# Isomorphic Substitution and Postsynthesis Incorporation of Zirconium into MCM-48 Mesoporous Silica

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We describe the introduction of zirconium metal centers into the cubic phase of mesoporous silica. Two methods of zirconium incorporation were compared consisting of hydrothermal Si/Zr coprecipitation and postsynthesis functionalization of surface silanols with zirconium propoxide. Nitrogen sorption and X-ray powder diffraction confirmed that both the structure, high surface area, and narrow pore size distribution were maintained. FTIR, UV/Vis, and EXAFS were then employed to characterize the local metal atom bonding and coordination environment. Grafting with zirconium propoxide was found to produce the most isolated metal species.

### Introduction

Zirconium has been used in catalysis due to both its moderate acidity and oxidizing capabilities.1 As with most pure or supported metal oxides, these materials are limited by their low surface area and absence of size-selectivity. Microporous zirconium silicates such as Zr-ZSM5<sup>2</sup> on the other hand are accessible to molecules with a kinetic diameter less than the pore aperture (5.5 Å for silicalite<sup>3</sup>). To extend the catalytic potential to larger organic substrates used in fine chemistry we have used the cubic phase of mesoporous silica<sup>4</sup> (MCM-48) as a host for zirconium. With its branching, 3-dimensional pore array, MCM-48 possesses a high surface area  $(1000-1400 \text{ m}^2/$ g) and pore volume, plus a uniform distribution of pore diameters in the 20-30 Å range. Since the silica wall material is amorphous, we have found that it is possible to isomorphically incorporate large transition-metal atoms during syntheses. Recently, zirconium was doped into MCM-41 and found to be active toward the dehydration of isopropyl alcohol.<sup>5</sup>

The second method of zirconium incorporation involves covalently bonding the metal directly to the surface by reacting a metal alkoxide with the surface silanol groups that result after calcination to remove the surfactant template. This technique generates isolated and accessible Zr metal centers on the silica surface and maintains the high surface area with minor constriction of the pores. X-ray powder diffraction and nitrogen adsorption were used to determine the extent of structural retention following incorporation of Zr into the silica matrix when compared to the pure silica isomorph. The nature of the structure and bonding of the local Zr environment was determined by UV/Visible, photoacoustic (PAS)-FTIR, and EXAFS techniques to compare the two synthetic pathways.

### **Experimental Section**

Reagent grade tetraethyl orthosilicate (TEOS) was provided by Fisher, cetylbenzyl dimethylammonium chloride CBDAC was obtained from Kodak, and zirconium(IV) propoxide (70% in 1-propanol) was purchased from Aldrich. All chemicals were used as received.

For a pure silica, cubic mesopore (denoted MCM-48 or blank), 7.88 g (19 mmol) of CBDAC was dissolved in 171 g (9.5 mol) deionized water with heating. The surfactant CBDAC was chosen because it was found to favor the MCM-48 mesophase. The pH was raised to  $\sim$ 13 with 10 g (20 mmol) of 2M TMAOH followed by 10.42 g (50 mmol) TEOS. This solution was rapidly stirred for 2 h and then transferred to a 500 mL Teflon bottle and placed in a 100 °C oven for 15 days. The product was filtered then returned to the 100 °C oven for an additional 8 days to give a more crystalline product by X-ray powder diffraction. This procedure was repeated with the addition of zirconium propoxide approximately 2 min after adding the TEOS to obtain Zr-MCM-48. Since Zr(OPr)<sub>4</sub> hydrolyzes much more rapidly than TEOS, the timing is crucial to ensure simultaneous coprecipitation. Both final products were filtered, washed with water followed by methanol, and calcined at 550 °C for 6 h in N<sub>2</sub> then air to remove the surfactant. The vield was approximately 80% based on TEOS (Si).

Grafted zirconium samples were made by first dehydrating a calcined sample of pure silica MCM-48 at 200 °C under a rough vacuum overnight. The sample was then mixed with a

 TABLE 1: Nitrogen Sorption Pore Diameter, Surface Area

 Analysis, and Elemental Analysis Results

sample	surface area (m²/g)	pore diameter (Å)	unit cell parameter ( <i>a</i> )	Zr/Si atomic ratio
MCM-48	1283	25.8	86.2	0
XS-Zr	1045	24.3	84.3	1/8.4
Zr-MCM-48	1175	26.4	86.2	1/16



**Figure 1.** X-ray powder diffraction patterns of (A) pure silica MCM-48, (B) 11.9 at. % Zr grafted, XS–Zr, and (C) hydrothermally prepared Zr–MCM-48.

 $Zr(OPr)_4$ /hexane solution corresponding to a stoichiometric excess (XS–Zr) based on an approximate surface silanol density<sup>6</sup> of 1.4 OH/nm<sup>2</sup> in an argon-purged glovebag and reacted according to the following equation:

## $(\equiv SiOH)_x + Zr(OPr)_4 \rightarrow (\equiv Si-O-)_xZr(OPr)_{4-x} + xHOPr$

The zirconium alkoxide route was chosen because it was found to give better dispersion than a zirconyl nitrate (aqueous), incipient wetness approach which can lead to  $ZrO_2$  clustering.<sup>7</sup> After reacting for 2 h, the product was filtered and washed with hexane to remove unreacted precursor and then calcined at 400 °C under O<sub>2</sub> for 4 h to convert  $-Zr(OPr)_n$  groups to  $-Zr(OH)_n$ groups. Samples prepared by both methods were found to resist degradation in water after being annealed at 800 °C for 20 h. This heat treatment lead to an average 15% shrinkage of pore diameter from additional silicate condensation and a reduction in XRD peak resolution.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN and are listed in Table 1.

X-ray powder diffraction patterns (Figure 1) were obtained on a Scintag PADX diffractometer using Cu K $\alpha$  radiation with a liquid nitrogen cooled solid state detector at 45 kV and 40 mA. Nitrogen absorption/desorption isotherms were measured on a Micromeritics ASAP 2000 apparatus. All samples were outgassed initially at room-temperature, then at 200 °C until a pressure <1  $\mu$ m Torr was achieved. Surface areas were calculated by the BET (Brunauer–Emmet–Teller) method<sup>8</sup> for each material. Pore diameter distribution curves were calculated by the BJH (Barrett–Joyner–Halenda) method using the Halsey equation for multilayer thickness and came from the analysis of the adsorption branch of the isotherm (Table 1).

The UV/Visible spectra were measured with a Cary 5 UV/ Vis-NIR spectrophotometer equipped with the Varian diffuse reflectance accessory. The halon/quartz cover slide that covers the sample was subtracted out of every scan. The Teflon integrating sphere that was used has a very low absorbance in the range of our scans, and hence has negligible influence on our results. The standard Kubelka Munk function<sup>9</sup> was used to analyze the data.

The mid-infrared spectra presented in Figure 3 have been collected on the Nicolet Magna 850 FT/IR spectrometer by the coaddition of 150 scans at a 4 cm<sup>-1</sup> resolution, using an MTEC photoacoustic (PAS–FTIR) detector and ultrapure He as a gas vector. The photoacoustic detector allows pure sample to be run, avoiding KBr dilution errors and structural changes during pellet making. Subtraction spectra were made from spectra with normalized intensities, with the blank being subtracted from the zirconium-containing sample.

The X-ray absorption spectra were recorded at the storage ring DORIS III (HASYLAB at DESY, Hamburg, Germany) on the RÖMOII beam line which was equipped with a Si(311) double-crystal monochromator. To reduce contributions from higher harmonics, the second monochromator crystal was detuned to 50% of the maximum intensity. The slit before the monochromator as well as that in front of the first ion chamber was set to 1 mm height. The spectra were calibrated against the first inflection point of the Mo K edge (20000 eV) of a Mo metal foil which was measured simultaneously. All spectra were recorded at room temperature using a continuous scan technique (QEXAFS).<sup>10</sup> The counting time per data point was 0.4 s, and the distance between data points was 2 eV. All samples were prepared as pressed polyethylene pellets in which the Zr content



Figure 2. Pore diameter distribution curves and nitrogen sorption isotherms for (a) pure silica MCM-48, (b) Zr-MCM-48, and (c) XS-Zr grafted.



**Figure 3.** UV–Visible spectra for (a) Zr–MCM-48, (b) ZrO<sub>2</sub> reference, and (c) XS–Zr grafted.

was adjusted to yield an absorption jump  $\Delta$  of about 0.4–0.7 at the Zr K edge. For further data analyses, the program WinXas<sup>11</sup> was used. Theoretical calculations of the phase shifts and backscattering amplitudes were calculated using FEFF 6.01.<sup>12</sup>

#### **Results and Discussion**

X-ray powder diffraction patterns for pure silica MCM-48 support and Zr-containing samples after template removal are shown in Figure 1. Each plot exhibits the characteristic pattern of the MCM-48 cubic phase which can be indexed to the Ia3d space group.<sup>13</sup> Many of the higher angle peaks are visible indicating a high degree of order in the arrangement of the pore network. Zr–MCM-48 shows a nearly identical powder pattern and unit cell (*a*) parameter (Table 1) compared with the pure silica blank indicating the disordered wall material can easily accommodate the larger Zr<sup>4+</sup> ion.

Grafting Zr causes a noticeable decrease in XRD intensity coupled with a 2.2% shrinkage of the unit cell (*a*) parameter for the XS–Zr sample. This is partially due to the equalization of X-ray scattering density within the pores and the walls. When the blank is subjected to the same heating conditions used in grafting, its (*a*) parameter decreases by about 1% due to additional condensation of surface silanols. The difference of 1.2% could be attributed to the formation of multiple Si–O– Zr bonds, which effectively "reign in" the amorphous and flexible walls and has been observed for vanadium grafted on MCM-48.<sup>23</sup> In the Zr-containing samples, no peaks due to crystalline ZrO<sub>2</sub> clusters (>50 nm) were observed at higher angles.

Nitrogen adsorption data are listed in Table 1. All samples possess a narrow pore size distribution and lack any noticeable hysteresis in the type IV isotherms inferring capillary condensation within uniform, cylindrical channels throughout the solids. Zr–MCM-48 has a smaller surface area and pore volume but a slightly larger pore diameter than the blank (Figure 2a,b). Grafting zirconium on a portion of the blank causes an expected decrease in all three properties measured. It should be noted that in the XS–Zr sample, the pore distribution is still narrow, indicating an even dispersion of Zr metal centers on the pore surface and the avoidance of ZrO<sub>2</sub> clusters (Figure 2c). Fullwidth half-maximum values for pore size are 5, 5.4, and 5 Å for the blank, Zr–MCM-48 and XS–Zr, respectively. Zirconia



**Figure 4.** Normalized photoacoustic FTIR spectra of (A) XS–Zr grafted on (B) pure silica MCM-48 support with (c) spectral subtraction result.

deposition by reaction with zirconium propoxide was uniform since zirconia clusters deposited predominantly at the pore openings would have constricted the pores, leading to a H2 type hysteresis loop.<sup>14</sup>

UV/Visible Spectroscopy. After confirming structural retention and bulk characteristics by XRD and N<sub>2</sub> adsorption, we can begin to elucidate the Zr metal center environment by spectroscopic methods. UV/Visible spectroscopy has successfully been used to determine the degree of isolation of Zr ions incorporated into two different silica matrixes. Zirconiumcontaining mesoporous silica, Zr-MS was found to have an absorption at 205-215 nm.<sup>15</sup> In Zr-ZSM5 an absorption is seen at 212 nm.16 Both absorptions are attributed to ligand-to-metal charge transfer from an  $O^{2-}$  to an isolated  $Zr^{4+}$  ion in a tetrahedral configuration. In ZrO<sub>2</sub> where there is full connectivity of Zr-O-Zr linkages, the LMCT shifts to lower energy of about 230 nm. Similarly, Zr-MCM-48 was found to have an absorption at about 207 nm indicating isolated Zr<sup>4+</sup> ions in the amorphous silica walls (Figure 3) accompanied by a small shoulder at 250 nm indicating nanoscopic regions of Zr-O-Zr linkages. In the case of grafting, a sample with about 5 atomic % Zr shows an absorbance band centered at about 200 nm. At maximum loading by grafting (XS-Zr; 11.9 at. %), the peak shifts to 207 nm with a gradual shoulder, implying a possible formation of Zr–O–Zr bonds on the surface.

FTIR with Photoacoustic Detection (PAS–FTIR). Further information concerning bonding and local environments of Zr metal centers was obtained by FTIR–PAS. In (Figure 4b), the spectra of the pure silica MCM-48 blank is shown. In the higherfrequency vibration region, isolated and hydrogen-bonded silanols are clearly present at 3745 and 3550 cm<sup>-1</sup>, respectively.<sup>17</sup> In the silica framework region (1300–800 cm<sup>-1</sup>) asymmetric ( $\nu_{as}$  1243, 1083 cm<sup>-1</sup>) and symmetric ( $\nu_{s}$  817 cm<sup>-1</sup>) stretches of the Si–O–Si bond are seen.<sup>18</sup> At 978 cm<sup>-1</sup>, a sharp peak is seen which is attributed to the Si–O stretch of silanol defects.<sup>19</sup>

Upon grafting of Zr onto the silica mesopore structure (Figure 4a), each of the above features undergoes profound changes that are seen clearly in the spectra subtraction results, in which the vibrations from the blank used for the support are removed. Both vibrations due to silanols at 3745 and 978 cm<sup>-1</sup> are reduced in intensity confirming the role of the surface silanols as reactive sites being consumed by the Zr(OPr)<sub>4</sub> precursor. Some isolated surface silanols remain most likely due to steric inaccessibility. More important is the formation of a new band at 942 cm<sup>-1</sup>

TABLE 2: Fitting Results of Zr, EXAFS for Zr-Containing Samples, and Reference Compound

	Zr-O			Zr-O			Zr–Zr		
	C.N.	R (Å)	$\Delta\sigma^2(A_2)$	C.N.	<i>R</i> (Å)	$\Delta\sigma^2(A_2)$	C.N.	R (Å)	$\Delta \sigma^2(A_2)$
Zr-MCM-48	4.14	2.07	0.0023	3.18	2.23	0.0023	1.29	3.41	0.0035
5% Zr	3.83	2.05	0.0017	3.08	2.22	0.0017	0.54	3.38	0.0035
XS-Zr	4.16	2.05	0.0026	3.02	2.23	0.0026	0.86	3.38	0.0035
	Zr-O			Zr-Zr			Zr-Zr		
	C.N.	R (Å)	$\Delta\sigma^2(A_2)$	C.N.	R (Å)	$\Delta \sigma^2(A_2)$	C.N.	<i>R</i> (Å)	$\Delta\sigma^2(A_2)$
<i>m</i> -ZrO <sub>2</sub>	7.02	2.13	0.0056	7.01	3.45	0.0046	3.98	3.98	0.0060



**Figure 5.** Normalized photoacoustic FTIR spectra of (A) Zr–MCM-48, (B) pure silica MCM-48, and (C) spectral subtraction result.

which is absent from the pure silica blank. The frequency of this new band is consistent with that seen for Zr grafted to amorphous silica at 945 cm<sup>-1</sup> and is attributed to the formation of a Si-O-Zr bond.<sup>20</sup> Two additional peaks are seen in the subtraction spectra at 680 and 515 cm<sup>-1</sup>. These absorbances are shifted upward in frequency from those reported in thin films from a Zr(OPr)<sub>4</sub> and acetic acid mixture<sup>21</sup> and can be tentatively assigned to Zr-O and Zr-O-Zr vibrations occurring at 650 and 475 cm<sup>-1</sup>, respectively. In the subtraction spectra result for Zr-MCM-48, the 940 cm<sup>-1</sup> is also observed (Figure 5a) and is interpreted as the vibration of a Zr<sup>4+</sup> ion surrounded by four silica groups within the walls, or near the surface of a pore.

EXAFS. X-ray absorption spectra were recorded from all three mesoporous compounds as well as for the monoclinic ZrO<sub>2</sub> which was used as reference compound.<sup>22</sup> The Fourier transforms (FTs) of the EXAFS spectra show the Zr-O and the Zr-Zr coordination sphere for all compounds (Figure 6). The Zr-Zr coordination sphere is strongly reduced in intensity for the MCM-48 type of material compared to the crystalline reference compound. In the case of the mesoporous compounds, best fits could be obtained by using two shells for the Zr-O coordination sphere (Table 2). Within experimental error, all three compounds show four oxygen atoms at a short distance and three at a larger distance. The three oxygen atoms which compose the longer Zr-O bonds probably serve as strained linkages to the silicate network, whereas the four more tightly bonded oxygen atoms are probably from water molecules or OH groups completing the coordination sphere. The larger bond distance for the first Zr-O shell in case of Zr-MCM-48 can be explained by the partial embedding of the Zr-O units within the network structure which introduces some strain and hinders a full relaxation of the coordination sphere leading to a closer structural arrangement and shorter distances, respectively. The second Zr-O bond length is similar for all three compounds, indicating the same type of oxygen atom coordination. Due to



**Figure 6.** Fourier transforms (FT  $(\chi(k)*k^3)$  of the Zr K-EXAFS of *m*-ZrO<sub>2</sub> and the pure silica and Zr-modified mesoporous compounds.

the larger first Zr-O shell in case of Zr-MCM-48 the difference between both Zr-O shells is smaller which leads to a Zr-Ocoordination sphere which cannot be resolved by EXAFS.

The second peak in the FT at 340 pm represents the Zr-Zr coordination sphere which can be seen for all compounds, but is much less pronounced for the mesoporous materials in which the Zr species are dispersed and immobilized by grafting onto the silica surface. Zr-MCM-48 shows a greater than two times larger coordination number of Zr atoms which is a strong indication for more Zr-O-Zr bonds in this type of material and for the existence of Zr-O-Zr units within the network structure. In addition, the bond length is also larger than in the "grafting"-type of materials which is due to the same structural strains we previously discussed in connection with the Zr-O coordination sphere. An increase of the Zr content in case of the latter compounds leads also to a larger coordination number, but without changing the bond length. Attempts to fit the Zr-Zr coordination sphere with a Zr-Zr and a Zr-Si shell did not lead to reasonable results. This coordination sphere is mainly dominated by Zr-Zr interactions but additional contributions from further Zr-Si shells cannot be fully quantified. Summarizing, one can say that a better dispersion of the Zr with a lower degree of Zr-Zr interactions can be obtained by using the "grafting" method.

#### Conclusions

Zirconium has been successfully incorporated into the silica MCM-48 system by two synthetic methods. Complimentary analytical techniques have shown a relatively homogeneous dispersion of zirconium centers in the walls of the Zr-MCM-48 material and on the surface of the grafted samples. The zirconium environment in each of these products is predominantly tetrahedral. Some regions of Zr-O-Zr bonding are suspected but occur around the detection limit for each analytical technique so their nature and domain size cannot be fully ascertained. These new materials feature high surface areas and an ordered pore array with a uniform pore diameter, which are accessible to molecules with kinetic diameters over 20 Å. For catalytic applications, the grafted materials are proposed to be superior to Zr-MCM-48 since the Zr concentration is controllable over a wider range and each Zr center is located on the surface. We previously reported the grafting of vanadium and titanium in the same manner and Ti/MCM-48 was found to be catalytically active as a biomimic for haloperoxidase enzymes.<sup>23,24</sup> The catalytic activity of zirconium-grafted and hydrothermally made Zr-MCM-48 toward the bromination of large organic dye molecules such as phenol red with hydrogen peroxide will be compared with tungsten and molybdenum in a subsequent paper.

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