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Photoionization of N, N, N'N'-tetramethylbenzidine in chromium silicoaluminophosphate microporous materials

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Received 20th March 2001, Accepted 14th May 2001 First published as an Advance Article on the web 20th June 2001

Silicoaluminophosphate (SAPO) microporous materials with Cr incorporated by ion-exchange and by direct synthesis were impregnated with N,N,N'N'-tetramethylbenzidine (TMB) and photoionized with 300 nm light at room temperature. TMB⁺ cation radicals are produced and characterized by electron paramagnetic resonance and diffuse reflectance spectroscopy. The photoyield is negligible for H-SAPO-*n* materials indicating that the chromium ion serves as an electron acceptor to enhance the yield of photoproduced TMB⁺ cation radical. The photoyield is dependent on the valence, amount and reduction potential of the metal ion and on the pore size of the SAPO material. Chromium SAPO materials are efficient hosts for the formation and stabilization of TMB⁺ cation radicals.

Introduction

Photoinduced charge separation in heterogeneous systems continues to attract attention.¹⁻³ One objective in this field is to design new materials which can sustain and maintain the charge-separated state long enough so that the free energy of the photoproduced cation can be utilized in driving a chemical reaction. A main problem in achieving long-lived charge separation is the rapid and thermodynamically favorable reverse electron transfer. This charge recombination results in the loss of the stored energy into heat.

Many systems such as vesicles, micelles, silica gels and molecular sieves have been examined as potential hosts to improve the efficiency of photoproduced energy storage.^{4–6} Such systems provide appropriate spatial and electronic organization of the donor and acceptor molecules to retard the reverse electron transfer. Thus, by appropriately tuning the electronic and spatial properties of the host system, one can maintain the integrity of the charge-separated state for a longer period of time.

N,N,N'N'-tetramethylbenzidine (TMB) has a low gas phase ionization potential $(6.1-6.8 \text{ eV})^7$ and undergoes efficient photoionization in solution. It has been known for a long time that TMB⁺ can be produced in polar organic solvents by photolysis or chemical oxidation.⁸ TMB can be easily oxidized by ultraviolet irradiation to form TMB⁺ which can be characterized by electron paramagnetic resonance (EPR) and optical spectroscopy.⁹

Silicoaluminophosphates (SAPO) are microporous materials that have been tested as catalysis for several reactions.^{10,11} SAPO-11, SAPO-5 and SAPO-8 have channel diameters of 6.3, 7.3 and 8.7 Å respectively. TMB has molecular dimensions of ~5 Å by 13 Å and hence it can be incorporated into the channels of SAPO-11, SAPO-5 and SAPO-8 microporous materials. Such host systems can provide an appropriate spatial environment to stabilize corresponding photoinduced radical cations.

The photoionization of TMB in micelles and vesicles has been extensively studied in our laboratory.^{12–16} However, one drawback of micelle and vesicle systems is the fact that the photoproduced TMB cation radical is not stable at room temperature so that previous photoionization studies were carried out at 77 K to detect stable TMB cation radicals. Only a couple of reports exist on the photoionization of TMB in heterogeneous solid systems.^{17,18} We have recently reported the photoinduced charge separation of N-methylphenothiazine in ion-exchanged Cr-SAPO-n and as-synthesized CrAPSO-n (n = 5, 8, 11) materials.¹⁹ The stability and the photoyield of the photoproduced methylphenothiazine cation radicals was higher when Cr ion was present in these systems. Thus, it is important to assess whether this enhanced charge separation extends to other photoionizable molecules like TMB. In the present study we have examined the photoionization of TMB in as-synthesized SAPO-n (n = 5, 8, 11) materials containing Cr introduced by ion-exchanged and by direct synthesis. The photoyield is found to depend on the nature of the metal, the amount of the metal ion, the redox potential of the metal ion and the pore size of the SAPO material.

Experimental

Syntheses of SAPO-n (n = 5, 8, 11)

The synthesis of the SAPO-5, SAPO-11 and SAPO-8 microporous materials have been described earlier.¹⁹ The X-ray diffraction (XRD) patterns of the as-synthesized and calcined materials are consistent with literature reports.^{20–22}

Preparation of M-SAPO-n

Metal ions were incorporated into both framework and extraframework positions. To incorporate metal ions into extraframework positions, liquid state ion exchange of the protons of the calcined H-SAPO-*n* materials with suitable metal ions was carried out. The samples prepared by liquid ion exchange are designated as CrH-SAPO-*n*(l). To incorporate Cr ions into framework positions, Cr(NO₃)₃ was added to the synthesis gel and all other conditions were similar to the ones used for the synthesis of SAPO-5.¹⁹ This synthesized material is designated as CrAPSO-*n*.

TMB incorporation

TMB was incorporated by immersing 0.1 g of SAPO in 1 ml of 1×10^{-2} M TMB in benzene for ~6 h in the dark. Benzene was removed by flowing nitrogen gas over the sample

for 1 h in the dark. For EPR measurements, 0.1 g of the sample was transferred into Suprasil quartz tubes (2 mm i.d. \times 3 mm o.d.) which were sealed at one end. For preliminary studies, the samples were evacuated below 1 Torr for ~ 3 h and flame sealed at the other end. It was observed that the photovield of the samples subjected to evacuation was similar to the photovield for samples that were not evacuated. Hence, further photoionization experiments were carried out without evacuation. For diffuse reflectance spectroscopy (DRS) the samples were loaded into a cylindrical quartz sample cell (22 mm diameter \times 20 mm path length).

Characterization

X-Ray diffraction powder patterns were recorded on a Siemens 5000 X-ray diffractometer using Cu Ka radiation of wavelength 1.541 Å in the range $10^{\circ} < 2\theta < 50^{\circ}$. Chemical analysis was performed by electron probe micro-analysis on a JEOL JXA-8600 spectrometer. The composition of the CrH-SAPO-n and CrAPSO-n materials was determined by calibration with known standards and by averaging over several defocused areas to give the bulk composition. EPR spectra were recorded at room temperature at 9.5 GHz using a Bruker ESP 300 spectrometer with a 100 kHz field modulation and low micropower to avoid power saturation. Photoproduced TMB radical cation (TMB⁺) yields were determined by double integration of the EPR spectra using the ESP 300 software. Each photoyield is an average of six determinations. The diffuse reflectance spectra were recorded at room temperature using a Perkin-Elmer 330 spectrophotometer equipped with an integrating sphere.

Photoirradiation

The TMB impregnated SAPO materials were irradiated using a 300 W Cermax xenon lamp (ILC-LX 300 UV) at room temperature. The light was passed through a 10 cm water filter to prevent infrared radiation and through a Corning No. 7-51 filter to give light of 300 ± 20 nm. The samples, sealed in quartz tubes were placed in a quartz dewar and rotated at a speed of 4 rpm to ensure even irradiation. The photoproduced TMB cation radicals were identified by EPR spectroscopy and diffuse reflectance spectroscopy.

Results

The pore sizes of the SAPO materials employed in the present study range from 6.3 Å in SAPO-11, 7.3 Å in SAPO-5 to 8.7 Å in SAPO-8. These are bigger than the molecular dimensions of the TMB molecule which are 5 Å by 13 Å and hence it is possible to incorporate TMB into these SAPO materials. Preliminary experiments were carried out in SAPO-5 materials. The XRD patterns of the SAPO materials synthesized showed the samples to be highly crystalline and the X-ray diffraction patterns agree well with literature data. However for SAPO-11 samples, the sample crystallinity was found to decrease by $\sim 20\%$ and $\sim 30\%$ after calcination and ionexchange respectively.

UV-Vis spectra

The spectra of calcined CrAPSO-5 samples show typically four bands at 270 nm, 350 nm, 450 nm and a broad band centered around 620 nm as shown in Fig. 1. The intensities of the bands increase monotonically with increase in Cr content. The higher energy bands (270 nm and 350 nm) are typically assigned to charge-transfer transitions associated with Cr(vI).²³ However, we did not detect any Cr(vI) in our calcined samples. To test for extraframework Cr(vi), 1 g of CrAPSO-5 was stirred in 20 ml of 1 M Ca(NO₃)₂ solution overnight. The filtrate was collected and 1 M AgNO₃ was added dropwise to test for CrO_4^{2-} , but no precipitate due to



0.0 500 600 700 800 200 300 400 Wavelength/nm

Fig. 1 Diffuse reflectance spectra of CrAPSO-5 samples (a) Cr/Si = 6.2×10^{-3} , (b) Cr/Si = 9.5×10^{-3} , (c) Cr/Si = 1.7×10^{-2} and (d) Cr/Si = 7.7×10^{-2} .

 Ag_2CrO_4 was formed. However, d-d optical transitions of Cr(v) occur in the same region.²⁴ Hence, we assign these optical bands to Cr(v) formed by the oxidation of Cr(III) during calcination. The EPR studies described later also suggest that Cr(v) is present in the calcined samples and hence we assign these optical bands to Cr(v). In the case of a Cr(III) liquid state ion-exchanged sample, typically three bands at 270 nm, 430 nm and 629 nm are observed. The bands at 430 nm and 630 nm are typical of octahedral Cr(III) in accordance with the literature.²⁵

Thus, the four bands obtained in calcined, hydrated CrAPSO-5 materials can be assigned to Cr(v) in either square pyramidal or distorted octahedral coordination, where the additional coordination is due to water molecules. In the case of liquid state ion-exchanged samples, Cr exists in the +3 oxidation state. The Cr(v) assignments in CrAPSO-5 and Cr(III) assignments in Cr-SAPO-n(1) (n = 5, 8, 11) agree well with EPR results.

EPR spectra

Absorbance (arbitrary units)

The EPR spectra of Cr ion liquid state ion-exchanged SAPO material (CrH-SAPO) show a very weak and broad signal at g = 1.97 assigned to Cr(III). On impregnation of TMB (prior to irradiation) a new signal at g = 2.00 assigned to TMB⁺ is seen. The intensity of the signal at g = 1.97 is much weaker in comparison with the signal at g = 2.00 assigned to TMB⁺ and hence can be considered to be negligible. This shows that some TMB⁺ cation radicals are produced during the sample preparation. After being irradiated at room temperature for 5 min, the samples show strong EPR signals. With further increase in irradiation time the intensity of the EPR signal increases further and then reaches a plateau in ~ 30 min. On further irradiation, the EPR intensity remains the same or decreases. An irradiation time of 30 min was hence selected for comparative photovield and stability studies. The weak EPR signals arising before irradiation have the same line shape as those observed after irradiation. Also a visual change in the color of the SAPO/TMB samples is easily seen; the samples prior to irradiation are pale green in color but turn dark green after irradiation, characteristic of TMB⁺ cation radicals in solid heterogeneous systems. The *g* value of 2.00 and the peak-to-peak linewidth of 24 G are similar to those of TMB⁺ in other heterogeneous systems and so the EPR line is reasonably assigned to TMB⁺ ion.^{26,27}

Fig. 2 shows the changes in the intensity of the EPR signal due to TMB⁺ cation radicals in liquid ion-exchanged MH-SAPO-5(1) samples. From Fig. 2 we can see that the highest yield is obtained for CrH-SAPO-5(1)/TMB. The intensity of the EPR signal for the Cr(III) and Mn(II) containing SAPO-5 samples rapidly increase during the first 10 min and then reach a plateau in about 30 min. For H-SAPO-5 there is virtually no increase in the intensity of the EPR signal due to TMB⁺ cation radical suggesting that the metal ion containing SAPO-5 materials are better hosts for forming and stabilizing TMB⁺ cation radicals. The rate of formation of the TMB⁺ cation radicals can be evaluated from the initial slopes of Fig. 2 assuming first order kinetics. The calculated rate constants for the formation of TMB⁺ cation radicals are $k = 2.2 \times 10^{-3}$ s⁻¹ for CrH-SAPO-5(l) and $k = 1.6 \times 10^{-3}$ s⁻¹ for MnH-SAPO-5(1). The order of the rate constants is consistent with the order of the photoyields.

The stability of the photoproduced TMB⁺ cation radicals is an important factor in designing efficient photoredox systems. The intensity of the EPR signal due to TMB⁺ cation radicals after 30 min irradiation was monitored as a function of time in order to determine the stability of the photoproduced TMB⁺ cation radicals. The decay of the TMB⁺ cation radicals can be calculated assuming first order kinetics in TMB⁺ from eqn. (1).

$$\mathbf{M}^{(n-1)+} + \mathbf{T}\mathbf{M}\mathbf{B}^{+} \to \mathbf{M}^{n+} + \mathbf{T}\mathbf{M}\mathbf{B}$$
(1)

The rate constants were evaluated assuming an exponential first order decay. The half-life $(t_{1/2})$ of the photoproduced TMB⁺ cation radicals was calculated to be $t_{1/2} \sim 20$ min for MnH-SAPO-5(l) and $t_{1/2} = 50$ min for CrHSAPO-5(l).

Cr ion-exchanged SAPO-5 has been found to exhibit higher photoyields and stability compared to either H-SAPO-5 or MnH-SAPO-5 samples. In our previous study, we had observed enhanced stability of photoproduced methylphenothiazine cation radicals in Cr as-synthesized SAPO-5 (CrAPSO-5) sample compared to CrH-SAPO-5(l).¹⁹ Hence, it is of interest to compare the photoyield and the stability of TMB⁺ cation radicals in CrAPSO-5 and CrH-SAPO-5(l) samples. Fig. 3 shows the increase in EPR intensity of TMB⁺ cation radicals vs. irradiation time in CrAPSO-5 (Cr/ Si = 4×10^{-3}) and CrH-SAPO-5(l) (Cr/Si = 6.2×10^{-3}) samples. Although the chromium content in these two samples is comparable it is clear that the photoyield is higher in CrAPSO-5 as compared to CrH-SAPO-5(l). The rate of for-



Fig. 2 Room temperature photoinduced TMB⁺ radical cation yield measured by EPR vs. irradiation time for MH-SAPO-5(l)/TMB (M = Cr, Mn and H).



Fig. 3 Room temperature photoinduced TMB⁺ radical cation yield measured by EPR vs. irradiation time for CrH-SAPO-5(l)/TMB (Cr/Si = 6.2×10^{-3}) and CrAPSO-5/TMB (Cr/Si = 4.0×10^{-3}).

mation of TMB⁺ cation radicals was calculated to be $k = 2.6 \times 10^{-2} \text{ s}^{-1}$ in CrAPSO-5(l) which is approximately ten times higher compared to the rate constant obtained for CrH-SAPO-5(l) ($k = 2.2 \times 10^{-3} \text{ s}^{-1}$). Fig. 4 shows the decay of EPR signal due to TMB⁺ cation radical in CrAPSO-5 (Cr/Si = 4×10^{-3}) and CrH-SAPO-5(l) (Cr/Si = 6.2×10^{-3}) samples at room temperature after irradiation for 30 min. The half-life of the photoproduced TMB⁺ cation radical is calculated to be $t_{1/2} = 175$ min for CrAPSO-5 (Cr/Si = 4×10^{-3}) whereas it was found to be only $t_{1/2} = 50$ min for CrHSAPO-5(l). Thus, we see that the photoproduced TMB⁺ cation radical is more stable in CrAPSO-5 compared to CrHSAPO-5(l).

In order to understand the influence of Cr content on the photoyield and stability, the photoionization of TMB was carried out in CrAPSO-5 samples with different Cr amounts. All the CrAPSO-5 samples show a signal at g = 1.97 assigned to the g_{\perp} component of Cr(v), possibly in square pyramidal coordination, while the g_{\parallel} component is not clearly resolved at room temperature. When the EPR measurements were carried out at 77 K for CrAPSO-5 samples, two signals were observed, a strong signal at q = 1.97 and a weak shoulder at g = 1.951. The intensity of the EPR signal at g = 1.97 was found to increase with an increase in Cr content. Zhu et al.28 have reported similar spectra for calcined, hydrated CrAPSO-11 at 77 K. They observed two EPR signals, one at g = 1.972and another weak signal at g = 1.947. The assignment of the EPR signal to Cr(v) in square pyramidal coordination is based on the g expression²⁹ for square pyramidal coordination. According to the g expressions, $g_{\perp} = g_e - 2\lambda/\Delta_0$ and $g_{\parallel} = g_{\rm e} - 8\lambda/\Delta_1$ where λ is the spin-orbit coupling constant



Fig. 4 Decay of photoproduced TMB⁺ cation radical at room temperature for CrH-SAPO-5(l)/TMB(Cr/Si = 6.2×10^{-3}) and CrAPSO-5/TMB (Cr/Si = 4.0×10^{-3}) after 30 min irradiation.

(a) (b)

(c)



Fig. 5 EPR spectra of CrAPSO-5/TMB (Cr/Si = 1.7×10^{-2}) at room temperature upon UV irradiation at 300 nm for (a) 0 and (b) 20 min.

of 160 cm⁻¹ for Cr(v) in an oxide environment³⁰ and Δ_0 and Δ_1 are the two lowest energy UV transitions for calcined, hydrated CrAPSO-5; the calculated values are $g_{\perp} = 1.981$ and $g_{\parallel} = 1.946$. These are in agreement with the experimental values of $g_{\perp} = 1.970$ and $g_{\parallel} = 1.951$ which seem to support the assignment of the UV spectrum and the EPR spectrum to square pyramidal Cr(v). Fig. 5 shows the EPR spectra of CrAPSO-5/TMB (Cr/Si = 1.7×10^{-2}) before and after irradiation for 20 min. Fig. 5(a) shows two EPR signals, one due to TMB⁺ cation at g = 2.00 and another at g = 1.97 due to Cr(v). The signal at g = 1.97 is assigned to a g_{\perp} component of Cr(v) in square pyramidal coordination while the g_{\parallel} component is not clearly resolved at room temperature. Fig. 5(b) shows the EPR spectrum after irradiation for 20 min. There seems to be an increase in the relative intensity of the peak at



Fig. 6 Diffuse reflectance spectrum of CrAPSO-5 (Cr/ $\dot{Si} = 9.5 \times 10^{-3}$) at room temperature upon UV irradiation at (a) 0, (b) 10 and (c) 20 min.





CrAPSO-5 (Cr/ $Si = 7.7 \times 10^{-2}$) at room temperature upon UV irradiation at (a) 0, (b) 20 and (c) 30 min.

g = 2.00 and a decrease in the relative intensity of the peak at g = 1.97. For CrAPSO-5/TMB samples the EPR signals due to TMB⁺ cation and Cr(v) partially overlap. A direct measurement of the signal intensity for TMB⁺ cation by double integration is hence not accurate. The relative intensity for the TMB⁺ cations in CrAPSO-5 samples was calculated in the following manner. The signals before irradiation were subtracted from the signals after irradiation. The relative intensity of the TMB⁺ cation was then estimated from the height of the resulting line at g = 2.00. This method of estimating the relative intensity of the TMB⁺ cation seems reliable since the line at g = 2.00 is fairly sharp and intense compared to the line at g = 1.97. The variation in the relative intensity of these two peaks seems to suggest that there is an increase in the intensity of the EPR signal due to TMB⁺ cation and a decrease in the EPR signal due to Cr(v) at g = 1.97.

The photoyield initially increases as the Cr content increases but beyond a certain concentration of Cr the photoyield decreases. Thus, there is an optimum concentration of chromium at which the photoyield is maximum. The rate of formation of TMB⁺ cation radical in CrAPSO-5 samples was calculated to be $k = 2.6 \times 10^{-2} \text{ s}^{-1}$ for CrAPSO-5 (Cr/ Si = 4 × 10⁻³); $k = 2.5 \times 10^{-2} \text{ s}^{-1}$ for CrAPSO-5 (Cr/ Si = 9.5 × 10⁻³); $k = 2.4 \times 10^{-2} \text{ s}^{-1}$ for CrAPSO-5 $(Cr/Si = 1.7 \times 10^{-2})$ and $k = 1.2 \times 10^{-3} \text{ s}^{-1}$ for CrAPSO-5 $(Cr/Si = 7.7 \times 10^{-2})$. The rate constants for the formation of TMB^+ cation radical are essentially the same for all the CrAPSO-5 containing samples except the sample with the highest Cr content. The half-life $(t_{1/2})$ of the photoproduced TMB⁺ in all the CrAPSO-5 samples was found to be approximately 3 h. The solid state ion-exchange process introduces metal ions into nonframework sites similar to a liquid state ion-exchange process. CrH-SAPO-5(s) (Cr/Si = 1.8×10^{-2}) was prepared with ~ 2.0 g H-SAPO-5 and 0.02 g CrCl₃ ground together well and heated to 873 K for 18 h in air. The reaction product was slowly cooled to room temperature and ground to a fine powder. EPR results show that Cr exists as



Fig. 8 Room temperature photoinduced TMB⁺ radical cation yield measured by EPR vs. irradiation time for CrH-SAPO-n(1)/TMB (n = 5, 8, 11).

Cr(v) in CrH-SAPO-5(s). The photoyield of TMB⁺ in CrH-SAPO-5(s) (Cr/Si = 1.8×10^{-2}) was found to be 2.5 times lower as compared to CrAPSO-5 (Cr/Si = 1.7×10^{-2}). The reason for the lower activity of CrH-SAPO-5(s) is not clearly understood at present.

Diffuse reflectance spectroscopic studies of the CrAPSO-5/ TMB samples are shown in Fig. 6 and Fig. 7. Fig. 6 shows the diffuse reflectance spectrum of CrAPSO-5 (Cr/Si = 9.5×10^{-3}). Curve (a) is the diffuse reflectance spectrum before irradiation. The absorption peak at 300 nm is assigned to TMB in the sample.^{31,32} In addition, there is absorption from 420 nm to 500 nm with characteristic vibronic fine structure. This is assigned to TMB⁺ ion in the sample. This is consistent with EPR results that indicate some TMB⁺ cation radicals are produced prior to irradiation during the sample preparation. Curve (b) shows the diffuse reflectance spectrum after irradiation for 10 min. After irradiation, the color of the sample became dark green and the optical spectrum shows a small decrease in the intensity of the peak due to TMB at 300 nm and an increase in the absorption from 400 nm to 500 nm, indicating that more TMB⁺ ions are produced in the CrAPSO-5 sample. In addition, there is a new absorption around 400 nm between the absorption peaks due to TMB and TMB⁺ ion. This is tentatively assigned to $(TMB)_2^{2^+}$. Curve (c) shows the diffuse reflectance spectrum after irradiation for 20 min. There is a further increase in absorption from 400 nm to 500 nm.



Fig. 9 Decay of photoproduced TMB⁺ cation radical at room temperature for CrH-SAPO-n(1)/TMB (n = 5, 8, 11) after 30 min irradiation.

Fig. 7 shows the diffuse reflectance spectrum of CrAPSO-5 $(Cr/Si = 7.7 \times 10^{-2})$. The diffuse reflectance spectrum is similar to the one described earlier except that the intensity of the peak due to $(TMB)_2^{2^+}$ is stronger and in addition it can be seen that some amount of $(TMB)_2^{2^+}$ exists in this sample prior to UV irradiation.

The pore size of the host system also plays a role in the photoyield and stability of the photoproduced radical cations. In order to understand the role of pore size, the photoionization of TMB was examined in CrH-SAPO-n(l) (n = 5, 8, 11) samples. The results obtained from the photoionization experiments are shown in Fig. 8. The photoyield decreases monotonically with increase in pore size. The stability of the photoproduced TMB⁺ cation radical was examined (Fig. 9) and the half-life estimated to be 72 min for CrH-SAPO-11(l) and only 21 min for CrH-SAPO-8(l).

Discussion

The EPR results clearly confirm the photooxidation of TMB molecules into TMB⁺ cation radicals in the SAPO materials at room temperature. The increase in the intensity of the EPR signal due to TMB⁺ cation radicals with time for ion-exchanged CrH-SAPO-*n* and as-synthesized CrAPSO-*n* materials suggests that Cr ion assists the photoionization of TMB. The role of metal ions as electron acceptors is clearly evident from the fact that there is net photoionization of TMB only in Cr and Mn containing SAPO materials and not in H-SAPO-5. The H-SAPO-5/TMB samples show very weak EPR signals after irradiation and almost no color indicating that TMB⁺ cation radicals are not stabilized.

Other evidence for the role of the Cr ion as the electron acceptor comes from the fact that the total EPR intensity of the sample prior to and after incorporation of TMB remains the same, but a decrease in the spin concentration of the Cr ion is observed. Fig. 6 seems to indicate a role of Cr(v) as an electron acceptor. After 20 min irradiation there is an increase in the relative intensity of the signal at g = 2.00 due to TMB⁺ cation and a decrease in the relative intensity of the signal at g = 1.97 due to Cr(v) as indicated by eqn. (2).

$$Cr(v) + TMB \rightarrow Cr(v) + TMB^{+}$$
 (2)

These points seem to suggest that Cr(v) acts as an electron acceptor and assists in stabilizing the TMB⁺ cation radical.

SAPO-5 containing Cr(III) and Mn(II) shows strong EPR signal due to TMB⁺ cation radical. The presence of Cr in SAPO-5 enhances the photoyield compared to Mn. The higher photoyield and stability of the TMB⁺ cation radical in CrH-SAPO-5(l) compared to MnH-SAPO-5(l) can be rationalized by the more positive reduction potential of Cr³⁺ $(E^0 \text{ Cr}^{3+/2+} = -0.407 \text{ V})$ compared to Mn²⁺ $(E^0$ $Mn^{2+/1+} = -3.0$ V).³³ The stability of TMB⁺ cation radical is related to the photoyield where a higher photoyield leads to higher stability of the TMB⁺ cation radical. For CrH-SAPO-5(1) the intensity of the EPR signal due to Cr(III) is much weaker compared to that of the TMB⁺ cation and hence the role of Cr(III) as an electron acceptor is not easily discernible. However the total EPR intensity of the sample prior to and after incorporation of TMB remains the same.

The photoyield and the stability of TMB⁺ cation radical in synthesized CrAPSO-5 containing Cr(v) were found to be higher compared to that in ion-exchanged CrH-SAPO-5(l) containing Cr(III). The higher photoyield and the greater stability of the photoproduced TMB⁺ cation radicals in CrAPSO-5 can be rationalized on the basis of the higher electron affinity of Cr(v) (E^0 Cr^{5+/4+} = 1.340 V)³⁴ as compared to Cr³⁺ (E^0 Cr^{3+/2+} = -0.407 V). The reduction potential of Cr(III) is negative making the reaction less favorable compared to Cr(v). The fact that the stability and the photoyield of TMB⁺ cation radical depend on the reduction potential of the metal ion suggests that the standard potential of the $M^{n+/(n-1)+}$ redox couple may be used as a guide for the efficiency of the process. Alkaitis *et al.*⁴ have similarly observed a dependence of the electron transfer rates from phenothiazine to metal ion acceptors in alcoholic micellar solutions and correlated this with the reduction potential of the metal ion.

CrAPSO-5 samples exhibit the highest photovield and stability towards TMB⁺ cation radical. The photoyield increases as the Cr amount increases, but beyond a certain concentration the photoyield decreases. Fig. 10 (inset) shows the relation between the amount of Cr(v) initially present and the amount of TMB⁺ produced after irradiation. The trend observed in the inset is similar to the trend observed in Fig. 7. Thus the amount of Cr(v) calculated from the spin concentration measured by EPR seems to influence the amount of TMB⁺ cation produced. Diffuse reflectance spectra of the CrAPSO-5 samples do not reveal the presence of any chromium oxide phase. In addition, the decay curves for TMB⁺ cation radical in all the CrAPSO-5 samples could be fit by a first order exponential decay. Also, the EPR spectra of the samples are symmetric which suggests the existence of only one paramagnetic species, namely the TMB⁺ cation radical. Thus, the lower activity exhibited by CrAPSO-5 (Cr/ $Si = 7.7 \times 10^{-2}$) is probably due to the formation of greater amounts of nonparamagnetic species. Diffuse reflectance spectra of CrAPSO-5 samples show an additional peak near 380 nm. This is assigned to the nonparamagnetic diaminediimine (TMB)₂²⁺ charge transfer (CT) complex formed with the structure suggested in Fig. 11.26

According to Awano *et al.*^{35,36} the oxidation of TMB leads to the formation of a band at 374 nm ascribed to a CT complex consisting of a neutral TMB molecule as a donor and the dication TMB²⁺ as an acceptor. TMB²⁺ assumes a diiminium structure or a quinoid structure and acts as a strong electron acceptor. Our results are in agreement with the results of Awano *et al.* and hence the assignment of the band at 380 nm to $(TMB)_2^{2+}$ seems best. The amount of $(TMB)_2^{2+}$ complex increases as the irradiation time increases but among the CrAPSO-5 samples studied, the intensity of the peak around 380 nm (assigned to $(TMB)_2^{2+}$) was highest for the sample containing the greatest amount of Cr. Thus the lower photoyield obtained for CrAPSO-5 (Cr/Si = 7.7×10^{-2}) is attributed to a greater amount of (TMB)₂²⁺ formation.

The pore size is also an important parameter affecting the photoyield and the stability of the photoproduced radical cations. This is related to the control of the spatial separation between the electron donor and the acceptor. The photoion-



Fig. 10 Room temperature photoinduced TMB⁺ radical cation yield measured by EPR vs. Cr/Si ratio for CrAPSO-5/TMB. The inset shows the amount of Cr(v) initially present and the amount of TMB⁺ radicals formed.





Fig. 11 Structures of TMB, TMB^+ and $(TMB)_2^{2+}$.

ization experiments show that the photoyield and the stability of the TMB⁺ cation radical decrease with increase in pore size. The photoyield decreases in the order CrH-SAPO-11 > CrH-SAPO-5 > CrH-SAPO-8. The pore size increases in the order SAPO-11 > SAPO-5 > SAPO-8. The decrease in the photoyield is attributed to the greater mobility of the TMB⁺ cation radical in the larger pores. This is consistent with the fact that the half-life of the TMB⁺ cation radical decreases with increase in pore size.

Conclusions

Cr ion-exchanged and as-synthesized SAPO-n (n = 5, 8, 11) materials were evaluated for the photoionization of TMB. The TMB⁺ cation radical yield was found to depend on the nature of the metal ion and the pore size of the host medium. In addition, the results indicate that the photoyield and stability of the TMB⁺ cation radical is dependent on the reduction potential of the metal ion incorporated into the SAPO material. The EPR studies seem to indicate a role of Cr(v) as an electron acceptor. EPR studies suggest a decrease in the relative intensity of the signal due to Cr(v) with irradiation time probably due to formation of Cr(IV) which is EPR silent.

Acknowledgement

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, the Texas Advanced Research Program and the Environmental Institute of Houston.

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