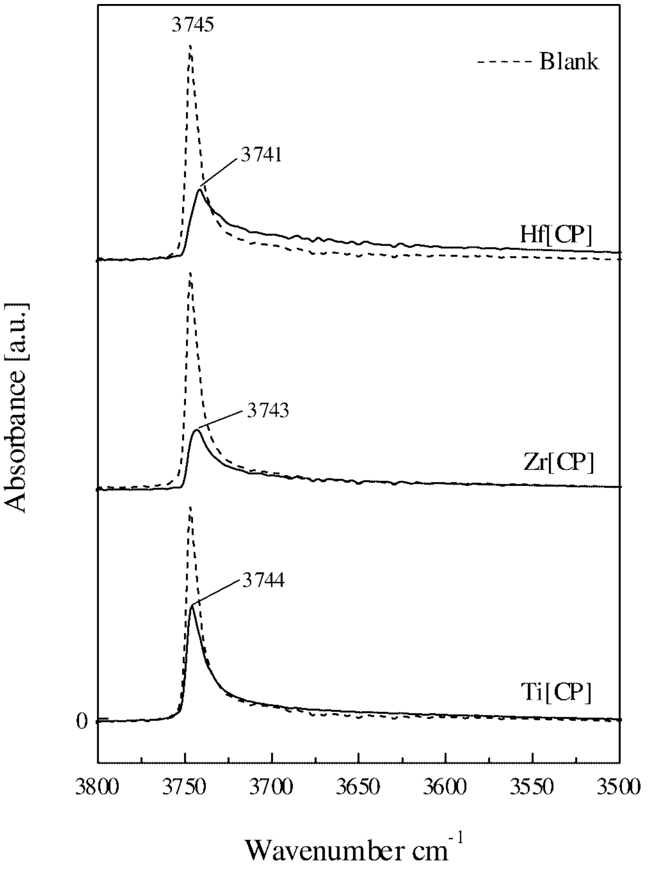

Figure 3. FTIR spectra of Ti[CP], Zr[CP] and Hf[CP] oxidised in 100 Torr O_2 at 550 °C and outgassed at the same temperature. The spectrum (- - -) of the siliceous parent (blank) is also reported for comparison.

Figures 4 and 5 show the effect of ammonia adsorption of the FT-IR spectra of Zr[CP] and Hf[CP], respectively. In both cases, the adsorption of ammonia was not completely reversible. For Zr[CP] (figure 4), after evacuation for 1 h at room temperature, weak bands were still visible at 3394, 3296 and 1608 cm^{-1} due, respectively, to the asymmetric stretching, the symmetric stretching and the bending deformation of NH_3 adsorbed onto Zr Lewis sites. For Hf[CP] (also evacuated for 1 h, figure 5) the analogous absorption bands were located at 3397, 3291 and 1609 cm^{-1}. For both Zr[CP] and Hf[CP], the absorption bands were shifted to lower frequencies with respect to ammonia adsorbed on pure silanol groups (see part 1 for spectra showing adsorption of ammonia on the blank, which was almost completely reversible) [1].

An absorption band was also present at 1466 cm^{-1} which remained after evacuation and is assigned to the bending de-

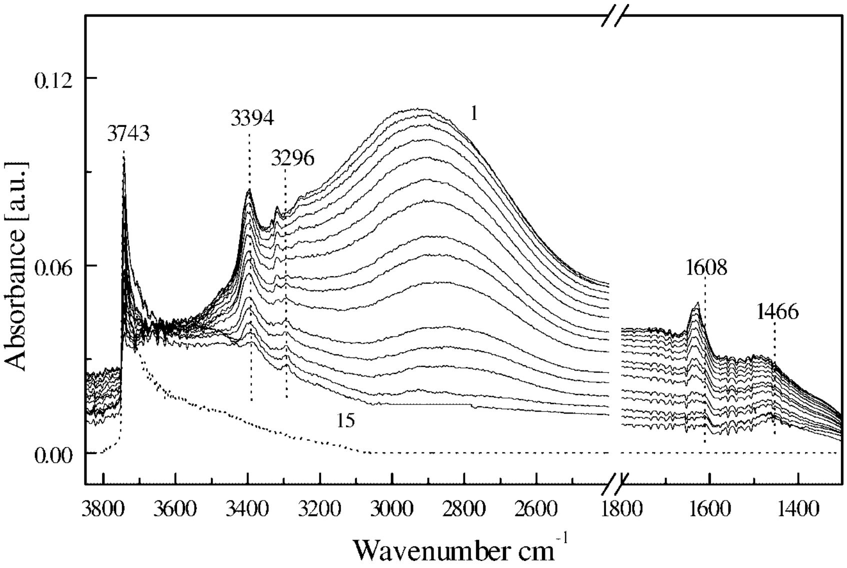

Figure 4. FTIR spectra for Zr[CP] *in vacuo* (- - -), and upon NH_3 adsorption (—). Curve (1) corresponds to the adsorption of 30 Torr NH_3, whilst curves (2)–(14) correspond to decreasing doses of NH_3. Spectrum (15) was obtained by evacuating the sample at room temperature for 30 min.

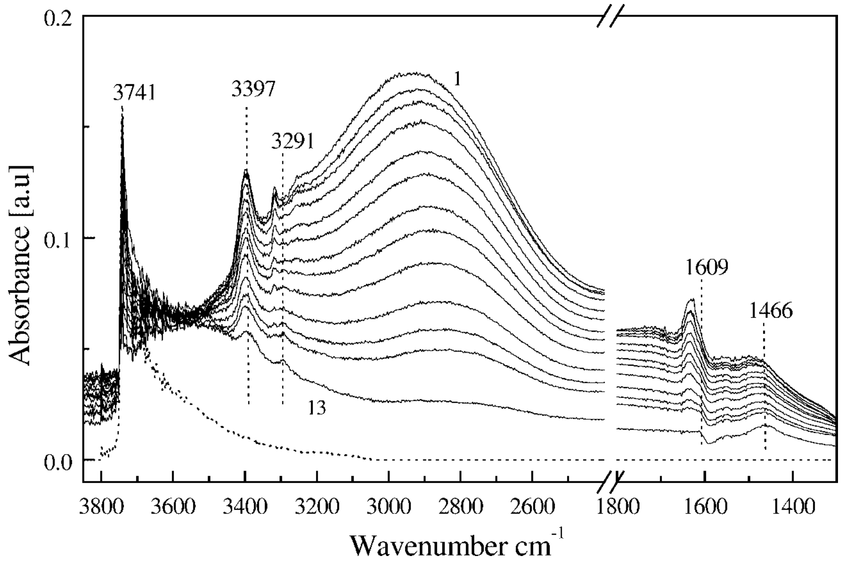

Figure 5. FTIR spectra for Hf[CP] *in vacuo* (- - -), and upon NH_3 adsorption (—). Curve (1) corresponds to the adsorption of 30 Torr NH_3, whilst curves (2)–(12) correspond to decreasing doses of NH_3. Spectrum (13) was obtained by evacuating the sample at room temperature for 30 min.

formation of NH_4^+ cations formed by protonation of ammonia by acidic surface –OH groups. Additionally, after evacuation of the Zr[CP] and Hf[CP] samples, the silanol absorption band (3740–3745 cm^{-1}) was broadened, and had a clear shoulder at lower frequencies indicating the irreversible formation of H-bonds resulting from the adsorption of ammonia molecules. Another interesting point is that the main absorption band produced on adsorbing ammonia, located at approximately 3000 cm^{-1}, was asymmetric and shifted depending on the amount of ammonia adsorbed. This was a characteristic observed for all three group IV transition-metal-incorporated materials, and was less pronounced for the blank, again indicating the presence of different surface hydroxide species in the Ti[CP], Zr[CP] and Hf[CP] materials.

Figure 6 shows the FTIR spectra resulting from the adsorption of 3 mbar NH_3 on the blank, Ti[CP], Zr[CP] and Hf[CP], in the region of the ammonia antisymmetric bending mode (in the case of OH bonded to silanols this mode is at 1637 cm^{-1}). Lower frequency shoulders are clearly visible for the materials containing Ti, Zr and Hf which are assigned to the bending mode of ammonia molecules adsorbed on the transition metal sites. These shoulders are located at 1606, 1608 and 1610 cm^{-1} for Ti[CP], Zr[CP] and Hf[CP], respectively.

The additional presence of a weak and broad band at 1466 cm^{-1} due to the bending mode of NH_4^+ ions suggests that some surface hydroxide species in the metal-incorporated materials were sufficiently acidic to protonate ammonia. Such acidic hydroxide groups did not appear to be

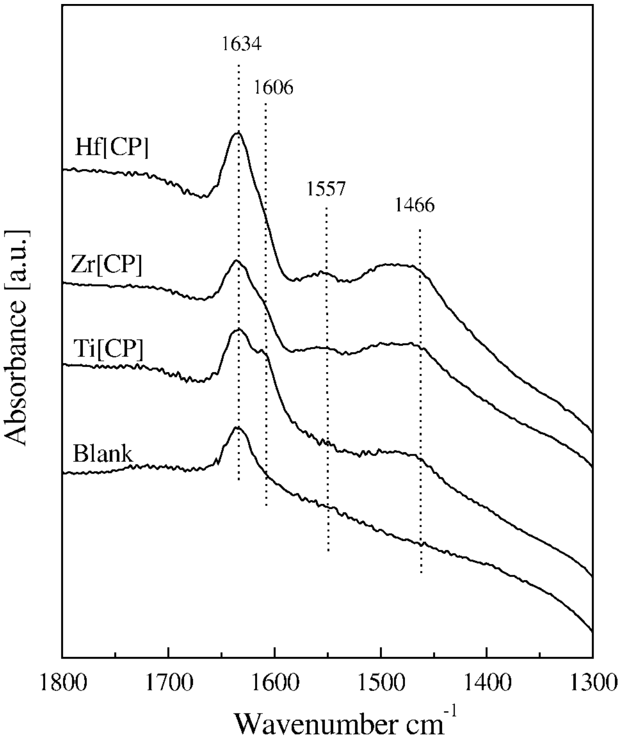

Figure 6. FTIR spectra for Zr[CP], Hf[CP], Ti[CP] and blank samples after NH_3 adsorption (3 mbar).

present in the purely siliceous solid (the precise nature of the groups is still under investigation). Interestingly, the intensity of the NH_4^+ ion bending mode was greatest for Hf[CP] and this may be correlated with the greater broadening and low frequency shift of the OH stretching absorption band (at 3741 cm^{-1}, see figure 3) with respect to the other materials. We can therefore hypothesize that the surface hydroxide species in Hf[CP] are more acidic than in the other materials, favouring the formation of a larger number of protonated ammonium species.

After outgassing NH_3 at 298 K, bands at *ca.* 3500 and 1557 cm^{-1} (see figures 4 and 5) are observed on Ti[CP], Zr[CP] and Hf[CP] materials. These bands are attributed to the irreversible reaction of NH_3 with distorted surface siloxane bridges (Si–O–Si) that produces Si–OH and Si–NH_2 groups [13,18]. The bands at 3500 and 1557 cm^{-1} are associated with the newly formed OH (stretching) and NH_2 (bending) groups, respectively.

4. Conclusion

UV-vis and FT-IR spectroscopic analyses of TLCT mesoporous silica doped with Ti, Zr and Hf have provided some interesting data shedding light on the nature of the surface species, and on their accessibility for probe molecules.

FTIR spectroscopy revealed that: (a) silanol groups are the locus where the metallocenes are anchored (the stretching mode of Si–OH groups at 3745 cm^{-1} is less intense for the metal-containing samples with respect to that of a purely siliceous (blank) sample); (b) only in metal-containing materials (Ti[CP], Zr[CP] and Hf[CP]), are Lewis acid centres present; (c) adsorption of ammonia onto the transition-metal-incorporated materials was partially irreversible, and the formation of ammonium cations demonstrated the presence of acidic surface hydroxide species.

DR UV-vis and photoluminescence spectroscopy yielded direct information on the metal ion dispersion only in the case of Ti[CP], where the presence of isolated tetrahedral Ti(IV) ions was revealed by an absorption band at 220 nm and emission bands at 435 and 480 nm. We did not detect any DR UV-vis and photoluminescence signals due to metal ions in Zr[CP] and Hf[CP] materials.

However, photoluminescence spectroscopy was proven to be a useful tool for monitoring traces of cyclopentadyl ligand decomposition products which are frequently present in our samples and which might have some influence on their catalytic performance.

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