Oxidizing Properties of Zeolite-Encapsulated Oxobis(2,2′-bipyridine)ruthenium(IV) Complexes Formed by Air Oxidation of Bis(2,2′-bipyridine)aquaruthenium(II)

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Several reports have appeared recently of zeolite-encapsulated complexes acting as oxidizing agents for hydrocarbon oxidation.[1] Peroxides or iodosylbenzene in solution phase has provided the oxidizing equivalents. Use of oxygen as the oxidant with selective oxidation taking place at a gas−zeolite interface should considerably enhance the scope of oxidation chemistry with zeolites. Polypyridine complexes of ruthenium-(IV) oxo compounds demonstrate excellent activity toward oxidation of alcohols, aldehydes, and unsaturated and aromatic hydrocarbons under mild conditions.[2] The problem with the homogeneous system is that the oxidizing equivalents need to come from Ce^{4+} or electrochemically, thus limiting general use. We report here that zeolite-encapsulated $\{(bpy)_2Ru(OH_2)_2\}^{2+}$ (bpy-2,2′-bipyridine) can be oxidized by air to form $\{(bpy)_2Ru^{4+}=O\}^{2+}$. The oxidizing ability of this terminal oxo complex was demonstrated by oxidation of triphenylphosphine (PPh_3) to triphenylphosphine oxide ($OPPh_3$). Even though this reaction is not synthetically useful, it has allowed us to unequivocally establish the mechanism of the reaction. The close correspondence we observe with solution chemistry[3] ensures that the more relevant hydrocarbon oxidations should also be feasible.

Moyer and Meyer have reported that on the basis of the reduction potential of $\{(bpy)_2pyRuO\}^{2+}$ to $\{(bpy)_2pyRu-(OH_2)\}^{2+}$ in the pH range of 2−8, O_2 should be thermodynamically capable of oxidizing Ru(II) to Ru(IV).[4] Under ambient conditions, however, the Ru(II) complex was found to be stable in aqueous solution. Kincaid and co-workers have reported that $(bpy)_2Ru^{2+}$-type complexes can be synthesized within zeolite Y supercages.[5] The starting material for synthesis of the bis-(bipyridyl) complex is intrazeolitic $Ru(NH_3)_6^{3+}$ obtained by ion exchange of zeolite with aqueous $Ru(NH_3)_6$ Cl_3. Upon heating this $Ru(NH_3)_6^{3+}$-exchanged zeolite with bpy at 90 °C under vacuum, the bis(bipyridyl) complex is formed. This procedure typically results in migration of a fraction of the ruthenium complexes to the zeolite exterior, which are removed by ion exchange with 1 M NaCl, until no complex is observed in the wash solution as confirmed by electronic spectroscopy (typically two exchanges). The excess bpy ligand is removed by Soxhlet extraction with ethanol, and this is followed by stirring in deionized water for 24 h. The diffuse reflectance spectrum of this material is shown in Figure 1a. The bands at 490, 345, 290, and 245 nm are typical of the *trans*-$\{Ru(bpy)_2(H_2O)_2\}^{2+}$
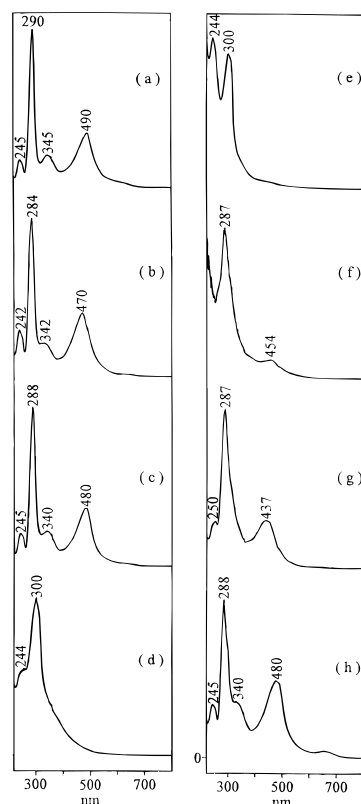

Figure 1. Diffuse reflectance spectra of zeolite-encapsulated (a) *trans*-$\{Ru^{II}(bpy)_2(H_2O)_2\}^{2+}$, (b) *cis*-$\{Ru^{II}(bpy)_2(H_2O)(OZ)\}$, (c) *cis*-$\{Ru^{II}(bpy)_2(H_2O)_2\}^{2+}$, and (d) $\{O=Ru^{IV}(bpy)_2(OZ)\}$. (e) Electronic spectrum of $\{O=Ru^{IV}(bpy)_2\}$ in solution obtained by acid dissolution of zeolite. Diffuse reflectance spectra of zeolite-encapsulated (f) $\{Ru^{II}(bpy)_2(PPh_3)(OZ)\}$, (g) $\{Ru^{II}(bpy)_2(CH_3CN)_2\}$, and (h) regenerated $\{Ru^{II}(bpy)_2(H_2O)_2\}$.

complex.[6] This intrazeolitic complex could only be released into solution by decomposing the zeolite framework with concentrated acid. The loading level of 1 $\{Ru(bpy)_2(H_2O)_2\}^{2+}$ per 8 zeolite supercages was determined by X-ray fluorescence.

$\{Ru(bpy)_2(H_2O)_2\}^{2+}$−zeolite was heated under a stream of nitrogen at 150 °C for 12 h to partially dehydrate the zeolite. This resulted in the electronic spectrum shown in Figure 1b, with bands at 470, 342, 284, and 242 nm. Upon rehydration of this sample, the peaks appeared at 480, 340, 288, and 245 nm as shown in Figure 1c. The shift of the MLCT band from 490 nm for the as-synthesized complex to 480 nm after thermal treatment and hydration is indicative of conversion of the trans to the cis structure.[6] This is not unexpected, since thermal conversion of trans to the cis form has been reported for $\{Ru-(bpy)_2(OH_2)_2\}^{2+}$ in solution.[6] We assign the species obtained upon heating and prior to hydration as *cis*-$\{(bpy)_2Ru^{II}(OH_2)-(OZ)\}$, where OZ represents a zeolitic oxygen. The aqua ligand is known to be weakly bound,[4] and is replaced by a zeolitic oxygen as water is driven out of the zeolite. Oxidation of this dehydrated species by air at 150 °C for 12 h leads to loss of the visible metal-to-ligand charge transfer band and appearance of a species characterized only by bands at 300 and 244 nm, shown in Figure 1d. These spectral characteristics are similar to that of $\{(bpy)_2(py)Ru^{IV}=O\}^{2+}$ or $\{(bpy)_2(H_2O)Ru^{IV}=O\}^{2+}$ reported earlier,[7] and can be assigned to $\{(bpy)_2(OZ)Ru^{IV}=O\}^{2+}$. This complex is not ion-exchangeable and can only be released by destroying the zeolite framework. Figure 1e shows the

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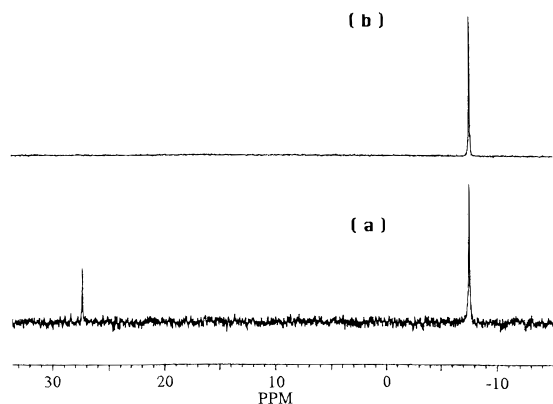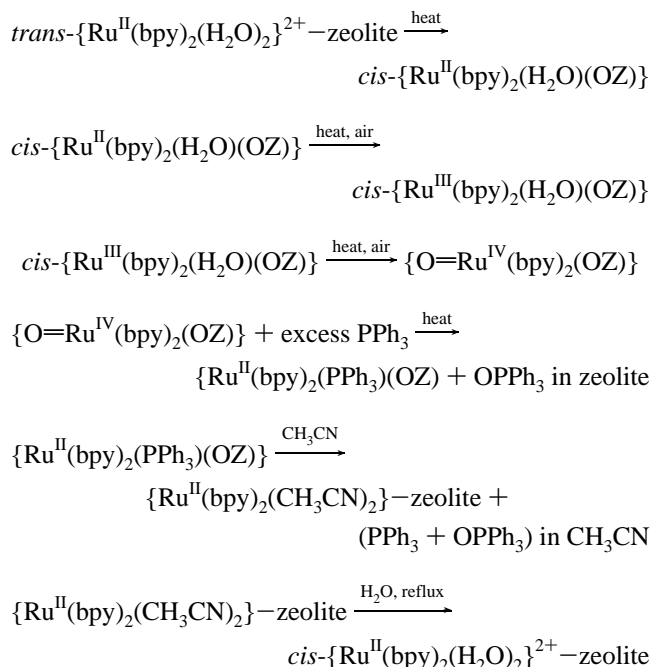
Figure 2. ^{31}P NMR spectra of acetonitrile extracted product after reaction of zeolite-encapsulated (a) {O=Ru[IV](bpy)$_2$(OZ)} and (b) Ru[II]-(bpy)$_2$(H$_2$O)$_2$}$^{2+}$ with excess phosphine under anaerobic conditions at 100 °C.

electronic spectrum of the complex recovered by acid dissolution (0.1 M HClO$_4$) of the zeolite; it is similar to that of the zeolite-entrapped complex and resembles the spectrum of the Ru[IV]=O complex generated electrochemically in solution.[7b] The dehydration and oxidation step can be done in a single step by heating in an air stream at 150 °C for 24 h. This oxidation proceeds through the Ru(III) complex and for incomplete oxidation in air (10 h at 150 °C or oxidation at temperatures below 120 °C) leads to the appearance of an intrazeolitic species with a band at 360 nm, characteristic of (bpy)$_2$Ru[III](OH$_2$)OZ.[7a] The formation of the Ru(III) intermediate is not unexpected, for it has been reported that air oxidation at elevated temperatures of solutions of {(bpy)$_2$Ru[II](OH$_2$)$_2$}$^{2+}$ will lead to the Ru(III) form.[6] However, previous reports in the literature have not shown that the Ru(IV) form is accessible by air oxidation. In solution, this oxidation is slow both with Ce^{4+} and electrochemically, because of the deprotonation step that is involved in making the oxo complex (Ru[III]—OH → Ru[IV]=O).[7a] We believe that the dehydrated environment in the zeolite promotes this deprotonation step and oxidation. The zeolite is a negatively charged framework, and dehydration causes electrostatic fields that can readily polarize covalent bonds and stabilize charge-separated species.[8] We found the optimum temperature of dehydration to be 150 °C to obtain complete conversion to the Ru[IV]=O species, without any apparent degradation.

In order to demonstrate the oxygen atom transfer capability of the intrazeolitic {(bpy)$_2$(OZ)Ru[IV]=O}, it was heated with excess PPh$_3$ (with a mole ratio of Ru:P of 1:2) in the solid state at 100 °C under strictly anaerobic conditions. The electronic spectrum of the intrazeolitic species is shown in Figure 1f, with bands at 454 and 287 nm. Note that the metal-to-ligand charge transfer (MLCT) band typical of the Ru[II] is recovered. This species is assigned to {(bpy)$_2$(OZ)Ru[II](PPh$_3$)$_3$}.[9] Upon refluxing in CH$_3$CN, the intrazeolitic species is characterized by bands at 437, 287, and 250 nm (Figure 1g) and is similar to {Ru[II](bpy)$_2$(py)(CH$_3$CN)$_2$ }$^{2+}$ reported in the literature.[4a] A white solid was recovered from the acetonitrile solution upon evaporation and was analyzed by IR, NMR, and MS. All these analyses supported the formation of OPPh$_3$, with a characteristic P=O stretch at 1200 cm^{-1} and a parent mass peak at *m/z* 278 amu. Figure 2 compares the ^{31}P NMR of the acetonitrile-extracted product formed by reaction of PPh$_3$ with {(bpy)$_2$(OZ)Ru[IV]=O} and zeolite Y—{(bpy)$_2$(H$_2$O)Ru[II]}$^{2+}$ done under identical conditions. The signal at 27.3 ppm (phosphoric acid as standard) is only observed with the Ru[IV]=O complex, and is indicative of formation of OPPh$_3$.[10]

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Upon heating of the zeolite—Ru[II](bpy)$_2$ (CH$_3$CN)$_2$ complex in air at 150 °C, no spectral changes were found, indicating that it cannot be oxidized to the Ru[IV] form. However, upon refluxing in water, zeolite-encapsulated *cis*-{Ru[II](bpy)$_2$(H$_2$O)$_2$}$^{2+}$- could be recovered, as is evident from the electronic spectrum shown in Figure 1h. This complex could be readily oxidized by air at 150 °C to regenerate the Ru[IV]=O complex, and used again for the transformation of PPh$_3$ to OPPh$_3$.

The chemistry is depicted below:

$$\textit{trans-}\{Ru^{II}(bpy)_2(H_2O)_2\}^{2+}-zeolite \xrightarrow{\text{heat}}$$
$$\textit{cis-}\{Ru^{II}(bpy)_2(H_2O)(OZ)\}$$

$$\textit{cis-}\{Ru^{II}(bpy)_2(H_2O)(OZ)\} \xrightarrow{\text{heat, air}}$$
$$\textit{cis-}\{Ru^{III}(bpy)_2(H_2O)(OZ)\}$$

$$\textit{cis-}\{Ru^{III}(bpy)_2(H_2O)(OZ)\} \xrightarrow{\text{heat, air}} \{O=Ru^{IV}(bpy)_2(OZ)\}$$

$$\{O=Ru^{IV}(bpy)_2(OZ)\} + \text{excess PPh}_3 \xrightarrow{\text{heat}}$$
$$\{Ru^{II}(bpy)_2(PPh_3)(OZ) + OPPh_3 \text{ in zeolite}$$

$$\{Ru^{II}(bpy)_2(PPh_3)(OZ)\} \xrightarrow{\text{CH}_3\text{CN}}$$
$$\{Ru^{II}(bpy)_2(CH_3CN)_2\}-zeolite +$$
$$(PPh_3 + OPPh_3) \text{ in CH}_3\text{CN}$$

$$\{Ru^{II}(bpy)_2(CH_3CN)_2\}-zeolite \xrightarrow{\text{H}_2\text{O, reflux}}$$
$$\textit{cis-}\{Ru^{II}(bpy)_2(H_2O)_2\}^{2+}-zeolite$$

There are several indispensable roles that the zeolite is playing in accomplishing the oxygen transfer chemistry. First, it is stabilizing the {Ru[II](bpy)$_2$(H$_2$O)$_2$ }$^{2+}$ complex in its higher oxidation states by encapsulation. In solution[11] and other substrates, e.g., clays,[12] such complexes will tend to dimerize upon oxidation and form the μ-oxoruthenium(III) complex. The presence of pyridine as a ligand will sterically hinder the oxo complex formation, but if the pyridine ligand dissociates, then the μ-oxoruthenium(III) is formed.[4b] In the zeolite, steric constraints as imposed by the 13 Å zeolite supercage are helping to stabilize the mononuclear complex. Molecular modeling demonstrates that dimer formation within a supercage is impossible. Second, dehydration of the zeolite host provides an environment where electrostatic fields promote the deprotonation and air oxidation of Ru(III) to Ru(IV). Third, the zeolite allows stabilization of the Ru(IV) complex without the necessity of a pyridine ligand. Fourth, since the Ru complex is now stabilized in the supercages, reactions between reactants in the gas phase and the complex can be carried out, obviating the necessity of using a solvent.

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