UV Resonance Raman Spectroscopic Identification of Titanium Atoms in the Framework of TS-1 Zeolite[**]

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Transition metal substituted zeolites have received great attention as new catalytic materials, and the synthesis and characterization of these new zeolites has become the subject of much interest.[1–4] Titanium-substituted silicalite-1 (TS-1) is the most extensively studied of the transition metal substituted zeolites because of its excellent catalytic properties in a range of selective oxidation reactions with aqueous hydrogen peroxide as the oxidant under mild conditions.[5–12] It is commonly believed that the isolated titanium atoms in the framework of TS-1, hereafter denoted as Ti-O-Si, are the active sites for selective oxidation. However, whether the titanium is actually in the framework has not been definitively resolved, although TS-1 has been extensively characterized by various techniques.[13–26] A vibrational band at 960 cm^{-1} in the Raman and IR spectra was used to characterize the framework titanium species of TS-1, but there is evidence that this band is possibly due to surface hydroxy groups (e.g. Si–OH)[24, 25] or defect sites.[26] Hence, the key question of how framework titanium atoms can be unambiguously identified still remains.

Here we present UV resonance Raman spectroscopic[27, 28] data that for the first time clearly distinguish framework titanium from framework silicon and nonframework titanium dioxide. The resonance Raman effect selectively enhances Raman bands that are associated with framework titanium atoms while leaving the other Raman bands unchanged. In addition, UV Raman spectroscopy significantly improves the quality of the Raman spectra of zeolites because it avoids fluorescence interference from zeolite samples.[28, 29] We found that resonance Raman bands due to the framework titanium atoms are selectively enhanced when the charge-transfer transition associated with framework titanium is excited by a UV laser. Thus, we were able to definitely distinguish the framework titanium atoms from the nonframework titanium species and other defect sites. This study opens up the possibility of identifying transition metal atoms in other zeolite frameworks.

UV Raman spectra were recorded on a home-made UV Raman spectrograph with a continuous-wave (CW) UV line at 244 nm as the source. The UV line was from a Coherent Innova 300 Fred CW UV laser equipped with an intracavity frequency-doubling system based on a β-barium borate (BBO) crystal. A line at 325 nm was obtained from a He–Cd laser. A spectrograph system was set up with a UV-sensitive CCD (Spex) and a triplemate (1877D, Jobin Yvon-Spex). Titanium silicalite-1 and silicalite-1 zeolites were prepared as reported.[5]

The UV/Vis diffuse reflectance spectra of TS-1 and silicalite-1 are shown in Figure 1a. TS-1 shows a typical absorption band centered at 220 nm, while no electronic absorption band is observed for silicalite-1. The band at 220 nm originates from the pπ–dπ charge-transfer transition between the titanium and oxygen atoms of the framework titanium species Ti-O-Si in the zeolite.[5, 17] Figure 1b shows the UV Raman spectra of TS-1 and silicalite-1 with excitation by the 244-nm line, which is close in energy to the charge-transfer band of TS-1 at 220 nm. The UV Raman spectrum of

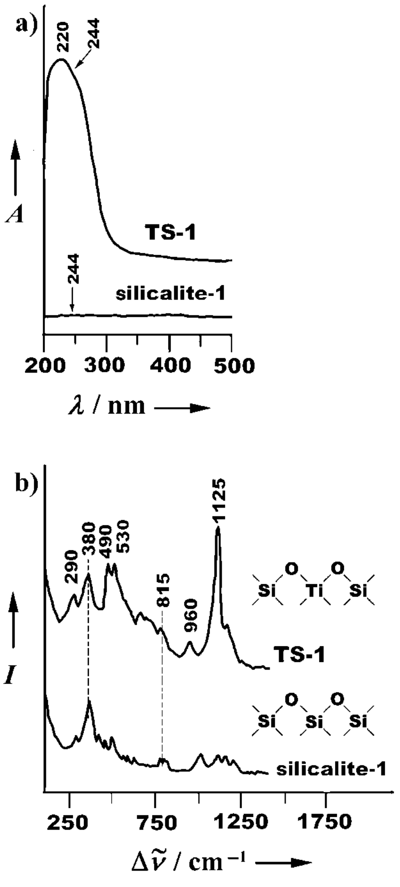

Figure 1. a) UV/Vis diffuse reflectance spectra of TS-1 and silicalite-1. The band in the 200–300 nm region is centered at 220 nm. b) UV resonance Raman spectra of TS-1 and silicalite-1 with excitation at 244 nm. A = absorbance, I = intensity.

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TS-1 is completely different from that of silicalite-1. The three strong Raman bands of TS-1 at 490, 530, and 1125 cm^{-1} are absent from the Raman spectrum of silicalite-1. These new bands are clearly due to the framework titanium species in TS-1. Several bands common to TS-1 and silicalite-1 at 290, 380, and 815 cm^{-1} indicate that the structure of TS-1 retains the main features of silicalite-1, except that some silicon atoms have been replaced with titanium atoms.

The strong bands at 490, 530, and 1125 cm^{-1} are observed only when TS-1 is excited at 244 nm, and not when the wavelength of the excitation source is 325 or 488 nm. Clearly these bands are due to the UV resonance Raman bands because 244 nm is very close to the center of the electronic absorption band of TS-1, while the lines at 325 and 488 nm lie outside of the absorption band of TS-1 (Figure 1 a).

The bands at 490, 530 and 1125 cm^{-1} are not detected for silicalite-1 on excitation with lines from the visible to ultraviolet regions. No resonance Raman phenomenon was observed for silicalite-1. This is in good agreement with the UV/Vis diffuse reflectance spectrum in Figure 1 a, which shows no electronic absorption band for silicalite-1. This is further confirmation that the bands at 490, 530, and 1125 cm^{-1} are solely associated with the framework titanium atoms of TS-1.

The resonance-enhanced Raman bands at 490, 530, and 1125 cm^{-1} are attributed to framework titanium species in tetrahedral coordination environments. The bands at 490 and 530 cm^{-1} are assigned to the bending and symmetric stretching vibrations, respectively, of the framework Ti-O-Si species, and the band at 1125 cm^{-1} is attributed to the asymmetric stretching vibration of Ti-O-Si.[13, 15]

Raman spectra of TS-1 excited at 325 and 488 nm show the typical bands of TiO_2 (anatase) at 144, 390, and 637 cm^{-1}, and this indicates that the TS-1 sample also contains nonframework titanium species. However, these bands are absent from the UV Raman spectrum with excitation at 244 nm. It appears that visible Raman spectroscopy is sensitive to nonframework TiO_2, while UV Raman spectroscopy is exclusively sensitive to framework titanium species.

Prior to this work, the framework titanium atoms of TS-1 were characterized mainly by means of a band at 960 cm^{-1} by using FT-IR and normal Raman spectroscopy (with excitation at 488, 514, or 1064 nm). It was assumed that the band at 960 cm^{-1} proves that framework titanium is present in TS-1. However, the assignment of this band is controversial.[13, 15, 30] The band at 960 cm^{-1} was also detected for TS-1 by UV Raman and visible Raman spectroscopy in this study, but the relative intensity of this band remains unchanged when the excitation line is changed. This clearly indicates that the band at 960 cm^{-1} is not a resonance-related Raman band. Hence, this band is not directly associated with the framework titanium ions of TS-1, because the resonance Raman phenomenon originates from the charge-transfer transition between titanium cations and oxygen anions in the framework of TS-1.

The fraction of transition metal ions substituting for silicon in the framework of TS-1 and of other zeolites is limited to a few percent. It is estimated that only 2 % of silicon atoms are replaced by titanium atoms in TS-1 in our case. Framework titanium atoms in such low concentrations are hard to detect by usual spectroscopic techniques. However, the resonance Raman effect allows the sensitive and selective identification of the framework titanium species in TS-1. This demonstrates that UV resonance Raman spectroscopy can selectively and sensitively identify very small fractions of transition metal atoms in the framework of a zeolite.

The UV resonance Raman approach may be applicable to the identification of other transition metal atoms in the framework of a wide range of zeolites, because most zeolites with transition metal atoms as substituents have a charge-transfer transition in the UV or near UV region. This will also allow in situ characterization of zeolite synthesis and an understanding of how transition metal atoms are introduced into the framework of a zeolite or other molecular sieve.

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Porphyrin-Based Thin-Film Molecular Materials with Highly Adjustable Nanoscale Porosity and Permeability Characteristics**

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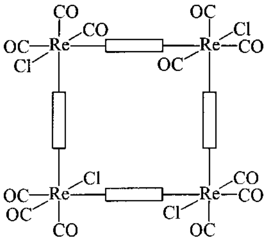
We have recently reported that $[\mathrm{Re^I(CO)_3(Cl)(\mu\text{-}L)}]_4$ metallocyclophanes ("molecular squares"), where L = pyrazine, 4,4′-bipyridine, and 4,4′-bis(pyridyl)ethylene, can form mesoporous thin films, where the porosity of the materials allows for the selective permeation of molecules based on their size.[1, 2] Notably, the observed permeation cutoffs correspond closely to the dimensions of individual molecular cavities. In addition, X-ray studies (albeit with single crystals rather than films) show that the cavities can align to form extended, one-dimensional, zeolite-like channels.[1a,c] Atomic force microscopy studies, however, indicate that films typically comprises micron and submicron-sized crystallites; these presumably account for the well-defined sieving behavior.[1d] We now report on the transport properties associated with thin films of a larger square (**1**; Re···Re edge distance approximately 20 Å) based on zinc 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-bis(4-pyridyl)porphyrin (Zn-$\mathrm{Py_2P'}$) as a bridging ligand.[1c]



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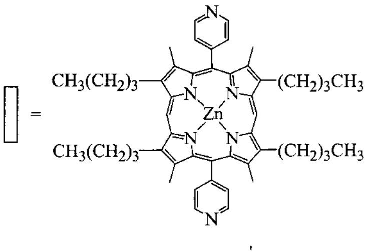

Zn-$\mathrm{Py_2P'}$

A key structural feature of **1**, exploited here, is the presence of multiple binding sites (Zn atoms) that allow for rapid chemical derivatization of walls and cavities.[1e] Other important features include: a) the absence of channel-blocking counter ions, b) very good solubility in polar organic solvents, which thus permits film preparation by simple evaporative casting, and c) complete insolubility in water, which facilitates investigations and applications in aqueous environments. Derivatization of compound **1** could prove particularly effective for: 1) adjusting the size-cutoff for permeation, 2) modifying the shape of the cavity and inducing shape-selective transport, and 3) changing the chemical affinity of the cavity. The resulting materials would potentially be useful in sensing applications, where the sieving properties of the films could be used to exclude large interfering species, while the tailored cavity would induce preferential partitioning of specific target molecules. Additionally, the mesoporous nature of the material suggests applications in membrane-based separations and catalysis.

Electrochemical techniques (cyclic voltammetry (CV) and rotating disk electrochemistry (RDE)) can be used to determine the size cutoff for permeation through films of **1** (Figure 1). Briefly, a thin film is evaporatively cast at the surface of an electrode and then exposed to an aqueous solution of an electroactive probe molecule (permeant). If permeation takes place through the pores of molecular dimensions then faradaic current will flow only if the electroactive probe is small enough to pass through the available pores (since the film thickness is much larger than the maximum achievable charge transfer distance). We find that thin films of **1** are permeable to small organic molecules (hydroquinone and nitrobenzene), small main group ions (for example, $\mathrm{I^-}$; diameter (d) ≈2.4 Å), and small and intermediate-size metal complexes, such as ferrocenemethanol ($\mathrm{FcCH_2OH}$ ($d \approx 4.5$ Å), $\mathrm{[Fe(CN)_6]^{3-}}$ ($d \approx 6.0$ Å), $\mathrm{[Ru(NH_3)_5(4\text{-}picoline)]^{2+}}$ ($d \approx 6.7$ Å), $\mathrm{[M(LL)_3]^{2+}}$ (M = Co or Fe, LL = 2,2′-bipyridine (bpy; $d \approx 11$ Å), 1,10-phenanthroline (phen; $d \sim 13$ Å), or 3,4,7,8-tetramethyl-1,10-phenanthroline ($d \approx 15$ Å)). However, the films are impermeable to $\mathrm{[Fe(bphenSO_3)_3]^{4-}}$ ($d \approx 24$ Å; $\mathrm{bphenSO_3}$ = disulphonated bathophenanthroline (4,7-diphenyl-1,10-phenanthroline), Figure 2), which is consistent with an estimated minimum van der Waals cavity diameter of about 18 Å for **1**.

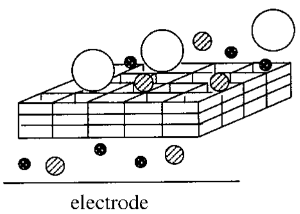

Figure 1. Schematic representation of film permeation studies using electrochemical techniques. (Note that the diagram is not meant to imply that all squares, channels, and domains within a given film are aligned normal to the electrode surface.)

Modification of the molecular square can be done in solution, prior to film casting, in cases where the Zn/guest binding constant is high. For example, the binding constants between 5,15-$\mathrm{H_2}$-tetrapyridylporphyrin ($\mathrm{H_2\text{-}Py_4P}$) and **1**, and between $\mathrm{H_2\text{-}Py_2P'}$ and **1** are on the order of 10^6–$10^7\,\mathrm{M^{-1}}$ in $\mathrm{CH_2Cl_2}$.[1c] Previous studies have indicated that $\mathrm{H_2\text{-}Py_2P'}$ and $\mathrm{H_4\text{-}Py_4P}$ bind to the interior of the square cavity through two- and four-point binding, respectively.[1c] Thus, upon incorpo-

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