Structure of Zirconium-Exchanged H-ZSM5 Prepared by Vapor Exchange of ZrCl4

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Received February 24, 2006. Revised Manuscript Received January 21, 2007

Zr dimers (Zr2O22+) interacting with two exchange sites and uniform in structure were prepared by grafting anhydrous ZrCl4(g) onto H-ZSM5 followed by hydrolysis and dehydration. This method led to selective exchange, without concurrent formation of crystalline ZrO2 aggregates, ubiquitously formed via aqueous exchange because of the slow diffusion of aquo oxo-ions within small channels. ZrCl4(g) reacts with acidic OH groups to form HCl and ZrCl42+−ZSM5 species. This exchange stoichiometry was confirmed by the number of HCl molecules evolved during hydrolysis, a process that forms ZrO(OH)3 species. These species then dehydroxylate via condensation with vicinal ZrO(OH)2 to form (O=Zr−O−Zr=O)2+ species interacting with two exchange sites and containing one bridging O-atom. This exchange process is consistent with the number of residual OH groups titrated by D2 and with the intensity of O−H infrared bands. X-ray diffraction, 27Al nuclear magnetic resonance, and infrared spectra showed that the exchange process did not influence zeolite crystallinity, led to Zr4+ introduction into the zeolite framework, or form residual Zr(OH)4 species at exchange sites. Weak Raman bands in the 960−1030 cm−1 region, absent in crystalline ZrO2 and H-ZSM5, were detected upon exchange. The maximum attainable Zr2+Al exchange ratios (0.6 ± 0.05) are consistent with Al radial structure distributions and with expected Al−Al distances required to anchor (O=Zr−O−Zr=O)2+ species in ZSM-5 with a statistical distribution of Al atoms. ZrCl4 species in excess of this saturation stoichiometry formed monoclinic ZrO2, detectable in Raman spectra and X-ray diffraction patterns.

1. Introduction

Cations exchanged onto microporous solids have been widely studied1−7 because they can introduce sites active in redox cycles and C−H bond activation.6,8−10 Aqueous media are effective for the exchange of monovalent and divalent cations into 8-ring and 10-ring zeolites.7,11−13 High-valent cations (Mn+, n = 2) form highly charged solvated oligomers in aqueous media and these species diffuse slowly into zeolite channels containing the exchange sites.14 Alternate strategies have exploited volatile oxides (MoO3),15 halides16 (FeCl3, WCl6),9,17 or carbonyls (Mo(CO)6),18 which form small neutral precursors in the gas phase.

Zirconium silicates (Zr,Si1−x O2) have been reported to form for several zeolite structures prepared by hydrothermal methods together with Zr4+ cations at framework positions (from infrared Zr−O−Si stretches at 940−960 cm−1; assigned by analogy with TS-1)19−22 and expanded unit cells (from X-ray diffraction).19−21 Postsynthesis exchange of Zr4+ oxo cations onto medium-pore Al-containing zeolites, however, has not been conclusively demonstrated. Exchange of [Al]−ZSM-5 with aqueous ZrOCl2 introduced only trace levels of Zr (Zr/Al < 0.06), indicating that Zr4+-oxo species in aqueous media did not diffuse into 10-ring zeolite channels.13 Isolated Zr-oxo species at exchange sites are likely to show adsorption and catalytic functions different from crystalline ZrO2 or Zr,Si1−x O2. ZrO2 species grafted onto SiO2 have been reported as active photocatalysts for CH4 coupling23 and ZrO2 species prepared by impregnation

of ZrOCl₂ onto ZSM-5 catalyzed m-xylene ammoxidation.12

Here, we describe nonaqueous exchange protocols and robust structural assessment strategies to form and characterize Zr⁴⁺-oxo species for a range of Zr/Al (0–0.5) ratios in H-ZSM5. Chemical and spectroscopic characterization methods showed that Zr⁴⁺-oxo species form (O=Zr–O–Zr=O)²⁺ cations by replacing two H⁺ at vicinal Al sites; the formation of these species resemble those reported earlier for W, Fe, and V species grafted onto H-ZSM5 using metal-chloride or oxychloride exchange precursors.9,17,24–26

2. Experimental Methods

2.1. Synthesis of Zr-ZSM5 Materials. H-ZSM5 was prepared from NH₄-ZSM5 (7–8 g; AlSiPenta, Si/Al = 12.5; <0.03 wt % Na) by treating in flowing dry air (1.67 cm³ s⁻¹ g⁻¹. Airgas, 99.999%) while heating to 623 K at 0.05 K s⁻¹ and holding at 623 K for 3 h to remove adsorbed H₂O. The temperature was then increased to 773 K at 0.017 K s⁻¹ and the sample held at 773 K for 5 h to convert NH₄-ZSM5 into its H-form. The silanol content, reported previously, was represented 8% of all the OH groups in H-ZSM5.

Zr-ZSM5 was prepared from ZrCl₄ and H-ZSM5 using anhydrous exchange methods previously reported for the synthesis of W-oxo species via grafting of WCl⁶(g) onto H-ZSM5.9 The synthesis was carried out in a Schlenk line capable of a dynamic vacuum of 0.13 Pa and equipped with a mechanical pump (Welch 1405) and a liquid N₂ trap. H-ZSM5 (2 g) was treated in vacuum at 573 K for 1 h to remove adsorbed water. Anhydrous ZrCl₄ powder (Aldrich, 99.9%+) was isolated from H-ZSM5 during dehydration by a valve; the ZrCl₄ and H-ZSM5 were combined after H-ZSM5 dehydration and the resulting ZrCl₄/H-ZSM5 physical mixture was sealed within an ampule under vacuum, agitated in a sonicator for 0.1 h to mix the components, and then heated to 650 K at 0.17 K s⁻¹ and held at 650 K for 5 h.

The contents of this ampule (in 0.2–0.5 g batches) were transferred into a quartz cell and heated to 373 K at 0.017 K s⁻¹ in 1 cm³ s⁻¹ He (Praxair, 99.999%). The flow was then switched to a 20% O₂/He stream (1 cm³ s⁻¹; Praxair, 99.999%) contacted with liquid water held in a saturator at 273 K to introduce 0.5 kPa H₂O. The sample temperature was increased to 623 K at 0.17 K s⁻¹ and held at 623 K for 0.5 h. The saturator was then bypassed and the sample treated in dry 20% O₂/He (Praxair, 99.999%) while heating the temperature to 973 K at 0.017 K s⁻¹ and holding at 973 K for 1 h. The residual Cl content in ZrCl₄/H-ZSM5 was measured from the amount of HCl evolved (by mass spectrometry, 36 amu) during contact with the H₂O-containing stream. The mass spectrometer response factor was determined by hydrolysis of anhydrous ZrCl₄ powders with 20% O₂/containing 0.5 kPa H₂O while heating the sample to 973 K at 0.17 K s⁻¹. H₂O (18 amu), H₂ (2 amu), and Cl₂ (70–74 amu) were detected by mass spectrometry (MKS, Minilab) with a time resolution of 2 s.

2.2. Isotopic Titration of Residual OH Groups with D₂. Samples (0.2 g) were treated at 773 K in flowing dry air (1 cm³ s⁻¹; Praxair, 99.999%), cooled rapidly to ambient temperature, and treated in He before contacting them with D₂(5%/Ar) (4.2 cm³ s⁻¹ g⁻¹) as the temperature was increased to 973 K at 0.17 K s⁻¹ and held for 1 h. The number of OH groups was measured from the amounts of HD and H₂ formed and also from the amount of D₂ consumed. The response factors for H₂ and D₂ were determined from mixtures of known composition, while that for HD (3 amu) was obtained equilibrating H₂–D₂ mixtures on a P/ZrO₂ catalyst at 773 K.

2.3. X-ray Diffraction. X-ray diffraction patterns were measured with a Siemens diffractometer (Model D500) and Cu Kα radiation (0.15418 nm wavelength) using powders (0.03 g) ground with KCl (0.03 g) and uniformly spread with Vaseline onto a glass slide. Diffraction data were collected for 2θ angles of 20–35° at 0.02° intervals with a 40 s hold. KCl was used as an internal standard for angles (2θ = 28.341°) and intensities. Lattice parameters were obtained by structural refinement after background subtraction using EXPGUIT28,29 and Al-free ZSM-5 structures (silicalite; monoclinic, P2₁/c, a = 19.879, b = 20.107, c = 13.369, β = 90.67°).

2.4. Infrared and Raman Spectroscopies. Infrared spectra were measured in transmission mode (Mattson RS 10000) using sample wafers (15 mg cm⁻²) treated at 673 K in dry air (0.8 cm³ s⁻¹; Praxair, 99.999%) for 1 h within a cell sealed with CaF₂ windows. Spectra were measured at 673 K with a 2 cm⁻¹ resolution using 1000 scans. Infrared band intensities were divided by the intensity of framework overtone bands (1730–2100 cm⁻¹) for H-ZSM5.

Raman spectra were measured with a HoloLab 5000 Research Raman Spectrometer (Kaiser Optical Systems, Inc.) using a 532 nm laser. Hydrocarbons adsorbed on ZSM-5 from ambient air dehydrogenate during thermal treatment to form unsaturated hydrocarbons, which fluorescing during laser irradiation. These residues were removed before measuring Raman spectra by heating Zr-ZSM5 (after exchange and hydrolysis) to 1023 K at 0.17 K s⁻¹ in dry air (1.7 cm³ s⁻¹; Praxair, 99.999%) and holding at 1023 K for 0.1 h. Zeolites were transferred to the Raman cell after cooling and then heated to 823 K at 0.17 K s⁻¹ in dry air (1 cm³ s⁻¹; Praxair, 99.999%) to remove any H₂O adsorbed during transfer. Spectra were measured at 298 K using 20 scans each acquired for 20 s while rotating samples at 7 Hz to avoid local heating by the incident laser.

2.5. Nuclear Magnetic Resonance Spectroscopy. ²⁷Al nuclear magnetic resonance was measured with magic angle spinning (NMR-MAS) using a Bruker AV-500 (11.7 T) spectrometer. Spectra were recorded at 130.3 MHz with a spinning rate of 14 kHz using a single 9° pulse (1.22 μs), a 1 s recycle delay, 3600 scans, and a sweep width of 500 kHz. Chemical shifts are reported relative to those in a 1 M Al(NO₃)₃ aqueous solution.

2.6. Density Functional Theory. Bond lengths and angles of Si–O–M (M = Si, Al, or Zr) in MFI zeolites were estimated using density functional theory (DFT) with Gaussian 03 to optimize silicate-1 structures. Silicate-1 was represented using the T-12
site in a 5T cluster (a T-site is a tetrahedral site). Terminal T-sites were bonded with hydrogen (–SiH₃) and fixed. A hybrid Becke’s exchange functional, with the Lee, Yang, and Parr correlation functional (B3LYP) was used for electronic structure calculations, and a 6-31G(d) basis set was used to add polarized character to all atoms except hydrogen.

3. Results and Discussion

HCl evolves during hydrolysis of ZrCl₄-ZSM5 as a single peak at all Zr/Alₜ ratios (Alₜ: framework Al) ratios (Figure 1). Samples with Zr/Alₜ ratios of 0.44 and 0.8 formed HCl at higher temperatures than samples with a Zr/Alₜ ratio of 0.22, apparently because some of the evolved HCl re-adsorbs as HCl concentrations increase with increasing Zr content. The amount of HCl evolved was 2.8 ± 0.1 HCl/Zr for all samples, indicating that ZrCl₄/H-ZSM5 mixtures led to ZrCl₄ reactions with H⁺ at 650 K to form HCl and ZrCl₄; these data are consistent with an initial exchange stoichiometry of one Zr per OH group.

X-ray diffraction patterns after removal of chloride from Zr-ZSM5 resembled those for the parent zeolite (Figure 2), indicating that zeolite structures were preserved during contact with ZrCl₄ and subsequent hydrolysis. The unit cell volume (UCV) in aluminosilicates is sensitive to Al framework content, thus, changes in lattice constants can be used to detect Al removal or Zr incorporation during sublimation of ZrCl₄ and subsequent hydrolysis. Lattice cell volumes (Table 1) in H-ZSM5 (6.7 Al/u.c.) were higher than those in silicalite (the pure SiO₂ form of ZSM-5; 5383.5 Å³), and inconsistent with any Al extraction or Zr incorporation during exchange. Thus, our ZrCl₄ grafting protocols place Zr-oxo species onto the exchange site without detectable replacement of framework Al atoms.

The local structure of Al atoms in Zr-ZSM5 and H-ZSM5 was also probed using ²⁷Al NMR-MAS (Figure 3). ²⁷Si NMR did not provide conclusive evidence for Zr framework incorporation because chemical shifts arising from framework Si–O–Al cannot be distinguished from those for Si–O–Zr structures in H-ZSM5. ²⁷Al NMR spectra showed two lines with chemical shifts at 54 and 0 ppm for tetrahedral framework Al and octahedral extraframework Al, respectively. The line at 54 ppm became broader after Zr exchange and acquired a shoulder at lower chemical shifts; both trends continue as Zr/Alₜ ratios increased. The line at 0 ppm also broadened but was similar in intensity for all samples. For samples with Zr/Alₜ < 0.8, ²⁷Al NMR spectra reflect contributions from Al atoms interacting with H⁺ and with exchanged Zr⁴⁺-oxo cations, which lead to nonuniform Al coordinations and broader Al NMR features, a reflection of unresolved multiple lines shifted slightly from those for Al atoms interacting with protons.

Residual OH groups after ZrCl₄(g) contact with H-ZSM5 and subsequent hydrolysis and dehydration were detected from the amount of HD (and H₂) formed by D₂ reactions with OH (Figure 4). The parent H-ZSM5 gave 1.07 ± 0.05 OH/Alₜ, as expected from charge balance requirements (1:1 H:Al) and the presence of trace silanols. The number of residual OH groups decreased linearly with increasing Zr/Alₜ ratio; the corresponding slope gives 1.2 ± 0.1 OH removed per Zr atom for Zr/Alₜ ratios below 0.5, consistent with an exchange stoichiometry near unity (Table 3). This

Figure 1. HCl formation rate during exposure of ZrCl₄-ZSM5 (0 < Zr < 0.8, Si/Alₜ = 13.4) to 1 cm³ s⁻¹ 20 kPa O₂/0.5 kPa H₂O/80 kPa He after exchange of H-ZSM5 with ZrCl₄ at 650 K for 4 h. H-ZSM5 was dehydrated prior to contacting with anhydrous ZrCl₄. Values in parentheses represent the integrated mol of HCl per mol of Zr (HCl/Zr) for different Zr to Alₜ ratios (Zr/Alₜ) in Zr-ZSM5.

M–O (M = framework Si, Al, or Zr) bond lengths. We have confirmed these conclusions using density functional theory calculations of M–O bond lengths in silicalite as various cations are inserted into T-12 sites within a theoretical 5T cluster (Table 2). M–O distances are longer for Zr–O (0.188 nm) than for Al–O (0.172 nm) bonds, consistent with the trend in volume expansions observed in experiments. Distances of Zr–O bonds of 0.194 nm in Zr-silicalite-2, measured using EXAFS, have also been reported by Ramaswamy et al. In view of these estimates, X-ray diffraction with structural refinement was used here to detect any incorporation of Zr into the ZSM-5 framework during exchange.

Dealumination and Zr incorporation into framework positions may occur during contact with ZrCl₄, by analogy with reported zeolite dealumination protocols using SiCl₄. Such processes would increase the unit cell volume, based on the data shown in Table 2. The replacement of 1 Al with Zr in each unit cell (Zr/Alₜ = 0.15) would increase unit cell volumes by 33 Å³. Cell volumes measured from diffractionograms were 5387 ± 4 Å³ for all Zr-ZSM5 in our study; these values are identical, within experimental accuracy, to those for the parent H-ZSM5 (5383.5 Å³), and inconsistent with any Al extraction or Zr incorporation during exchange. Thus, our ZrCl₄ grafting protocols place Zr-oxo species onto the exchange site without detectable replacement of framework Al atoms.

The local structure of Al atoms in Zr-ZSM5 and H-ZSM5 was also probed using ²⁷Al NMR-MAS (Figure 3). ²⁷Si NMR-MAS (Figure 3). ²⁷Si NMR did not provide conclusive evidence for Zr framework incorporation because chemical shifts arising from framework Si–O–Al cannot be distinguished from those for Si–O–Zr structures in H-ZSM5. ²⁷Al NMR spectra showed two lines with chemical shifts at 54 and 0 ppm for tetrahedral framework Al and octahedral extraframework Al, respectively. The line at 54 ppm became broader after Zr exchange and acquired a shoulder at lower chemical shifts; both trends continue as Zr/Alₜ ratios increased. The line at 0 ppm also broadened but was similar in intensity for all samples. For samples with Zr/Alₜ < 0.8, ²⁷Al NMR spectra reflect contributions from Al atoms interacting with H⁺ and with exchanged Zr⁴⁺-oxo cations, which lead to nonuniform Al coordinations and broader Al NMR features, a reflection of unresolved multiple lines shifted slightly from those for Al atoms interacting with protons.

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exchange stoichiometry is lower (0.78 OH/Zr) for the sample with the higher Zr/Al ratio (0.8).

Infrared spectra of OH stretches gave trends similar to D₂-OH exchange experiments with Zr/Al ratio (Figure 5). The intensity of the band at ~3600 cm⁻¹, corresponding to acidic OH groups (the weak band at 3740 cm⁻¹ arises from silanols), decreased with increasing Zr/Al ratios. Figure 6 shows Δ(OH)/Al values from D₂-OH and infrared data as a function of Zr/Al ratio. These two independent sets of data agree within their respective accuracies and give an exchange stoichiometry of 1.2 ± 0.1 Δ(OH)/Zr for Zr/Al ratios lower than 0.5. For the sample with a higher Zr/Al ratio (0.8), the infrared spectra gives a Δ(OH)/Zr ratio of 0.7 ± 0.1, which also resembles the value obtained from isotopic exchange data.

Charge neutrality requires that exchanged Zr⁴⁺-oxo species be present as either ZrO²⁺ monomers (Chart 1, Structure I) or Zr₂O₄²⁻ dimers (Chart 1, Structure II), each interacting with two next-nearest neighbor Al sites. Only dimers are consistent with the exchange stoichiometry measured for Zr/Al ratios below 0.5 (1.2 ± 0.1 Δ(OH)/Zr). Experimental

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Table 1. Unit Cell Parameters for Zr-ZSM5 (0 ≤ Zr ≤ 0.8, Si/Al₁ = 13.4) ¹

<table>
<thead>
<tr>
<th>Zr/Al₁</th>
<th>lattice dimensions (Å)</th>
<th>β (deg)</th>
<th>UCV (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.85(3) 20.18(7) 13.43(2)</td>
<td>90.54(2)</td>
<td>5383.5(5)</td>
</tr>
<tr>
<td>0.22</td>
<td>19.87(1) 20.20(4) 13.43(1)</td>
<td>90.56(2)</td>
<td>5391.0(0)</td>
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<tr>
<td>0.44</td>
<td>19.94(3) 20.20(5) 13.36(4)</td>
<td>90.51(8)</td>
<td>5385.2(2)</td>
</tr>
<tr>
<td>0.8</td>
<td>19.88(7) 20.15(2) 13.43(5)</td>
<td>90.57(9)</td>
<td>5384.4(4)</td>
</tr>
</tbody>
</table>

¹ Crystal parameters were refined from silicalite-1 using KCl as internal standard. Diffraction patterns were fit between 2θ angles of 20° and 35°.

Table 2. Average M—O Distance and Experimental Change in Unit Cell Volume (ΔUCV) per Metal Content for Framework Si, Al, and Zr Atoms in ZSM-5 Structures ²

<table>
<thead>
<tr>
<th>metal</th>
<th>average M—O distance (Å)</th>
<th>ΔUCV/metal (Å³ M⁻¹)</th>
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<tbody>
<tr>
<td>Si</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.72</td>
<td>7</td>
</tr>
<tr>
<td>Zr</td>
<td>1.88</td>
<td>40</td>
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² Average M—O distances were calculated using density functional theory simulations of the T-12 site in a 5T ZSM-5 cluster.

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Figure 2. X-ray diffraction patterns of Zr-ZSM5 (0 ≤ Zr ≤ 0.8, Si/Al₁ = 13.4) between 2θ of (a) 22–25 and (b) 5–50.

Table 3. Change in Hydroxyl Content per Al or Zr Atom in Zr-ZSM5 (0 ≤ Zr ≤ 0.8) (Δ(OH)/Zr) Measured Using D₂-OH Exchange and Infrared Hydroxyl Stretching Bands

<table>
<thead>
<tr>
<th>Zr/Al₁</th>
<th>Δ(OH)/Al ²</th>
<th>Δ(OH)/Zr</th>
<th>Δ(OH)/Al ²</th>
<th>Δ(OH)/Zr</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.20</td>
<td>0</td>
<td>1.7</td>
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<tr>
<td>0.12</td>
<td>0.15</td>
<td>1.27</td>
<td>0.20</td>
<td>1.7</td>
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<tr>
<td>0.44</td>
<td>0.26</td>
<td>1.19</td>
<td>0.53</td>
<td>1.2</td>
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<tr>
<td>0.8</td>
<td>0.61</td>
<td>1.05</td>
<td>0.55</td>
<td>0.7</td>
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</table>

² Amount of OH per framework Al (Al₁) in the sample is calculated by HD formation; estimated uncertainty is 0.05 OH/Al₁. ³ Area of band at 3600 cm⁻¹ for H-ZSM5 normalized; estimated uncertainty is 0.1 OH/Al₁.
As a result, ZrO(OH)\(^+\) are very sensitive to crystalline ZrO\(_2\). We have examined the latter possibility using Raman spectra,

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presence of trace moisture to exchange with another OH or neighboring OH groups to form less stable ZrO\(_2\) monomers both require site pairs with Al–Al distances consistent with the size of Zr-oxo structures; clearly, this requirement cannot be satisfied by all Al sites in ZSM-5. Random and thermodynamic arrangements of Al atoms can be used to estimate radial distribution functions in ZSM-5.\(^{38,39}\) These results, taken together with the expected dimensions of (O–Zr–μO–Zr–O)\(^{2+}\) structures estimated from Zr–O bond lengths (0.20–0.24 nm) measured by neutron diffraction,\(^{40}\) can be used to estimate the number of Al–Al pairs that can interact with Zr-oxo dimers and thus the maximum Zr/Al\(_f\) ratios for which dimers can form. Zr-oxo dimers require Al–Al distances smaller than 0.92 nm; the fraction of Al atoms in Al–Al pairs satisfying this requirement (from calculated radial structure functions\(^{38}\)) for a Si/Al\(_f\) ratio of 12 was 0.34 dimers/Al\(_f\), corresponding to a maximum Zr/Al\(_f\) ratio of 0.68 for the maximum Zr content at which dimers can form as the sole Zr-oxo structure. This estimate is slightly larger than the highest Δ(OH)/Al\(_f\) exchange ratio (0.55–0.61 ± 0.05) measured from D\(_2\)–OH exchange and infrared spectra (Table 3). These slight differences may reflect small differences in Al\(_f\) content between our ZSM-5 (Si/Al\(_f\) = 13.4) and that in the reported simulations (Si/Al\(_f\) = 12).\(^{38}\) We conclude that Zr atoms exceeding those required for a Zr/Al\(_f\) ratio of 0.68 cannot form either structure I or structure II; thus, ZrO(OH)\(^+\) species de-anchor during hydrolysis or dehydroxylation to form ZrO\(_2\) nuclei at extraframework positions probably at external surfaces.

Next we examine Raman spectra of Zr-ZSM5 samples for evidence of Zr-oxo species present as monomers, dimers, or crystalline ZrO\(_2\). Figure 7 shows Raman vibrational spectra for Zr-ZSM5, H-ZSM5, and monoclinic ZrO\(_2\). Zr-ZSM5 samples gave Raman bands between 960 and 1030 cm\(^{-1}\) (Figure 7b), absent in H-ZSM5. These bands are broader but similar in frequency to Zr–O–Si bands in crystalline Zr\(_2\)Si\(_5\)–O\(_2\) at 940–960 cm\(^{-1}\).\(^{19–22}\) Zr–O modes in Zr\(_4\)-oxo species on ZSM-5 are expected to be weak because of the

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nonuniform binding sites that stabilize grafted isolated structures. Structure II contains Zr–O–Si, Zr–O–Al, and Zr=O linkages, which would be Raman-active because of the $C_2V$ symmetry of $\text{Zr}_2\text{O}_3^{2+}$ dimers, and would give bands at $\sim 1000 \text{ cm}^{-1}$, as found in zirconyl salts$^{41}$ and in analogous Mo$^{6+}$ and V$^{5+}$ oxo-dimers exchanged onto H-ZSM5.$^{24,42}$ The observed bands in the spectra for Zr-ZSM5 were too small for a conclusive spectral assignment, especially in Zr-ZSM5 with Zr/Al$\text{f}$ ratios below 0.44; therefore, these spectra cannot provide definitive evidence for structures I or II.

Crystalline ZrO$_2$ gives no detectable bands above 900 cm$^{-1}$ for any of its stable monoclinic, tetragonal, or cubic phases.$^{43-47}$ Below 800 cm$^{-1}$ (Figure 7a), the Raman spectra for Zr-ZSM5 samples with Zr/Al$\text{f}$ ratios of 0.12 and 0.22 are identical to those for unexchanged H-ZSM5. Monoclinic ZrO$_2$ ($m$-ZrO$_2$) bands were evident on Zr-ZSM5 samples with Zr/Al$\text{f}$ ratios of 0.44 and 0.8, as also detected by X-ray diffraction (not shown in Figure 2). X-ray diffraction patterns showed evidence of crystalline $m$-ZrO$_2$ (with intensity calibrated from $m$-ZrO$_2$/H-ZSM5 mixtures), present in Zr-ZSM5 at 15% and 25% of total Zr for Zr/Al$\text{f}$ ratios of 0.44 and 0.8, respectively. The amount of ZrO$_2$ formed in the 0.8 Zr/Al$\text{f}$ sample (corresponding to 0.2 Zr/Al$\text{f}$) is somewhat higher than predicted from the deviations from a unity exchange stoichiometry in these samples (0.12 ± 0.05 Zr/Al$\text{f}$, assuming a maximum Zr/Al$\text{f}$ ratio of 0.68 for dimers). This small discrepancy reflects the formation of some ZrO$_2^{2+}$ monomers, which require two Al sites per Zr, and thus decrease the maximum Zr/Al$\text{f}$ dimer ratio. The presence of ZrO$_2^{2+}$ monomers is also evident from the measured exchanged stoichiometry (1.2 ± 0.1 O$_\text{H}$/Zr), which is slightly higher than that expected from dimers.

4. Conclusions

Zr$^{4+}$ cations were grafted selectively onto exchange sites in H-ZSM5 using ZrCl$_4$ vapor under anhydrous conditions. Structures with ZrCl$_3^{+}$ stoichiometry formed initially and their Cl ligands were removed by subsequent hydrolysis at 623 K. In samples with low Zr/Al$\text{f}$ ratios, each Zr$^{4+}$ cation replaced 1.2 ± 0.1 O$_\text{H}$ by forming predominantly Zr$_2$O$_3^{2+}$ dimers. At higher Zr/Al$\text{f}$ ratios, the change in O$_\text{H}$ content per Zr approached a constant value of $\sim 0.6$ as a result of the limited number of Al–Al pairs. X-ray diffraction and $^{27}$Al MAS NMR spectra showed that the zeolite structure remains intact during exposure to ZrCl$_4$(g) and subsequent thermal treatments and that Zr was not incorporated into the zeolite framework.

Acknowledgment. The authors acknowledge financial support from the Ford Foundation through the Ford Catalysis Fellowship administered by the Berkeley Catalysis Center. Drs. Stacey Zones, Allen Burton, and C. Y. Chen (Chevron Corp.) are also acknowledged for their technical guidance in the simulation and characterization of the structure of the materials reported here.