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Characterization of Nitrosyl Intermediates Formed during the Decomposition of $[Ru(NH_3)_6]^{3+}$ Complexes in Zeolites

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Upon decomposition under an O_2 atmosphere of $[Ru(NH_3)_6]^{3+}$ complexes in X- andY-type zeolites, a variety of intermediates were observed which have been characterized by diffuse reflectance, infrared, and X-ray photoelectron spectroscopies. After heating to 450 K in flowing O_2, the predominant Ru complex in both the X- and Y-type zeolites is a mixed ammine–nitrosyl species, $[Ru(O_{zeol})_3(NH_3)_x(NO)]$, in which the value of x is 1 or 2. This mixed ammine–nitrosyl complex may be decomposed either in O_2 or under high vacuum at 530 K. In the former case, RuO_2 is the major product, while in the latter, deammination is complete, leaving a reduced form of ruthenium inside the zeolite.

Introduction

The high activity of supported ruthenium metal as a heterogeneous catalyst for a surprising variety of reactions is now well recognized.[1-3] This is in keeping with the general nature of the group 8 metals, all of which display some very desirable behavior as heterogeneous catalysts. This of course has led to a tremendous effort on the part scientists worldwide and has resulted in an enormous body of literature. While no attempt is made to review the extensive literature in this short space, some salient points concerning supported ruthenium in zeolitic systems are of interest.

In the past several years, ruthenium has been introduced into zeolites by ion exchange with $[Ru(H_2O)_6]^{3+}$, $[Ru(NH_3)_5N_2]^{2+}$, and $[Ru(NH_3)_6]^{3+}$.[4-7] The procedure utilizing the hexaaquo complex has serious limitations since it is easily hydrolyzed to form poorly defined polymeric products.[4] Furthermore, the low pH required to maintain the integrity of the $[Ru(H_2O)_6]^{3+}$ complex can lead to the decomposition of zeolitic framework. The preparation of Ru-containing zeolites via the ammine complexes has been much more successful and shows promise as an advantageous route to industrially important catalysts.

The chemistry of the zeolitic ruthenium–ammine complexes is fascinating in that many of the derivatives which can be formed from these precursors are unprecedented in homogeneous systems. Interest was recently stirred when one such derivative (a mixed ammine–carbonyl complex of Ru(III)) was shown in a preliminary report to be a much more active water–gas shift catalyst than those which are commercially available.[3] Unfortunately, the present level of understanding of such novel complexes in zeolites did not allow its detailed characterization. Much more work will obviously be necessary before a clear description of ruthenium complexes on zeolite supports can evolve.

The present paper outlines the formation and characterization of a ruthenium–nitrosyl complex which is produced from $[Ru(NH_3)_6]^{3+}$ in X- and Y-type zeolites. As was expected, similar complexes have not been observed in homogeneous systems. It was found that, by using a suitable pretreatment procedure, a stable ionic ruthenium mononitrosyl ammine complex could be formed within the zeolite. The preservation of ionic ruthenium is not possible when traditional activation techniques (e.g., heating under vacuum) are employed since under these conditions much of the ruthenium from the hexammine complex is reduced to the metallic state, accompanied by the liberation of N_2.[7]

Experimental Methods

Materials and Sample Preparation. The sodium forms of zeolites X and Y were obtained from Linde Co. (SK-20 and SK-40). Ruthenium hexammine trichloride was purchased from Strem Chemicals. Matheson NO was purified by repeated vacuum distillation at the melting point of pentane (144 K). Nitrogen-15 labeled NO was purchased from Stohler Isotope Chemicals and was similarly purified. Deuterium-enriched ammonia (99% ND_3) was supplied by Merck & Co. Ultrahigh purity O_2 and anhydrous NH_3 were obtained from Matheson and were used as received.

Samples of RuX and RuY zeolites containing ca. 2% Ru by weight were prepared from the corresponding NaX and NaY by ion exchange with $[Ru(NH_3)_6]Cl_3$. For this ion exchange, 20 g of the sodium zeolites were stirred in 10 L of deionized H_2O along with the desired equivalents of Ru complex. The exchange was carried out at 298 K for 24 h. The solid zeolite was separated from the exchange solution by centrifugation, repeatedly rinsed with H_2O, and finally air-dried. The samples prepared in this fashion were analyzed for ruthenium by atomic absorption spectroscopy following digestion of the zeolite with HF. The error in the analysis is estimated to be ±10%. Both the X and Y samples contained 3.5 ruthenium ions/unit cell, which corresponds to 12 and 19% of the cation-exchange capacity, respectively.

Standard pretreatment of the zeolites consisted of heating samples slowly (approximately 1 K/min) under a continuous flow of O_2 at 80 cm^3/min. This procedure was interrupted at selected temperatures to record desired spectra.

Spectroscopic Methods. Infrared (IR) spectra were obtained with use of Beckman IR-9 spectrophotometer. The zeolite samples for IR studies were in the form of self-supporting wafers having a single-beam transmission of ~50%. The Pyrex IR cell was equipped with KCl windows and was designed so that all pretreatments could be performed in situ. The resolution of the IR spectra reported in this text is estimated to be ±2 cm^{-1}.

The quartz cell for diffuse reflectance studies was also designed to allow in situ heating in the O_2 flow. Diffuse reflectance spectra (DRS) were recorded in the range from 1000 to 200 nm with use of a Cary 17 spectrophotometer equipped with a type II reflectance attachment. An Eastman white reflectance standard was employed as the DRS reference.

ESCA spectra of selected samples were obtained with use of a Hewlett-Packard 5950-A instrument with Al Kα X-rays (1366.6 eV). This instrument was fitted with a glovebox filled with dry N_2 so that samples could be introduced without exposure to H_2O or O_2. ESCA binding energies were referenced to the Si 2s line of the zeolite which was taken to have a binding energy of 154.0 eV. With use of this instrument, binding energies were reproducible within an error of ±0.2 eV.

Results

Diffuse Reflectance Results. The DRS of X and Y zeolites containing the hexaammineruthenium(III) cation after treatment in flowing O_2 at various temperatures are shown in Figure 1. For the most part, these spectra are complex and arise from a mixture of Ru complexes on the zeolitic

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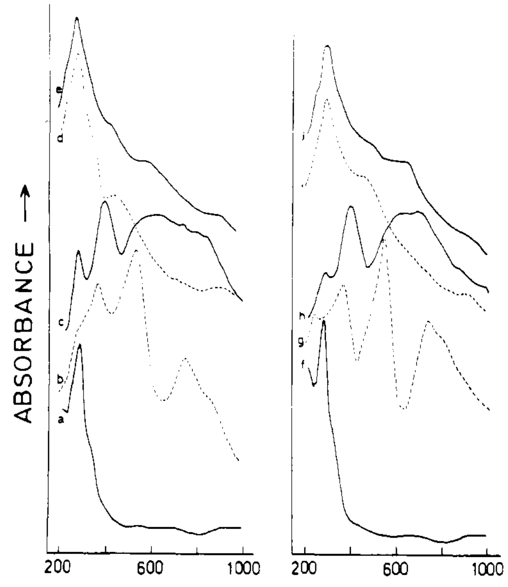

Figure 1. Selected diffuse reflectance spectra of RuX and RuY zeolites: (a) RuX starting zeolite; (b–d) RuX treated in flowing O_2 at 343, 383, and 450 K; (e) RuX treated in flowing O_2 at 450 K followed by heating in vacuo to 530 K; (f) RuY starting zeolite; (g–i) RuY treated in flowing O_2 at 343, 383, and 450 K; (j) RuY treated in flowing O_2 at 450 K followed by heating in vacuo to 530 K. Spectra are displaced along the ordinate for clarity.

surface. Some of these complexes have been characterized in the homogeneous phase and are readily identified. Others are unknown, and we can only speculate as to their identity.

The freshly prepared RuX and RuY samples (Figure 1a,f) both displayed a single adsorbance at 280 nm which is characteristic of the $[Ru(NH_3)_6]^{3+}$ cation.[8] This suggests that the ion exchange was accomplished without decomposition of the hexaammine complex. However, upon heating in O_2 to 343 K, the RuX and RuY zeolites turned purple with intense bands appearing at 360, 540, and 740 nm (Figure 1b,g).

After heating the RuX and RuY samples to 383 K in flowing O_2, both samples were black and displayed the DRS in Figure 1c,h, respectively. The 540-nm band, while greatly attenuated, was still evident. A weaker absorbance at 260 nm and a very broad asymmetric band between 500 and 800 nm were also noted for these samples. After treatment at 450 K in flowing O_2 the RuX and RuY zeolites were orange-pink in color. The DRS of these samples, reproduced in Figure 1d,i, display major bands at 270 nm with long-wavelength shoulders at 450 nm.

Heating RuX and RuY zeolites above 473 K in the oxygen atmosphere resulted in the samples again turning black. This was due to the formation and sintering of RuO_2, a reaction which was easily confirmed by the appearance of several characteristic reflections of RuO_2 in the X-ray powder diffraction profile (RuO_2, tetragonal, $a = b = 4.48$ Å, $c = 3.11$ Å).[9]

When the O_2 flow was discontinued at 450 K followed by heating to 530 K under high vacuum ($<10^{-5}$ torr), the DRS shown in Figure 1e,j were obtained. The samples treated in this manner were brown due to the appearance of a weak absorbance at ca. 600 nm. A continuation of the vacuum treatment to 575 K intensified the broad band at 600 nm and attenuated the 270-nm absorption. It should be noted that zeolites containing metallic ruthenium have been reported to have this color.[7,10]

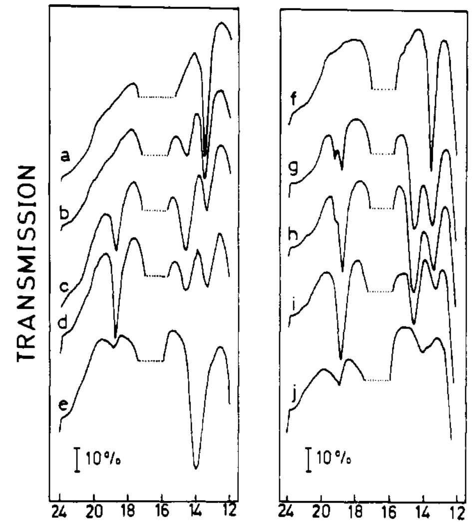

Figure 2. Infrared spectra (transmission mode) of selected RuX and RuY zeolites: (a) RuX starting zeolite; (b–e) RuX heated in flowing O_2 to 343, 383, 450, and 530 K; (f) RuY starting zeolite; (g–j) RuY heated in flowing O_2 to 343, 383, 450, and 530 K. The band at 1650 cm^{-1} is not shown for clarity.

Infrared Results. The infrared (IR) spectra between 2400 and 1200 cm^{-1} for the freshly prepared RuX and RuY zeolites are shown in Figure 2a,f. Two intense bands are visible in each spectrum at 1650 and 1355 cm^{-1}. The 1355-cm^{-1} band is the δ(sym) mode of the coordinated NH_3 in the $[Ru(NH_3)_6]^{3+}$ complex while the 1650-cm^{-1} band is a combination of the δ(deg) mode of coordinated NH_3 and the δ(sym) mode of zeolitic H_2O.[11]

The IR spectra of the RuX sample after heating in flowing O_2 at 343, 383, and 450 K are reproduced in Figure 2b–d, respectively. The corresponding spectra for RuY are found in Figure 2g–i. A brief examination of these spectra yields some interesting information. First, the deformation band of coordinated NH_3 is sharply reduced in intensity during the heating process in both the X and Y zeolites. There is also a small downward shift in the wavenumber of these bands. After heating to 450 K, they are observed at 1340 and 1335 cm^{-1} for the RuX and RuY samples, respectively. Second, an intense band appears at 1460 cm^{-1} during the heating process for both samples. This arises from the interaction of free NH_3 with Brønsted acid sites of the zeolites, a reaction which generally produces a deformation band, $\delta(NH_4^+)$, in this region.[11] NH_3 is liberated by the partial decomposition of the $[Ru(NH_3)_6]^{3+}$ complex. The relative intensities of the 1335–1340 and 1460 cm^{-1} bands in both RuX and RuY appear to follow qualitatively the expected reciprocal relationship.

Several IR bands appeared during the process of heating in flowing O_2 which were at wavenumbers typical of the stretching mode of coordinated nitrosyl ligands, ν(NO). In the case of RuX, a single band was observed at 1870 cm^{-1}. It was evident after treatment at 383 K and displayed a maximum in intensity after treatment at 450 K. A subsequent evacuation of the sample at 450 K decreased only slightly the intensity of this 1870-cm^{-1} band, an indication of a very stable complex.

For the RuY sample, two distinct bands were visible at 1925 and 1875 cm^{-1} after heating in O_2 to 343 K. The complex

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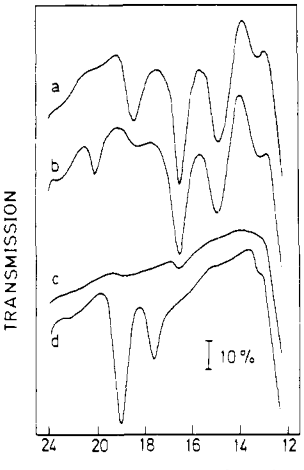

Figure 3. Infrared spectra (transmission mode) of selected RuY zeolites: (a) treated in flowing O_2 at 450 K followed by exposure to 50 torr of NH_3 at 298 K; (b) as in (a) but subsequently heated to 423 K under 50 torr of NH_3; (c) treated in flowing O_2 to 450 K followed by heating in vacuo to 530 K; (d) as in (c) but subsequently exposed to 10 torr of NO at 298 K.

responsible for the band at 1925 cm^{-1} was not stable at higher temperatures in the O_2 atmosphere, and after treatment at 450 K, it was not observed. The band at 1875 cm^{-1} in the RuY zeolite behaved in the same manner as the single band at 1870 cm^{-1} noted for the RuX, so it is probable that an identical complex was present in both samples after treatment at 450 K in flowing O_2. The small difference in wavenumber ($\sim$5 cm^{-1}) between these bands in the two zeolites is attributed to the greater negative charge density of the X-type zeolite lattice.

After heating in O_2 above 473 K, the spectra in Figure 2e,j were observed for the X and Y zeolites, respectively. Following this treatment all of the bands of interest were removed. They were replaced by a very strong band at ca. 1400 cm^{-1} in the case of RuX and a weak band in the same region for the RuY sample.

To characterize further the ruthenium–nitrosyl complex formed in RuY by heating in flowing O_2 to 450 K, this sample was thoroughly evacuated and subsequently exposed to 50 torr of NH_3 at ambient temperature. The resultant IR spectrum is shown in Figure 3a. The nitrosyl band, while retaining its intensity, has been shifted from its original 1875 to 1840 cm^{-1}. The intensity of the NH_4^+ band at 1460 cm^{-1} was increased sharply by the addition of gas-phase NH_3 while that of the coordinated NH_3 band at 1335 cm^{-1} was unaffected. A lengthy evacuation of the sample at this point restored the nitrosyl band to its original position at 1875 cm^{-1}. This reversible behavior was likewise observed for the RuX zeolite sample.

When the sample just described was heated while still in contact with 50 torr of NH_3, the nitrosyl band at 1840 cm^{-1} was attenuated and a new band appeared at 2000 cm^{-1}. This exchange was evident at temperatures as low as 323 K and was virtually complete at 423 K. The IR spectrum at this point is reproduced in Figure 3b. The alternative use of ND_3 did not change the wavenumber of the new band at 2000 cm^{-1}.

The IR spectrum in Figure 3c is that of RuY which had been heated to 450 K in flowing O_2 followed by heating in vacuum to 530 K. All bands of interest have been removed. However, if the RuY pretreated in this fashion was exposed further to 10 torr of NO at 298 K, the IR spectrum in Figure 3d was observed. The two major bands which appeared were at 1895 and 1750 cm^{-1}. A similar spectrum was obtained when 10 torr of NO was exposed to a RuY sample at 298 K which had been reduced in H_2 at 683 K for 20 h. Substitution of ^{15}NO for ^{14}NO resulted in a shift of the two bands to 1860 and 1720 cm^{-1}, respectively.

ESCA Results. Portions of the ESCA spectra in which the 1s level of nitrogen (395–410 eV) and the 3d level of ruthenium (275–290 eV) generally appear were monitored for three selected RuY samples. These include the freshly prepared starting material, the sample after heating in flowing O_2 to 450 K, and the sample treated in O_2 at 450 K and subsequently heated to 530 K under high vacuum. The peaks in the region of the N 1s energy for the first two samples are complex as might be anticipated from the variety of N-containing complexes which may be present.[12] However, after evacuation at 530 K, virtually all nitrogeneous material was removed from the zeolite surface.

It is unfortunate that the Ru 3d levels lie so close to the C 1s peak at 285 eV. The only peak which can be assigend unambiguously to ruthenium was observed at 281.6 eV after treatment in flowing O_2 to 450 K followed by evacuation at 530 K.

Discussion

Following decomposition in O_2 at 343 K the DRS indicates that several different ruthenium complexes may be present. As pointed out by Madhusudhan et al.,[13] the 540-nm adsorption in the DRS probably arises from "Ru red", $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$, a complex which in solution displays a strong absorption at this wavelength.[14,15] The bands at 360 and 740 nm are more difficult to assign. However, the infrared band at 1870 cm^{-1}, in the region typical of coordinated nitrosyl ligands, also appeared after this pretreatment. It is therefore probable that the 360- and 740-nm bands are due to one or more ruthenium–nitrosyl complexes.

In the case of RuY at least two forms of nitrosyl bands are indicated by the infrared bands at 1875 and 1925 cm^{-1}. The band at 1925 cm^{-1} could arise from several different ruthenium–nitrosyl complexes including $[Ru(NH_3)_5NO]^{3+}$[6,16] or $[Ru(NH_3)_4(NO)(OH_2)]^{3+}$.[17] It is interesting to note that a similar band has been observed by the exposure of a zeolite containing $Ru(NH_3)_6^{3+}$ to nitric oxide at room temperature in the absence of O_2.[18]

It was originally suspected that the black samples formed upon treatment in O_2 to 383 K were due to the presence of "Ru brown", the one-electron oxidation product of Ru red. However, Ru brown is a well-known complex which displays a prominent optical absorbance around 460 nm.[14,15] As this band was not observed in these experiments, the presence of Ru brown is excluded. Although the infrared spectra indicate the presence of ruthenium–nitrosyl complexes, we find no literature references which would account for the black samples observed following this treatment.

Very little can be deduced concerning this sample since it still contained a rather intractable mixture of ruthenium complexes (perhaps polynuclear), each of which could have arisen from a number of precursors. Furthermore, the ligands which could have been present in the coordination sphere of Ru include H_2O, NH_3, OH^-, O^{2-}, and NO.[8,13-16,19] The

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(12) One might expect only one nitrogen moiety to be observed for the RuY starting material, i.e., coordinated NH_3. However, the combination of ultrahigh vacuum and heat generated by the X-ray beam of the ESCA instrument leads to partial decomposition of the hexaammine–ruthenium complex.

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present experimental techniques are not sufficient to resolve such complexity.

It is possible, however, to surmise the most probable identity of the orange-pink complex observed after O_2 treatment at 450 K by considering the following summary of results. First, the IR spectra show that the predominant Ru complex in both the X and Y samples is a nitrosyl. The single, symmetric band observed in either zeolite would further indicate that this complex is a mononitrosyl. The wavenumbers of these nitrosyl bands (1870 and 1875 cm^{-1} for X and Y, respectively) are in the region generally attributed to nitric oxide coordinated as the nitrosonium ion, NO^+.[20] It is also evident from the residual bands at 1335 cm^{-1} in the IR spectra that a small amount of NH_3 remains in the ligand sphere of Ru.

The ESCA spectra of these samples demonstrate that the ruthenium retains it ionic character after this treatment at 450 K, with the most probable oxidation states being 2+ or 3+.[21,22] This range of oxidation states typically exhibits bands in the region of 282–283 eV[21] which is completely obscured by the C 1s peak. However, significant reduction would have been reflected in the appearance of obervable shoulders on the C 1s peak at 285 eV.

Finally, it appears that the ruthenium–nitrosyl complex in question is mononuclear. We have performed the X-ray crystal structures of both the RuX and RuY powder samples pretreated in this fashion.[23] The results of that study show that the Ru cations are located at site II where they are coordinated directly to three oxygens of the zeolite lattice, O_{zeol}. After consideration of this data, the most likely form of this novel complex is $[Ru(O_{zeol})_3(NH_3)_x(NO)]$. Since a coordination number greater than 6 is highly unlikely for a cation located at the site II, the value of x in this formula must be either 1 or 2.

There are two possible explanations for the behavior of the X and Y samples containing the $[Ru(O_{zeol})_3(NH_3)_x(NO)]$ complex on exposure to NH_3 at 298 K. One should recall that the nitrosyl stretching frequency was shifted by about 30 cm^{-1} to lower wavenumbers upon NH_3 addition but was restored to its original position by lengthy evacuation. The wavenumber shift might have been due to weak interactions between the nitrosyl ligand and the gaseous NH_3 saturating the zeolitic cavities. However, it is unlikely that such an interaction wöuld result in a shift as large as 30 cm^{-1}. It is more probable that $x = 1$ and the NH_3 interacted directly with the ruthenium by entering the coordination sphere of the complex. A similar type of complex where the ammine ligand is trans to the nitrosyl ligand has been reported for cobalt in a Y-type zeolite.[24] For such a model, the trans ammine ligand would give rise to a second IR band for coordinated ammine which is probably present but not observed due to the strong adsorption by the support below ca. 1300 cm^{-1}.

The interaction of the $[Ru(O_{zeol})_3(NH_3)_x(NO)]$ complex with NH_3 at higher temperatures resulted in the loss of the nitrosyl ligand with the appearance of a new band at 2000 cm^{-1}. This band is in a region which is typical of metal hydrides,[25] but the substitution of ND_3 for NH_3 did not alter the spectrum, and therefore the formation of a metal hydride is ruled out. This led to the conclusion that the 2000-cm^{-1} band was due to strongly adsorbed or coordinated N_2 which is known to be infrared active in this region of the spectrum.[26] It should be noted that Laing et al.[6] have prepared $[Ru(NH_3)_5N_2]^{2+}$ in a Y-type zeolite by reduction of $[Ru(NH_3)_5NO]^{3+}$ at room temmperature with hydrazine.

The decomposition of the mixed ammine–nitrosyl complex above 473 K and in the presence of O_2 produced RuO_2. The appearance of a band at 1400 cm^{-1} is indicative of the formation of a surface nitrate moiety.[25,27] Following decomposition under vacuum, the IR and ESCA spectra both show that virtually all of the nitrogenous material was removed at 530 K. The appearance of a peak in the ESCA spectrum at 281.6 eV would indicate that some of the ruthenium has undergone reduction; however, the assignment of this peak is not straight forward as Pedersen and Lunsford[21] have shown that the binding energy for Ru $3d_{5/2}$ may vary with either particle size or oxidation state.

The readsorption of nitric oxide at 298 K again produced nitrosyl complexes, but it is not clear whether the two IR bands at 1890 and 1750 cm^{-1} arose from a dinitrosyl complex of ruthenium or from two distinct mononitrosyls, perhaps of ruthenium in different oxidation states. Attempts to distinguish between these possibilities using a mixture of ^{14}NO and ^{15}NO were futile due to the large widths of the IR bands. Similar spectra have been reported following the adsorption of NO on silica-supported ruthenium metal particles.[28,29] Likewise, in this study bands at these wavenumbers were observed following NO adsorption on reduced ruthenium in the zeolite. It has been postulated that nitric oxide dissociatively adsorbs on ruthenium, resulting in a partially oxidized surface.[28] When nitric oxide is adsorbed onto this partially oxidized surface, two mononitrosyl species were observed. The possible oxidation of the ruthenium surface by nitric oxide tends to make the assignment of this species somewhat ambiguous.

It is significant that the RuX and RuY samples containing $[Ru(NH_3)_6]^{3+}$ may be partially deamminated, and a very stable $[Ru(O_{zeol})_3(NH_3)_x(NO)]$ complex formed at site II without a major fraction of the Ru being reduced to the metal. One should recall that the deammination of RuX and RuY by heating only *in vacuo* yields a large fraction of ruthenium metal.[7,10] In view of the catalytic activity of homogeneous ruthenium nitrosyl complexes, it will be of interest in future work to explore the catalytic properties of this novel ionic ruthenium nitrosyl complex in the zeolites.

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