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The Structure of the Peroxo Species in the TS-1 Catalyst as Investigated by Resonant Raman Spectroscopy**

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Carlo Lamberti, and Adriano Zecchina

Ti-silicalite-1 (TS-1)[1] has exhibited a remarkably high efficiency and molecular selectivity in oxidation reactions with H_2O_2 under mild conditions, such as for olefin epoxidation, phenol hydroxylation, cyclohexanone ammoximation, and conversions of ammonia to hydroxylamine, secondary alcohols to ketones, and secondary amines to dialkylhydroxylamines[2] (Figure 1). Because of its relevance in industrial applications, it has been one of the most studied materials in heterogeneous catalysis in recent years.[3–13]

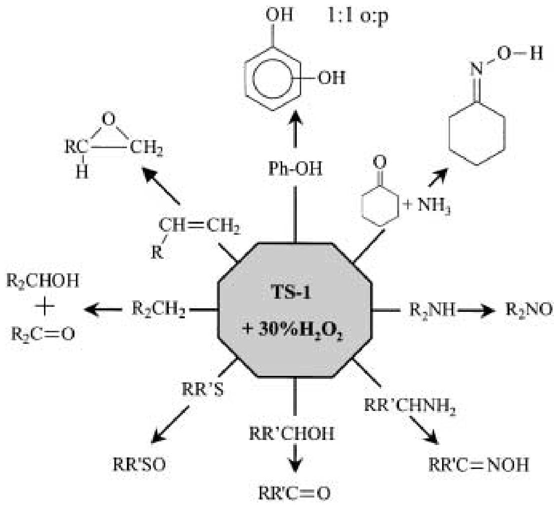

Figure 1. Schematic representation of the most relevant oxidation reactions catalyzed by TS-1.

It has been shown that the active species is a Ti^{IV} atom isomorphically inserted into the MFI-type framework.[1] TS-1 is characterized by an increase of the unit cell volume proportional to the Ti content[1,5,7,14] and by the presence of a "fingerprint" IR absorption component[1,6b,8–10,13] centered at 960 cm^{-1}, the intensity of which grows proportionally with increased Ti content. This band is clearly visible in IR spectra appearing on the low-energy tail of the very strong absorption resulting from the ν_{asym}(Si-O-Si) modes that appear in the broad 1250–1030 cm^{-1} region. In addition to the component at

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960 cm^{-1}, Raman experiments[9] have also revealed the presence of a second fingerprint band at 1125 cm^{-1} which is not obscured by the ν_{asym}(Si-O-Si) modes (very weak in Raman spectra). Conventional Raman spectroscopy is, however, a critical technique when applied to these systems because of both the high dilution of Ti centers in the MFI framework (less than 3 wt% in TiO_2[4]) and the presence of a strong fluorescence background.

In this regard, a remarkable improvement has been achieved recently by Li et al.[12] who have collected Raman spectra of TS-1 using an excitation laser at $\lambda = 244$ nm (40984 cm^{-1}), that is, in the low-energy tail of the ligand (O) to metal (Ti) charge-transfer transition (LMCT) centered around 48000 cm^{-1} (208 nm,[8,10,13] Figure 2a). The transition occurs from the four nearly equivalent oxygen atoms coordinated to the Ti^{IV} center in the quasitetrahedral TiO_4 unit, and leads to the symmetric expansion of the tetrahedral unit.[13] Li et al. have demonstrated, for the first time, that the band at 1125 cm^{-1} undergoes a remarkable resonant enhancement, while the intensity of the 960 cm^{-1} component is almost unchanged. The reason for this behavior has been successfully explained in a combined ab initio and spectroscopic study,[13] in terms of the symmetry of the vibrational and electronic transitions that are involved.[15]

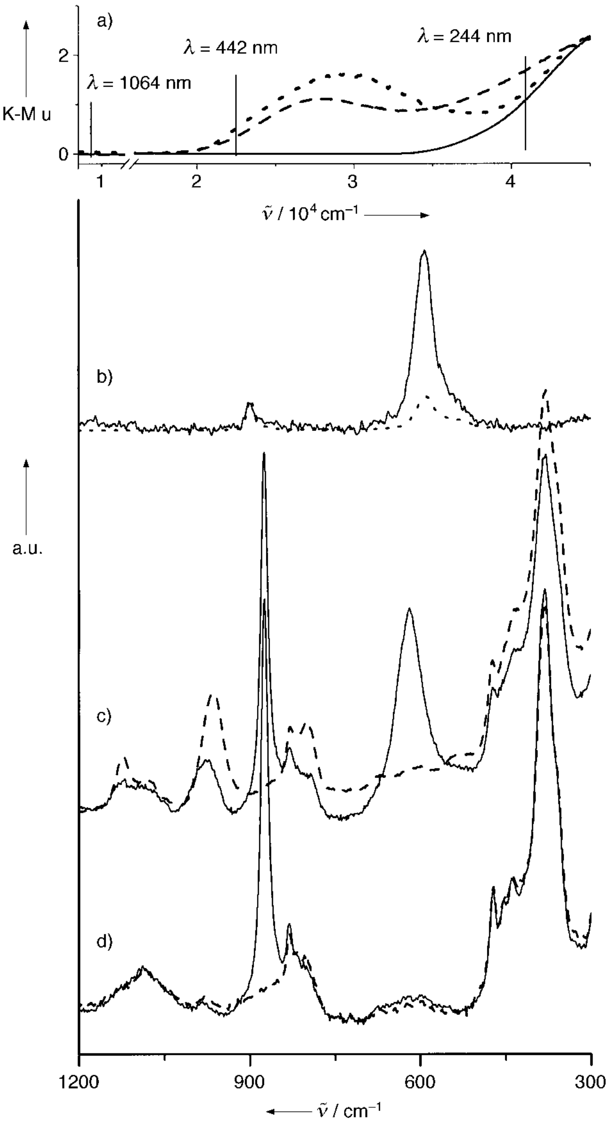

Figure 2. a) Diffuse reflectance UV/Vis spectra of a TS-1 sample in vacuo (——), in contact with a H_2O_2/H_2O solution (---), and of $[NH_4^+]_3[TiF_5O_2]^{3-}$ (••••); K-M u = Kubelka–Munk units. Vertical lines indicate the positions of the exciting Raman sources used in this work (λ = 1064 and 442 nm) and in two previous studies exploiting the resonant condition on TS-1 (λ = 244 nm);[12,13] b) Raman spectra of $[NH_4^+]_3[TiF_5O_2]^{3-}$ (λ = 1064 (••••) and 442 nm (——), respectively); c) Raman spectra (λ = 442 nm) of pure TS-1 (---) and in contact with a H_2O_2/H_2O solution (——); d) Raman spectra (λ = 442 nm) of pure silicalite (---) and contacted with a H_2O_2/H_2O solution (——).

In this work, we wish to extend the vibrational study of the TiO_4 groups in TS-1 through an investigation of the material in an H_2O_2/H_2O solution, which is the key reactant in partial oxidation reactions.[1–3] As a result of the presence of H_2O (which precludes an extended use of IR spectroscopy) and the high lability of complexes formed by H_2O_2 at the Ti^{IV} centers in TS-1, very few characterization papers have been reported on the TS-1/H_2O_2 system to date. The most commonly used technique is UV/Vis diffuse reflectance spectroscopy (DRS), which is not affected by the presence of H_2O. This technique has revealed the formation, upon contact with the H_2O_2/H_2O solution, of a new LMCT from the peroxidic moiety to the Ti center that appears at around 26000 cm^{-1} (385 nm, see Figure 2a).[16–18] Some other papers have appeared that use EPR,[16] IR,[19] Raman,[19] EXAFS,[18,20] and computational[19–21] approaches to investigate the complexes formed upon dosing H_2O_2 (or more complex species such as *tert*-butyl hydroperoxide) on titanosilicates. However, more than twenty years after the discovery of the material, the detailed structure of the peroxidic species formed at the catalytic center, which is thought to be the active intermediate in partial oxidation reactions, is still unknown. The two most frequently proposed structures are a "side-on" Ti–peroxo species or an "end-on" Ti–hydroperoxo species.

A previous Raman study[19] (exploiting a conventional 1064 nm exciting source) was only able to measure the O–O stretching frequency of peroxo complexes formed at the Ti sites in TS-1 upon contact with $H_2O_2/NH_3/H_2O$ (840 cm^{-1}) and H_2O_2/NaOH/H_2O (843 cm^{-1}) basic solutions.[22] The reason for this partial success is probably because in basic solutions the peroxo species are more stable and hence they are not readily destroyed by the laser beam. The same experiment with an H_2O_2/H_2O solution was not successful because of the labile nature of the complex. On this basis it is apparent that the only route that can be followed to improve the quality of the Raman spectra in this field is that reported by Li et al.[12] As the peroxo species absorb in the visible region, an exciting source in the same spectral region must be used, because in this way the vibration associated with the Ti–peroxo species can undergo a Raman enhancement phenomenon, if the selection rules are fulfilled.[15] We have used a 442 nm (22625 cm^{-1}) laser source, which lies on the low-energy tail of the LMCT band at around 26000 cm^{-1} that is typical of the TS-1/H_2O_2/H_2O system (see Figure 2a), and should stimulate the resonant enhanced response. Figure 2c shows the Raman spectra of TS-1 both before and after interaction with the H_2O_2/H_2O solution. Interaction with H_2O_2 causes: a) the reduction and blue shift of the 960 cm^{-1} mode, shifted to 976 cm^{-1}, b) the quenching of the 1125 cm^{-1}

mode, which results from a breakdown of the T_d-like symmetry,[13] c) the appearance of the strong and sharp O–O stretching mode at 875 cm^{-1}, resulting from the H_2O_2/H_2O solution being physisorbed into the zeolite channels, and d) the appearance of a strong and complex new feature centered at 618 cm^{-1}. Features a–c are also observed when the same experiment is performed with a 1064 nm laser source (spectra not reported, see Ref. [19]). Conversely, the 618 cm^{-1} vibration is only found in Raman spectra obtained with a 442 nm exciting source, and is therefore ascribed to a Raman-enhanced vibration mode of the Ti–peroxo complex. To assign this new feature, two control experiments have been performed, with the model compound $[NH_4^+]_3[TiF_5O_2]^{3-}$ [23] (Figure 2b), and with the Ti-free silicalite-1 molecular sieve, (Figure 2d) respectively. Interaction of the H_2O_2/H_2O solution with the Ti-free silicalite results only in the appearance of the 875 cm^{-1} mode, already assigned to H_2O_2 that is physisorbed into the zeolite channels. The Raman spectrum of $[NH_4^+]_3[TiF_5O_2]^{3-}$ exhibits a band at 898 cm^{-1} and a composite absorption with a maximum at 595 cm^{-1} which undergoes a distinct enhancement when the 442 nm excitation source is used. To assign this spectrum, it is useful to consider that the crystalline structure of $[NH_4^+]_3[TiF_5O_2]^{3-}$ (see Figure 3) consists of TiF_5O_2 units intercalated with NH_4^+ counterions. For this reason the discussion of the vibrational spectrum can be based on the TiF_5O_2 molecular unit and in particular the $Ti(O)_2$ fragment. The $Ti(O)_2$ unit has C_{2v} symmetry and Γ_{vib} for this moiety is $2A_1 + B_1$. The three normal modes, labeled ν_1, ν_2, and ν_3 following literature data on peroxo–metal complexes in argon matrices,[24] are assigned to: an O–O stretching vibration with A_1 symmetry (ν_1); a symmetric breathing mode of the $Ti(O)_2$ cycle with A_1 symmetry (ν_2); an asymmetric breathing mode of the $Ti(O)_2$ cycle with B_1 symmetry (ν_3). Literature data for the cyclic structures $Fe(O)_2$, $Co(O)_2$, $Ni(O)_2$, and $Ca(O)_2$ show that the ν_1 mode lies in the 990–742 cm^{-1} spectral range.[24] This suggests that the band at 898 cm^{-1} can be associated with the O–O stretching vibration. It is of note that even if this mode is totally symmetric (A_1 symmetry), its intensity is not substantially enhanced in the spectrum obtained with the 442 nm source. By analogy with the data obtained on the previously cited structures, this behavior can be explained by considering that among the two A_1 modes which meet the symmetry requirements, the ν(O–O) mode (where the Ti center is not directly involved) is not affected by the resonant Raman effect. Literature data[24] on $Fe(O)_2$, $Co(O)_2$, $Ni(O)_2$, and $Ca(O)_2$ show that ν_2 and ν_3 are usually only about 30 cm^{-1} apart and are located in the range 600–500 cm^{-1}. Because of the proximity of the two contributions, and with only the ν_2 mode being Raman enhanced, we associate the absorption centered at 595 cm^{-1} to the symmetric breathing mode of the $Ti(O)_2$ cycle, the asymmetric mode giving a minor contribution. The similarity between the spectroscopic features in both the UV/Vis (Figure 2a) and Raman (Figure 2b,c) spectra of the $[NH_4^+]_3[TiF_5O_2]^{3-}$ and TS-1/H_2O_2/H_2O systems allows us to conclude definitively that the species responsible for the band at 26000 cm^{-1} of the TS-1/H_2O_2/H_2O system is a "side-on" Ti–peroxo species, characterized by a Raman mode at 618 cm^{-1} which is resonance-enhanced upon laser excitation at a wavelength falling within the LMCT region.

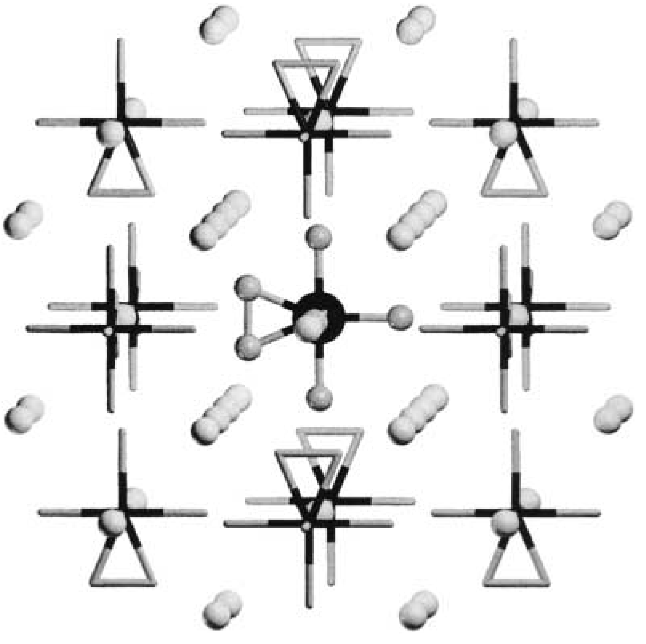

Figure 3. Graphical representation of the crystalline structure of $[NH_4^+]_3[TiF_5O_2]^{3-}$. The TiF_5O_2 unit is represented by balls and sticks: Ti^{IV} (black), O and F (gray). NH_4^+ counterions are represented by white spheres.

Experimental Section

TS-1 (3.0 TiO_2 wt%) and silicalite-1 samples have been synthesized in EniChem laboratories (now PolimeriEuropa) following a procedure described in the original patent.[1] The complete insertion of Ti atoms within the MFI framework has been proved by comparison of the amount of Ti, as determined by chemical analysis, with the cell volumes obtained by Rietveld refinement of powder X-ray diffraction data, according to Ref. [7]. TiO_2 extra-framework particles are below the detection limit (about 0.03 wt%) of the UV/Vis technique (Figure 2a).[25] X-ray absorption near-edge spectroscopy (XANES; from the width and intensity of the 4967 eV pre-edge peak[13]) and Raman[25] (from the absence of the 144 cm^{-1} band) analysis confirm the complete insertion of Ti into the framework. A sample of TS-1 was analyzed when in contact with a 30% H_2O_2 aqueous solution, which represents the working conditions of the catalyst.[2] The experiment is carried out in an excess of H_2O_2 molecules, with respect to Ti–peroxo complexes. Note that the presence of water is necessary, since it has been shown that the TS-1/H_2O_2/H_2O system loses its yellow color upon water desorption.[18] $[NH_4^+]_3[TiF_5O_2]^{3-}$ has been synthesized in the PolimeriEuropa laboratories and characterized by XRD (Figure 3), UV/Vis, (Figure 2a) and Raman spectroscopy (Figure 2b).

Raman spectra were obtained on a Perkin Elmer 2000 NIR-FT Raman spectrometer equipped with an InGaAs detector. The lasing medium was an Nd-YAG crystal pumped with a high-pressure krypton lamp, which results in an excitation wavelength of 1064 nm (9398 cm^{-1}). The power output was approximately 1 W. Resonance Raman spectra were obtained using a Renishaw Micro-Raman System 1000 by excitation with a He/Cd laser operating at 442 nm (22624 cm^{-1}). The photons scattered by the sample were dispersed by a 2400 lines mm^{-1} grating monochromator and simultaneously collected on a CCD camera; the collection optic was set at x20 objectivity. A laser output of 8.3 mW and an exposure time of 500 s per spectrum were used in case of zeolite samples. Care was taken with the measurements on $[NH_4^+]_3[TiF_5O_2]^{3-}$ in order to avoid decomposition, where a laser output of 0.3 mW and an exposure time of 200 s per spectrum were employed.[26] The diffuse reflectance UV/Vis spectra were obtained on a Varian Cary 5 spectrometer.

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Pd^0-Catalyzed Three-Component Tandem Double-Addition–Cyclization Reaction: Stereoselective Synthesis of *cis*-Pyrrolidine Derivatives[**]

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Pd^0-catalyzed cyclization reactions of functionalized allenes[1] leading to carbo- and heterocyclic compounds[2–4] has been studied extensively. In some of these reactions, the π-allyl palladium intermediate formed in situ[5] was trapped by an intramolecular nucleophile (path A, Scheme 1). Recently, development of multicomponent reactions to preserve atom economy[6] and stereoselectively construct an array of several stereogenic centers in one pot is attracting the attention of many chemists.[7] Therefore, if there is another potential electrophilic receptor such as an imine group in the reaction system, the Pd^0-catalyzed reaction of organohalides and allenes with a nucleophilic center would allow the formation of pyrrolidine derivatives (path B, $Nu = C$, Scheme 1). To make this concept synthetically attractive, we must address the issues of matched relay, regioselectivity (by excluding the formation of seven-membered product **6**), and diastereoselectivity (Scheme 1).

The construction of pyrrolidine skeletons, a frequently observed structural unit in various natural products, ligands, etc., is of current interest.[8,9] Although the transition-metal-catalyzed cyclization of γ-allenic amides to yield 2-substituted

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