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in mediation reaction like eq 1 when the reaction substrate already posesses fast heterogeneous rates and the reaction occurs at a polymeric monolayer has been anticipated by theory.[20]

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Registry No. I, 88000-69-5; II, 85185-57-5; III, 88000-70-8; IV, 88000-71-9; V, 88000-72-0; VI, 88000-73-1; VII, 85202-31-9; VIII, 88000-74-2; IX, 70811-29-9; X, 17112-07-1; XI, 88000-75-3; XII, 83605-44-1; XIII, 88000-77-5; XIV, 60804-74-2; XV, 15702-72-4; XVI, 88000-78-6; XVII, 88015-26-3; XVIII, 88000-80-0; poly-[(bpy)$_2$Os(vpy)$_2$]$^{3+}$, 88080-24-4; poly-[(bpy)$_2$Os(vpy)$_2$]$^{2+}$, 88080-25-5; Pt, 7440-06-4.

Photoassisted Catalytic Oxidation of Isopropyl Alcohol by Uranyl-Exchanged Zeolites

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Abstract: Suspensions of uranyl-exchanged zeolites mixed with solutions of isopropyl alcohol and acetonitrile undergo selective photocatalytic conversion of the alcohol to acetone. The photoassisted catalytic oxidation is sustained for over 300 h. Bulk photolysis experiments show that aging does occur. X-ray photoelectron spectroscopy experiments indicate that uranyl ions on the surface are slighly reduced with respect to the bulk. Luminescence lifetime measurements yield a range of long-lived components between 10 and 700 μs for the different zeolites. Quenching experiments show that the shortest lived components of crystalline uranyl-exchanged zeolites are responsible for this conversion to acetone. Liquid nitrogen and liquid helium temperature luminescence emission spectra show splittings of the vibrational rotational fine structure as the temperature is diminished. These splittings are indicative of site symmetry, and in the case of the uranyl-exchanged HZSM-5 with the isopropyl alcohol mixture, evidence is presented that the isopropyl alcohol binds to the excited uranyl ion. The nature of the active site and factors that are important in the mechanism of this reaction are described.

Introduction

Zeolites have received much attention recently in a wide range of contexts,[1] particularly in the area of catalysis. Their catalytic and absorptive properties, primarily in the cracking of petroleum,[2] as builders in detergents,[3] and as Fischer–Tropsch catalysts,[4] have been investigated in great detail. A large effort in related areas involving spectroscopic studies of zeolites including magic angle spinning nuclear magnetic resonance,[5] X-ray diffraction,[6] surface analysis,[7] and X-ray absorption[8] has brought about several fundamental questions regarding the structure and stability of these materials.

The role of light in the transformation of reagents inside zeolites and the use of photochemical techniques, such as luminescence methods[11,13] and photoacoustic spectroscopy,[12] are resonably well understood although the number of photochemical studies of zeolites falls far behind the enormous volumes concerning thermal activation.[9,10]

Some of the most interesting and promising reports concerning the photochemical behavior of inorganic species in zeolites have been the water-splitting studies by europium,[14] silver,[15] and titanium-exchanged zeolites,[16] as well as by Ru(bpy)$_3^{2+}$ complexes in zeolites.[17] Electron-transfer[12,18] and energy-transfer[19] reactions have also been reported recently. Further discussion of these studies can be found elsewhere.[20]

Since this time, work by Lunsford and Camera[21] has shown that infrared spectroscopy can be used to explore the photoaquation of transition metal complexes like iodopentaamminerhodium(III). Valuable information regarding quantum yields and scattering was obtained. Ammonia has also been photogenerated over zeolites.[22]

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To our knowledge, there has only been one report of the photochemical conversion of organic reagents by inorganic ions in zeolite matrices. In that preliminary report,[20] we showed that uranyl ions could be exchanged into zeolites and then photolyzed in the presence of isopropyl alcohol to form acetone. Selective conversion was observed only if the zeolites had intermediate or large pores *and* if they were crystalline. In addition, there was a good correlation between the presence of vibrational rotational fine structure in the room-temperature luminescence spectra and the degree of crystallinity as determined by X-ray powder diffraction experiments.

Several unanswered questions have been raised concerning our preliminary results on the photochemical conversion of isopropyl alcohol into acetone:[20] 1. Is the process catalytic? 2. What is the nature of the active site? 3. What is the mechanism of this reaction? 4. Are other factors such as aging and poisoning of the sites important?

This paper addresses these questions. The results of luminescence emission, luminescence lifetime, bulk photolysis, and surface analysis experiments are presented.

Experimental Section

Synthesis of Zeolite Materials. Uranyl ions were exchanged into zeolites NaY, NaX, NaA, NH_4Y, NH_4X, NaZSM-5, sodium mordenite, and hydrogen mordenite by adding 100 mL of a 0.01 M $UO_2(CH_3CO-O)_2{\cdot}2H_2O$ solution to 1 g of zeolite in a 250-mL round-bottom flask. The flasks were stoppered and sealed with Teflon sleeves; the mixtures were stirred for 24 h. The uranyl-exchanged zeolites were then washed with 15 mL of distilled deionized water. The solid exchanged zeolites were transferred to test tubes that were evacuated on a vacuum line to a pressure of 0.001 torr. Samples were stored in capped glass vials and sealed with parafilm for later use.

Zeolites A (Lot No. 061576), X (Lot No. 08077), and Y (Lot No. 042578, SK-40) were obtained in the sodium forms from the Alfa Ventron Corp., Danvers, MA. Zeolite ZSM-5 was synthesized according to procedures found elsewhere.[23] The NH_4Y (Lot No. 042578, SK-41) was purchased from Alfa Ventron. Hydrogen mordenite (Lot No. 10282-51) and sodium mordenite were purchased from Strem Chemicals Inc., Newburyport, MA. Uranyl acetate dihydrate, $UO_2(CH_3COO)_2{\cdot}2H_2O$, and other uranyl salts were purchased from Alfa Ventron Corp. All organic solvents such as isopropyl alcohol and acetonitrile were purchased from the Aldrich Chemical Co., and were triply distilled and the purified by freeze–pump–thaw techniques.

Bulk Photolysis Conditions. The barrel photolysis cell used in this study was 20 mm in diameter and 60 mm long. Cooling coils made of copper tubing ($^1/_8$-in. diameter) were used to cool the bottom of the barrel cell. The entry port (5-mm diameter) on the top of the cell was stoppered during photolyses. Independent volume measurements of the solutions before and after irradiation indicated no evaporation loss in this cell. The large dimension of the cell was designed to have a large area of irradiation.

The light source for irradiation of the zeolite and organic mixture was a 1000-W continuous output Xe lamp, Model LH-51, from the Kratos Corp. A Model LPS-255 arc lamp supply was used to control the output power which in our experiments ranged from 400 to 760 W. The light was filtered through a bottle (40-mm path length) of distilled water and then through a 400-nm cutoff filter No. GG400, from Schott Optical Glass, Duryea, PA. After photolysis times of 10 min to 300 h, samples were syringed out of the barrel cell into the gas chromatograph.

Chromatographic Analyses. Gas chromatographic analyses of the photolyzed mixtures were performed on a Hewlett-Packard Model 5880A system equipped with a thermal conductivity detector. Typically 1 μL of solution was injected onto the column. The injector temperature was set at 210 °C and the oven at 100 °C. The 10-ft columns used for the separation were prepared using 10% Carbowax 20M, on 60–80 mesh Anakrom C-22 firebrick obtained from Analabs Inc., North Haven, CT. Absolute retention times were 1.11 min (acetone), 1.95 min (isopropyl alcohol), and 3.5 min (acetonitrile).

Spectroscopic Characterization. X-ray Diffraction. X-ray powder diffraction analyses of the ion-exchanged zeolites before and after irradiation were made with a DIANO-XRD 8000 X-ray powder diffractometer equipped with a Philips Electronic source. Solid zeolite samples were mounted on glass slides that were lightly coated with vaseline. Copper Kα radiation was used and sample scans were done at 2° 2θ/min.

Table I. Long-Term Photolysis

zeolite[a]	lamp power[b]	illumination, h	acetone, mol	cycles[c]
UO_2ZSM-5	461	16.5	1.2×10^{-4}	9.2
UO_2ZSM-5	752	8	2.4×10^{-4}	17.4
UO_2ZSM-5	752	16.5	2.8×10^{-4}	20.3
UO_2ZSM-5	752	40.5	5.4×10^{-4}	40

[a] Using 0.3 g of exchanged zeolite, 1.3×10^{-5} mol of UO_2^{2+} exchanged in zeolite. [b] Power in watts. [c] Cycles given by number of moles of acetone produced per total moles of uranyl ion.

Luminescence Measurements. Luminescence spectra were recorded on a double Czerny-Turner scanning monochromator, Model 1902, Spex Fluorolog spectrofluorometer. Variation in the excitation radiation were automatically corrected by a reference detector. Two fresh rhodamine B solutions, one before the sample and one after the sample, are used for this purpose. Both excitation and emission spectra were initially recorded for all of the uranyl-exchanged zeolites by loading 0.3 g of material into a quartz cell.

Liquid helium temperature experiments were done at the NSF Regional Laser Laboratory in Philadelphia, Pa. Liquid nitrogen temperature emission experiments were also carried out, in the Spex Fluorolog. Samples (0.1 g) for liquid nitrogen and liquid helium temperature experiments were sealed in quartz tubes (3-mm o.d.) on a vacuum line and then immersed into a homemade optically transparent dewar. Further details concerning liquid nitrogen luminescence measurements can be found elsewhere.[20]

For liquid helium experiments, fluorescence was monitored through a 455-nm 3-mm Schott GG 455 filter. Resolution was 6 Å/min with an effective 2-Å line width. The slits into the monochromator and the photomultiplier tube were 0.375 mm. The laser source was a Coherent Radiation Model CR15 argon ion laser operated at 2 W of UV power. This was used to pump a Coherent 590 dye laser operated with a two-plate birefringent filter of about 1 wavenumber line width which is extremely small with respect to the sample signal. The monochromator was from Instruments SA, Model HR-640. Experiments were conducted in a He dewar with a quartz tail, and samples were immersed in liquid helium at 4 K. The dye was Stilbene-3 from Lambda Physik operated at a power of 100–200 mW attenuated by full power to a factor of 10 attenuation by a neutral density filter.

The lifetime measurements reported in this paper were made with a standard PRA Model 3000 system except that a pulsed nitrogen laser (PRA Nitromite) was used for the excitation source, and a UV–vis grating monochromator (Model 33-86-79) from Bausch and Lomb, Rochester, NY, was used between the sample compartment and the photomultiplier tube. Data were collected with the use of a Model 174 phosphorescence delay unit since all lifetimes were greater than 10 μs. A Tracor Northern multichannel analyzer and a PDP-1103 computer were used for data collection, storage, and manipulation. Deconvolution and statistical analyses were done with software provided by the PRA Corp. of London, Ontario, Canada.

Surface Analysis Measurements. X-ray photoelectron spectroscopy experiments were done on a Leybold-Heraeus, LHS-10 system at the Leybold-Heraeus Analysis Laboratory in Export, PA. A Mg Kα X-ray source having an excitation energy of 1253.6 eV was operated at 12 kV and 20 mA. Survey scans over the kinetic energy range of 300 to 1300 eV and selected narrower regions scans for the elements U, Na, O, Si, and Al were done. Further details concerning data manipulation can be found elsewhere.[45]

Ion scattering spectroscopy and secondary ion mass spectrometry experiments were done with a 520B ISS/SIMS spectrometer interfaced to a PDP8 minicomputer. Information concerning sputtering rates, sample preparation, and experimental conditions have been published elsewhere.[25]

Results

Bulk Photolyses. Bulk photolyses of the uranyl-exchanged zeolites with isopropyl alcohol are reported in Table I. The ZSM-5 zeolite was selected for long-term photolysis experiments because it was found to be most active and selective for acetone

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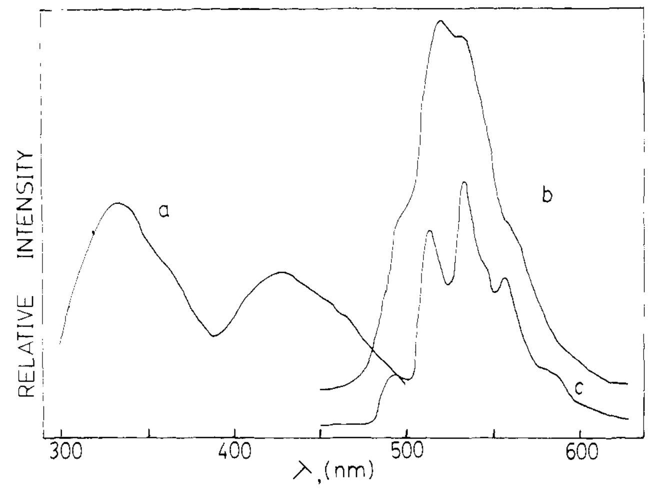

Figure 1. Luminescence spectra of UO_2NaY zeolite. (a) Excitation spectrum, room temperature. The emission wavelength was 518 nm. (b) Mission spectrum, room temperature. The excitation wavelength was 425 nm. (c) Emission spectrum, 77 K. The excitation wavelength was 425 nm.

production.[20] The number of moles of UO_2^{2+} ions exchanged into ZSM-5 as determined by energy dispersive X-ray analysis is 1.3×10^{-5}. This number was used in relation to the number of moles of acetone produced to calculate the number of cycles of acetone production. The amount of acetone was determined by gas chromatography. In terms of a mass balance, therefore, after 8 h of illumination with a lamp power of 752 W 17.4 cycles of acetone were produced. For purposes of comparison and evaluation of power, for a lamp power of 752 W, 6 mW of power at 425 nm is produced at the sample surface. The procedure used in determining this information can be found elsewhere.[24] The aging studies reported later in this paper also were done with a lamp power of 752 W.

X-ray powder diffraction analyses before and after the irradiation indicate that these materials are crystalline and no new peaks appear. Infrared and Fourier transform infrared experiments also show no new peaks after irradiation. The species UO_2^+ and UO_2 were not observed even as intermediates with electron paramagnetic resonance or with any other of the above techniques.

Luminescence Experiments. The luminescence excitation and emission spectra of zeolite UO_2Y are shown in Figures 1a and 1b, respectively. The room-temperature emission spectra of all of the zeolites discussed in the paper can be found elsewhere;[20] however, Figure 1b is included to show the degree of vibrational rotational fine structure for most materials at room temperature.

Table II contains information regarding the vibrational rotational fine structure for hydrated, dehydrated, and rehydrated zeolites at room temperature and at liquid nitrogen temperature. An example showing the added resolution of the fine structure at liquid nitrogen temperatures with respect to room temperature is shown in Figure 1c for uranyl-exchanged NaY zeolite.

Experiments performed at liquid helium temperature for the most part did not show any more resolution of the fine structure than samples at liquid nitrogen temperature. One notable exception to this trend occurred when the isopropyl alcohol solution was added to zeolite HZSM-5. The emission spectrum recorded at 4 K for this mixture is shown in Figure 2a. The same uranyl ZSM-5 zeolite without isopropyl alcohol present at liquid helium temperature is also plotted in Figure 2b for comparison.

Luminescence lifetime experiments for the uranyl-exchanged zeolites in the hydrated and dehyrated forms are reported in Table III. All of these samples, except for the dehydrated UO_2Na mordenite, contained two components, one of which was fairly short (25–100 μs) and the other which was long (90–900 μs). The percentages of each component are included. Lifetime data for uranyl ZSM-5 catalysts in the presence of increasing amounts of isopropyl alcohol are useful for quenching studies. For instance, the lifetime of UO_2NaZSM-5 zeolite is 25.8 μs (55.6%) in the solid state. As the isopropyl alcohol concentration is increased from 1.52×10^{-3} to 7.61×10^{-3} M, the lifetime (and percentage) decreases from 23.4 (34.0%) to 19.9 μs (20.2%). A representative plot of the lifetime data, including a plot of the sum of the squares of the residuals, is given in Figure 3. To give an appreciation for how these lifetime values fluctuate in different zeolites, a plot of Table III is represented in Figure 4.

Table II. Emission Spectra Data

sample	conditions[a,b]	emission peaks[c] and intensity[d]
UO_2 mordenite (Na)	RT, RT	490 (m), 503 (m), 513 (s), 535 (s), 550 (s), 575 (m), 600 (w)
UO_2 mordenite (Na)	RT, LN	487 (m), 495 (w, sh), 507 (m, p), 530 (s, p), 545 (s), 520 (m, sh), 555 (w)
UO_2 mordenite (Na)	370 °C, RT	495 (sh, br), 513 (s, br), 530 (m, sh), 600 (br)
UO_2 mordenite (Na)	H, RT	517 (s, p), 542 (s, p)
UO_2Y	RT, RT	495 (m, sh), 515 (s), 535 (s), 560 (m, sh, br)
UO_2Y	375 °C, RT	500 (m, p), 513 (s, p), 530 (s, p), 550 (w, br)
UO_2Y	H, RT	495 (m, sh), 515 (s), 535 (s), 560 (m, sh, br)
UO_2 mordenite (H)	RT, RT	495 (w, sh), 520 (m, br), 535 (br)
UO_2 mordenite (H)	RT, LN	495 (m, p), 520 (m, p), 545 (s, p), 576 (m, br), 600 (w, br)
UO_2 ZSM-5	RT, RT	520 (s, p), 545 (s, p)
UO_2 ZSM-5	RT, LN	497 (m, p), 512 (m, sh), 520 (s, p), 533 (s, p), 545 (s, p), 555 (m, sh), 570 (m, sh), 605 (w, br)
UO_2A	RT, RT	425 (s, br)
UO_2A	RT, LN	500 (vw, p), 525 (s, p), 545 (s, p), 565 (m, sh)
UO_2A	400 °C, RT (or LN)	no peaks
UO_2X	RT, RT	500 (m, sh), 520 (s, br), 543 (m, sh)
UO_2X	RT, LN	500 (w, sh), 517 (s, p), 53 (s, p), 560 (sh, br), 585 (m, br), 615 (w, br)

[a] Column a refers to thermal treatment of sample before emixxion spectra was taken: LN, liquid nitrogen; H, rehydrated after thermal treatment; RT, room temperature. [b] Column 6 refers to temperature of emission spectrum. [c] In nanometers. [d] sh, shoulder; w, weak, ; s, strong; m, medium; p, sharp peak; br, broad.

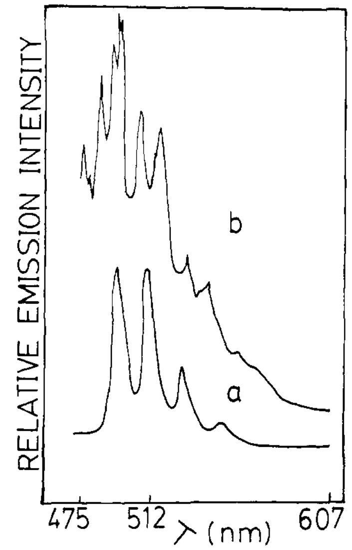

Figure 2. Luminescence emission spectrum of UO_2HZSM-5 at 4.2 K: (a) zeolite alone, (b) Zeolite with 1.0×10^{-5} M isopropyl alcohol in acetonitrile.

Surface Analysis. The survey scan of the X-ray photoelectron spectroscopy experiment shows peaks for U, O, Si, Al, and Na

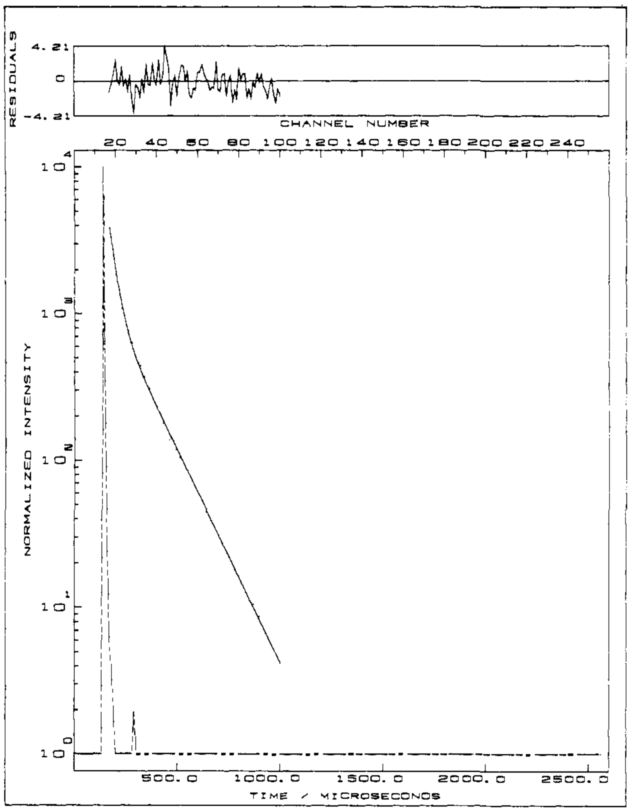

Figure 3. Typical luminescence lifetime decay for uranyl-exchanged zeolites. Residuals are given above the decay for UO_2NaY zeolite.

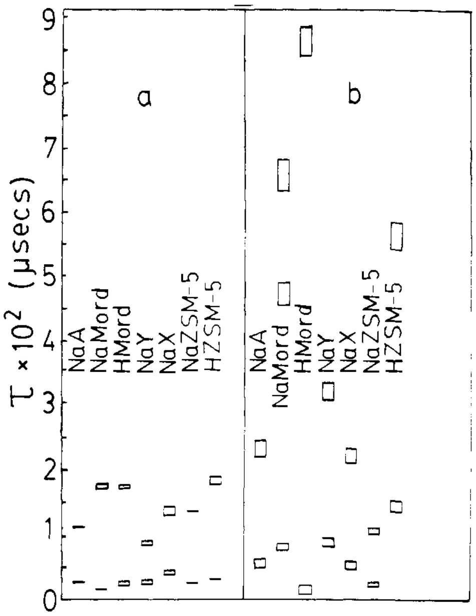

Figure 4. Plot of lifetime range for (a) hydrated and (b) dehydrated uranyl-exchanged zeolites at 375 °C.

for all of the uranyl zeolites. The semiquantitative analyses for Si, Al, and O gave ratios that were very consistent with the EDX analysis and with neutron activation and wet analyses of similar samples. The most interesting information obtained from several samples that we investigated as shown in Figure 5. The top spectrum reveals the kinetic energies of the $4f_{5/2}$ and the $4f_{7/2}$ (at higher kinetic energy) transitions of uranium in the as prepared UO_2Y zeolite. The kinetic energies in the lower spectrum are for the UO_2Y zeolite photolyzed for 7 h in the presence of the isopropyl alcohol–acetonitrile mixture. The results of the ISS–SIMS analysis of single crystals of faujasite exchanged with uranyl ions for 6 months can be found elsewhere.[25] The ISS–SIMS depth profile of the uranyl faujasite single crystals shows that the uranium concentration increases as one sputters away the upper layers of the crystal. The crater formed was imaged with electron microscopy techniques to check the depth of sputtering.

Table III. Luminescence Lifetimes of Hydrated and Dehydrated Uranyl-Exchanged Zeolites

sample	τ_1 (μs)	%	τ_2 (μs)	%	τ_3 (μs)	%
UO_2NaA	25.3	62.2	112	37.8		
$UO_2NaMord$	15.0	7.2	175	92.8		
UO_2HMord	25.0	10.1	176	89.9		
UO_2NaY	27.4	56.2	86.7	43.8		
UO_2NaX	41.7	47.9	139	52.1		
UO_2NaZSM-5	25.8	55.6	136	44.4		
UO_2HZSM-5	33.1	43.9	136	56.1		
UO_2NaA^a	57.1	42.3	235	57.7		
$UO_2NaMord^a$	82.8	*b*	473	*b*	657	*b*
UO_2HMord^a	14.5	34.7	866	65.3		
UO_2NaY^a	89.4	36.2	321	63.8		
UO_2NaX^a	54.6	40.8	224	59.2		
UO_2NaZSM-5^a	25.8	44.0	106	56.0		
UO_2HZSM-5^a	145	31.9	564	68.1		

[a] Dehydrated at 375 °C in vacuo. [b] Undetermined percentages, due to triple exponential behavior.

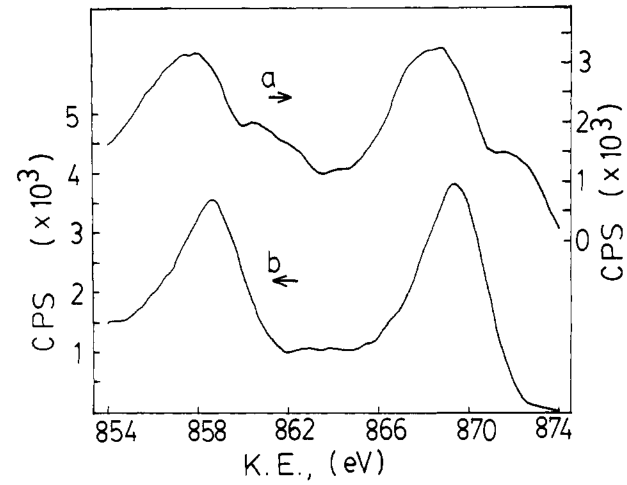

Figure 5. Uranium $4f_{5/2}$ and $4f_{7/2}$ transitions for (a) UO_2NaY zeolite and (b) photolyzed UO_2NaY with 1.0×10^{-5} M isopropyl alcohol.

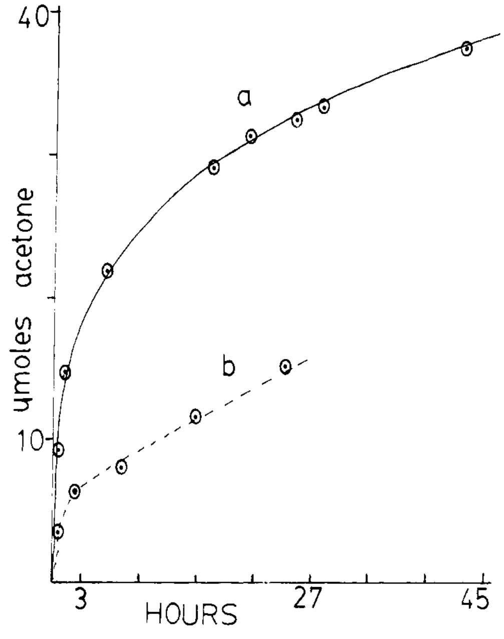

Figure 6. Plot of percent conversion vs. time for UO_2HZSM-5 in presence of isopropyl alcohol: (a) New catalyst, (b) used catalyst.

Aging Studies of the Catalysts. The uranyl-exchanged zeolites were photolyzed in the presence of the isopropyl alcohol solution for periods up to 300 h in order to monitor the percent conversion and how it changed with time. An example of a continuous photolysis of the same uranyl ZSM-5 zeolite catalyst for 300 h total is given in Figure 6. After each data point the zeolite is filtered, washed, and placed in the reactor with a fresh isopropyl alcohol–acetonitrile mixture and photolyzed. This means that the point at 41 h actually represents a *total* photolysis of the starting zeolite of 136 h. The lower curve shows that the catalyst indeed does deactivate since it represents taking the zeolite that was photolyzed for 136 h and restarting the experiment. The total amount of acetone produced diminishes by about a factor of 2 although the slopes of both curves at long photolysis time are approximately the same. The present conversion is still increasing at this point and the zeolite is still active (although somewhat diminished) even after a total of 207 h of photolysis. This particular zeolite catalyst was photolyzed for 100 h more with no decrease in activity or stability.

Discussion

A. Uranyl Photochemistry. The uranyl ion has a unique stereochemistry and very distinctive spectroscopic properties. Blue light is absorbed by the uranyl moiety and luminescence predominantly occurs in the green region of the visible spectrum. Jorgenson and Reisfeld[26] have noted that the emission is neither fluorescence nor phosphorescence and that Ω replaces J as a quantum number in linear symmetries. They have suggested that the luminescent eigenvalue of the uranyl ion is the lowest of the three eigenvalues for $\Omega = 4$. However, the uranyl ion in several environments is not an isolated linear moiety, and the quantum yield of luminescence and the lifetime are often influenced to a certain extent. Absorption, excitation, and emission spectra are indeed subject to environmental and geometrical effects. In fact, vibronic structure resolved in low-temperature optical experiments can be used to understand the importance of ligand-field effects. The details of uranyl photophysics have recently been reviewed.[26] A conclusion to be drawn from this review is that several researches have been investigating the uranyl moiety for decades and that much is still unknown about energy levels, electron-transfer bands, and the overall stereochemistry of the uranyl ion.

Nevertheless, it is widely known among researches in the area of uranyl photochemistry that the uranyl ion is unique with respect to other inorganic ions because it not only luminesces but also has the ability to photooxidize a variety of substrates. The lowest excited eigenvalue of the uranyl ion is strongly oxidizing and can abstract hydrogen atoms from several organic molecules. Excellent reviews of the photophysical and photochemical processes that are believed to occur in uranyl systems can be found elsewhere.[27]

The emission, excitation, and luminescence lifetime experiments as well as the bulk photolyses reported in this paper are very much in line with the general features of uranyl ions in other solid substances such as phosphate glasses[28] and inorganic coordination complexes. The excitation and emission spectra for the uranyl Y zeolites observed in Figure 1 closely resemble these related complexes. Although there is considerable disagreement in the literature about the orbitals that are used in the bonding of uranium to oxygen based on extended-Hückel[29] and Hartree–Fock[30] calculations and confusion concerning the mechanism of reaction of organic photooxidations,[31,32] we will attempt to clarify the chemistry of the uranyl ion in zeolites.

B. Photoassisted Catalysis. The data in Table I clearly show that significant amounts of acetone can be produced at room temperature via visible irradiation of isopropyl alcohol/uranyl-exchanged zeolite mixtures. Even under fairly low power (461 W) irradiation, catalytic amounts of acetone can be produced by using uranyl-exchanged zeolite ZSM-5. Previous results from our laboratory[20] have shown that ZSM-5 exchanged with uranyl ions gives the highest yield of acetone with respect to other zeolites like A, X, and Y. If the luminescent lifetime data reported in Table III are correlated with the percent conversion of isopropyl alcohol of the various zeolites, it is observed that the shortest lived components are the most active in this conversion. For instance, uranyl-exchanged ZSM-5 zeolites have short components of approximately 20 μsecs. The mordenite samples are very inactive and have longer lifetimes of approximately 175 microseconds. Further proof concerning the activity of a short lived component comes from the quenching studies. As more and more isopropyl alcohol is added, it quenches the uranyl ZSM-5 emission. The short component of about 26 μs continually decreases in amount as the quenching concentration increases.

C. Nature of Active Sites. The room-temperature emission and excitation spectra of the uranyl-exchanged zeolites provide a wealth of information. As observed in Figure 1a, vibrational rotational fine structure only occurs in the emission spectrum. The maximum in the excitation spectrum occurs at approximately 425 nm, although significant emission intensity is apparent at higher wavelengths up to about 475 nm. There is a good relationship between the amount of fine structure and the degree of crystallinity of the zeolite.[20] When uranyl ions are in certain ligand-field environments, the vibrational rotational fine structure sometimes increases as the temperature is lowered. At times the number of peaks and their position can be used to identify the stereochemistry of the uranyl environment.[33]

The emission spectrum in Figure 1c shows that the fine structure can be partially resolved for uranyl-exchanged Y zeolite at liquid nitrogen temperature. In fact, the data of Table II give the impression that even lower temperatures would yield sharp fine structure and therefore that an assignment of uranyl ion microenvironment in the zeolite would be possible. This belief is based on other low-temperature high-resolution optical studies.[34]

Luminescence emission spectra recorded at liquid helium temperature were for the most part just as broad as those taken at liquid nitrogen temperature. This was quite surprising and may indicate that molecular motion is still occuring at these low temperatures. The liquid helium temperature emission spectrum in Figure 2 recorded for ZSM-5 in the presence of isopropyl alcohol was a rare exception in contrast to the rest of the samples. The number of peaks in the emission spectrum alone indicates that isopropyl alcohol is binding to the uranyl ion. Although an unequivocal assignment cannot be made for the isopropyl alcohol–uranyl zeolite complex, the vibronic progression can be used to ascertain that the overall symmetry of the uranyl environment is less than D_{2h} and that the isopropyl alcohol is binding in an equatorial site. These conclusions are based on emission studies of the uranyl ion fine structure done at low temperatures for single crystals of uranyl inorganic salts[33,35] and hydrogen uranyl phosphate glass samples.[36] This is not meant to imply that the binding of isopropyl alcohol to the uranyl ion always occurs in the equatorial position for other zeolites or in solution phases.

A model that can be proposed for the environment of the uranyl ion in the active ZSM-5 catalyst is proposed below. The environment of the uranyl ion before introduction of the isopropyl alcohol is that of an eight-coordinate complex, having the usual linear UO_2^{2+} moiety surrounded by six equatorial ligands. The

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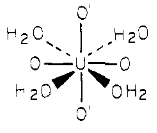
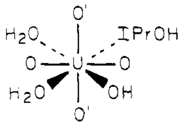
vibronic structure of the emission spectrum of zeolite Y indicates that the environment is exactly the same as that of uranyl acetate, the parent complex.[37] This means that the symmetry of the uranyl environment is D_{2h} with two trans framework oxygen molecules in the equatorial plane. This geometry has been depicted as compound I. The oxygens that are labeled with a prime are the original uranyl oxygens. These two bonds are the strongest and the shortest. The other oxygens are framework oxygen atoms located in the framework of the zeolite. The overall dimensions of this uranyl complex are too large for incorporation in the smaller sodalite cages. This assignment, which is based on luminescence emission data and a single-crystal uranyl acetate dihydrate structure,[37] has been independently confirmed by extended X-ray absorption fine structure experiments.[38]



I



II

On incorporation of the isopropyl alcohol, the weakest bonds may be broken. The water ligands are most easily replaced. The emission spectral features revealed at 4 K indicate a symmetry lower than D_{2h} which could correspond to the structure labled II above. This would account for the quenching of the uranyl emission and release of the acetone after hydrogen abstraction. Although we were not able to observe any more low-temperature active species for other zeolites like uranyl-exchanged X and Y, the excited-state intermediate complexes are probably similar.

The data reported in Figure 3 show that there are definitely two decaying species which we attribute to two different sites. The statistics are very reasonable and are a good indication that the data represent a double exponential decay. Attempts to fit these data to a single exponential were unsuccessful based on the nonrandomness of the residuals. The range of lifetimes of Figure 4 indicate how the lifetimes vary from one zeolite to another and after dehydration. Specific details concerning the lifetimes will be discussed later. Scattering of light off the zeolite particles is indicated by the laser trace. Most of the detected luminescence signal is due to the emission of the uranyl ion, and the correction for laser scattering off the zeolite particles is a minimal source of error in the analysis.

The luminescence lifetime data indicate that there are at least two different kinds of uranyl sites. One type of site has a relatively short lifetime of 20–50 μs and another of 80 to over 300 μs. Zeolite A is a small pore zeolite and the likelihood of having a site inside the pores like that of I or II is not high. The A material is amorphous and inactive in this conversion. The mordenite materials are also inactive, perhaps because of the type of channels. The mordenite channels are quasi-one-dimensional and there may be restrictions based on diffusion of molecules like isopropyl alcohol. Zeolites X and Y are large pore zeolites, and there are at least three sites in the supercage where the uranyl complex could reside, one of which seems to give the correct environment for isopropyl alcohol binding and conversion to acetone. This site is probably not in the center of the supercage and more likely involves framework oxygens of the 12-member window. This suggestion is based on the steric requirements of complexes I and II. The site location in ZSM-5 is more difficult to pin down, but the two framework oxygens could be part of the 10 ring.

Mechanistic Information. The mechanism for isopropyl alcohol conversion to acetone involves the reduction of the uranyl ion with concomitant oxidation of the organic substrate. In analogous solution-phase experiments the first step is reduction of the uranyl ion to uranium(V).[27] The second step involves the disproportionation of uranium(V) to uranium(IV) and regeneration of uranium(VI). It is not totally clear whether these two steps include intermolecular energy transfer, intramolecular energy transfer, or intermolecular hydrogen abstraction. In solution, the reduction of the uranyl ion to uranium(IV) eventually leads to a decrease in activity. The photolysis of uranyl salts or uranyl ions embedded in inorganic crystalline matrices with subsequent photooxidation of organic moieites in solution has not been reported until now.

To stop the decay of the uranyl ion, the disproportionation reaction must be prevented and the uranyl ion must be regenerated through some kind of oxidation process. The moderate tight binding of the uranyl ion to the zeolite lattice and the acidic environment of the zeolites should help prevent the disproportionation. Absorption maxima for U(V) between 625 and 1900 nm reported for silicates have not been observed, and photolyzed uranyl zeolite/isopropyl alcohol mixtures when analyzed in situ by EPR techniques show no signals for reduced uranium species or organic radicals. Reduced uranyl species [U(V)] have been proposed from solution EPR studies.[39]

Reduced uranium species in the zeolites have not been observed, perhaps because trace amounts of oxygen present in these solutions oxidize any U(V) back to UO_2^{2+}. Freeze–pump–thawed zeolite organic slurries show lower amounts of conversion.

Aging and Stability of the Catalysts. The aging studies reported in Figure 6 show that even after 300 h these catalysts are still active. The initial activity of the uranyl-exchanged zeolite has decreased after restarting the photolysis after 136 h. This means that there is some type of deactivation. Leaching of uranium species into solution, however, has not been found. This indicates that either the surface is changing or the active sites are dynamic.

All experiments that we have performed so far indicate that the activity is brought about by internal uranyl ions which bind isopropyl alcohol in the exited state leading to production of acetone. The only other evidence for deactivation comes from the X-ray PES studies represented in Figure 5. The upper spectrum of Figure 5 for the as-prepared zeolite shows both the $4f_{5/2}$ and $4f_{7/2}$ uranium transition at kinetic energies of 857.8 and 868.4 eV, respectively, as well as small shoulders at 860.8 and 872 eV. The lower spectrum of Figure 5 for the photolyzed samples shows the $4f_{5/2}$ and $4f_{/72}$ uranium transitions at kinetic energies of 858.7 and 869.1 eV, respectively, with no shoulders. The shift to higher kinetic energies after photolysis indicates that the uranium is in a more reduced oxidation state indicative of a reduced uranium(V) species.[40] Exposure of this sample to air regenerates the shoulders and shifts the U $f_{5/2}$ and $f_{7/2}$ transitions to lower kinetic energies again. The photolyzed sample was irradiated for 7 h under anaerobic conditions, filtered in a glove box, and loaded into the spectrometer under a nitrogen purge. Although these conditions are not absolutely the same as in our bulk photolysis experiments because of the ultra-high vacuum conditions, the X-ray PES results indicate that partial reduction of the uranyl ion may occur after long photolysis time.

Further evidence that the internal sites are the most active comes from the ISS–SIMS experiments.[25] These experiments involved measurements of uranium concentrations as a function of depth profiling into single crystals of faujasite and mordenite. These studies indicate that most of the uranium is concentrated in the interior of the single crystals. Microanalysis using wet chemical techniques and energy dispersive X-ray analysis have been used to generate ion-exchange isotherm data which also support the belief that the majority of uranium sites for these zeolites (except zeolite A) are internal.

These uranyl-exchanged zeolites are quite stable with respect to laser and lamp photolysis. The luminescence emission experiments of Table II show that several of these zeolites can be thermally heated to temperatures as high as 375 °C and then reversibly rehydrated. Zeolites X and Y fall into this classification. The uranyl-exchanged A zeolite totally breaks down at temper-

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atures about 375 °C and no emission is observed after thermal treatment. The mordenite samples change emission characteristics after thermal treatment and should be regarded as different materials after thermal activation. On dehydration, cations must bind to framework oxygen atoms. Channel blocking is also known to occur in mordenite and it has been suggested that cations on channel walls hinder or restrict diffusion.[43] After dehydration, these channels open up, and this may explain the new type of emission for sodium mordenite after thermal treatment. These uranyl-exchanged zeolites are stable to ion beams.[25] High-energy electron bombardment[44] can cause loss of crystallinity and mass.

Luminescence Lifetime Measurements. Luminescence lifetime experiments are important in the determination of the number of active sites. The correlation of high activity with a short-lifetime component is also an important observation. Further inspection of the lifetime data reveals several other conclusions. Figure 4 shows that dehydration at 375 °C in a 1×10^{-5} atm vacuum does significantly alter the lifetime. The lifetime can be used as a tracer of the microenvironment in the same way as emission experiments and other spectroscopic measurements. On rehydration of the dehydrated uranyl-exchanged X, Y, and ZSM-5 zeolites the lifetimes return to the same values of the as-prepared hydrated materials. Such information regarding the effects of thermal treatment of ions in zeolites is not always easily obtained.

The luminescence lifetime decay of 1% by weight of UO_2^{2+} in phosphate glass[28a,41] shows a two-component exponential which has been resolved into two lifetimes, one short of 115 μs and one long of 367 μs. Reisfeld and Jorgenson[41] attribute the short-lifetime process to a small concentration of uranyl pairs with a characteristic short U–U distance. Marcantonatos[42] has suggested that these species are excimers and has detected then in aqueous solution at a pH of 2. The uranyl-exchanged mordenite samples have lifetimes that are close to the excimer values. Excimers of uranyl ions could form more easily in a poor system like mordenite that is one dimensional. The emission spectrum of sodium mordenite has bands at 487 and 545 nm which compare well to that of the reported U_2O_2H[41] exciplex which emits at 488 and 544 nm. In any event, ground-state association of some sort should decrease the ability of excited uranyl ions to bind and oxidize isopropyl alcohol and other organic substrates. On dehydration of the mordenite, the channels open up[43] and the emission characteristics are different. Excited-state dimer formation is lowered because of new steric conditions.

Concluding Remarks

We have shown here that one can expect ion-exchanged zeolite molecular sieves to show a general ability to participate in photoassisted catalytic conversions and appear to remain stable for extended periods of time. It is clear that in applications involving zeolites there must be some way to increase the yield of these reactions either by decreasing scattering[21a] of the irradiation or by finding more efficient systems. Such developments would further support the use of zeolites in, for instance, solar conversion schemes. Our experiments suggest that these uranyl-exchanged zeolites are chemically and physically stable photocatalysts and could provide valuable hints concerning the selection of materials for efficient photochemical conversions.

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Registry No. Uranyl, 16637-16-4; isopropyl alcohol, 67-63-0; acetone, 67-64-1.

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Fluorescence Quenching Processes of Rhodamine B on Oxide Semiconductors and Light-Harvesting Action of Its Dimers

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Abstract: Fluorescence spectra, lifetime, and intensity of Rhodamine B (RhB) adsorbed onto SnO_2, TiO_2, and glass substrates were examined as a function of surface dye concentration. On the basis of the results, fluorescence quenching by RhB dimers and electron injection from the monomers and from the dimers are discussed. The relation with the electrochemical spectral sensitization is also discussed.

Introduction

The photophysical and photochemical behavior of dyes adsorbed on semiconductors are widely attracting recent interest. The spectral-sensitizing action of those dyes have had been playing an extremely important role in the photographic industry.[1] In recent investigations their functions are correlated to light-energy conversion[2] and a model of the primary processes of photosynthetic systems in vivo.[3] The amount of the dyes at interfaces is quite small in contrast to the importance of their functions, and this

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