QUARTERLY TECHNICAL PROGRESS REPORT

for period 4/1/96 to 6/30/96

on DOE/PETC Grant No. DE-FG-22-93PC93218

"Photochemical Coal Dissolution"

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Work begun and described for the previous quarter on electron transfer processes in porous media continued to be the focus of work this quarter. Work focused on diphenylamine and benzophenone individually doped into the supercages of cation-exchanged X-type faujasite zeolites. The results show that diphenylamine exhibits the major effect in Na-X, K-X and Rb-X while benzophenone generally serves only to suppress weak background signals.

Figure 1 shows the (integrated) EPR absorption spectrum from diphenylamine in the K-X zeolite. At this preliminary stage of analysis the spectrum is tentatively assigned all or in part to the diphenylamine cation radical powder pattern. Similar but weaker spectra are found in doped Na-X and Rb-X but no spectra are generated from diphenylamine in Li-X and Cs-X. Table 1 gives the integrated intensities, $A_{\text{doublet}}$ of these spectra and the cage occupancies $\Theta$ based on Na-X loading studies. Intensity data ($A_{\text{doublet}}$) are also given for half-filled peaks observed at lower temperatures, a subject that will be discussed later.

It is noteworthy that the intensity of the doublet signal grows with increasing cation atomic number from zero at Li, reaches a maximum at K and decreases again to zero at Cs. The results suggest that the reaction may depend on a resonance between the empty cation M orbital in M-X and the diphenylamine $\pi$ donor orbital. For Li-X sites and most Na-X sites the acceptor orbital may be so low as to empty the non-bonding orbital of diphenylamine resulting in a diamagnetic species. For Cs-X sites and most Rb-X sites the cation is such a weak acceptor that no transfer occurs. In the most resonant case of Na-X sites a biradical state is formed as shown in the biradical scheme of Figure 2.

The existence of a peak at half-field, shown in Figure 3, is indicative of the presence of a molecular triplet state. The transition is an accumulation of intensity from weakly allowed $\Delta m_s=\pm 2$ transitions between the sublevels of the triplet state. The position of the line indicates a zero field splitting parameter $D/\hbar c = 0.0095 \text{ cm}^{-1}$. A magnetic dipole interaction of this magnitude indicates that the two unpaired electrons are $2.6 \text{ Å}$ apart on the average. This would imply that the unpaired electrons are in the same molecule or complex. The temperature corrected intensities of the half-field peak are of the order of one-tenth the intensities of the $g=2$ peak. However, as the half-field peak is weakly allowed, its transition probability is difficult to predict for comparison. For practical reasons concerning relaxation phenomena, we have not observed the allowed part of the triplet spectrum. The allowed part may also be weakened due to its extending over a wide field range.

The triplet spectra appear to have a similar dependence on cation, suggesting that the existence of the triplet is also the result of a resonance between the $\pi$ orbital of diphenylamine and the $s$ orbital of the zeolitic cation. The existence of a molecular-type triplet state suggests that the triplet involves covalent bonding between the cation and the diphenylamine $\pi$ orbital, such as indicated in the triplet scheme of Figure 2.
We propose that the only difference between the biradical species and the triplet complex is basically the distance between cation and diphenylamine. The biradical is formed when little favorable interaction (overlap) is possible between the cation and the diphenylamine π system because the cation site is removed from the interior of the supercage. On the other hand, the triplet complex is formed with cations near the interior of the zeolite supercage which are favorable for overlap with the diphenylamine π system.

Experimental work planned for the next quarter involves the completion of the Li-X and Cs-X experiments and the repetition of the experiments with diphenylamine deuterated on the amine nitrogen. Analysis will focus on powder pattern simulations of the biradical spectrum. Further experimental and/or analytical (spectrum subtraction) efforts will be made to measure or isolate the allowed part of the triplet spectrum.

Table 1. Relative intensities A of the signals observed in diphenylamine (DP)-doped X-type faujasite zeolites that have been exchanged with the indicated cations. The fractional loading, θ, of the zeolite supercages, in each case is also indicated.

<table>
<thead>
<tr>
<th>System</th>
<th>$A_{\text{doublet}}^{(a,b)}$</th>
<th>$A_{\text{triplet}}^{(c)}$</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP in LiX</td>
<td>0</td>
<td>(d)</td>
<td>(d)</td>
</tr>
<tr>
<td>DP in NaX</td>
<td>8.4</td>
<td>64.7</td>
<td>0.702</td>
</tr>
<tr>
<td>DP in KX</td>
<td>25.8</td>
<td>119.0</td>
<td>0.412</td>
</tr>
<tr>
<td>DP in RbX</td>
<td>4.2</td>
<td>33.5</td>
<td>0.885</td>
</tr>
<tr>
<td>DP in CsX</td>
<td>0</td>
<td>(d)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

(a) Signal at $g = 2$; 293 K; not corrected for temperature
(b) Estimated uncertainties are ±0.5
(c) Half-field signal; 5 K; not corrected for temperature
(d) Incomplete
FIGURE CAPTIONS

1. Electron spin resonance (ESR) absorption spectrum at $g=2$ of K-exchanged X-type faujasite zeolite doped with diphenylamine.

2. Molecular orbital mixing and filling scheme for the resonance of cation orbitals with the highest occupied diphenylamine (DP) $\pi$ orbital.

3. Electron spin resonance (ESR) absorption spectrum of the half-field region of Rb-exchanged X-type faujasite zeolite doped with diphenylamine.
Figure 2

Triplet

Biradical
ESR ABSORPTION SPECTRUM

DP/Rb-X, 5 K, -20dB, integrated 6/17/96

Absorption Intensity (V*G)

Magnetic Field Strength (Gauss)