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ESR Investigation of Radical Cations Formed from Aromatics and Heteroaromatics Adsorbed on Mo-Al₂O₃ Surfaces

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Molybdena-alumina is an important model catalyst system that has attracted considerable attention over the years. The behavior of adsorbed species on catalytic surfaces is also of interest because this may lead to a better understanding of the reaction mechanisms involved in the catalytic process. Using electron spin resonance, we have continued our systematic study of the molybdena-alumina system to which various aromatics and heteroaromatics have been added. We have investigated electron-transfer reactions with the molybdena-alumina surface and have also investigated the structural and dynamical aspects of the resulting adsorbed cations. Computer fitting of the cation ESR spectra has been carried out for a more precise determination of spectral parameters, and a comparison with solution spectral parameters has also been made.

I. Introduction

The molybdena-alumina system is a chemically interesting model of many industrially significant catalysts, and as a result, it has received considerable attention.¹⁻⁵ The incorporation of molybdena in the alumina support and subsequent thermal treatments can effect significant changes in the solid-state and surface properties of the system. For example, it is quite well-known that molybdena, even though it is incorporated initially as a hexavalent species, shows a distribution of valences, the distribution being determined by the thermal history of the system.⁶⁻⁸ In addition, the surface acidity of the support is changed significantly by the molybdenum deposit, the changes being manifested by the radically different appearance of the IR⁹ and NMR¹⁰ spectra of adsorbed pyridine. Finally, the molybdena-alumina surface is sufficiently different from the alumina support to allow the former to enter readily into electron-transfer reactions with organic molecules that are adsorbed on its surface. These electron-transfer reactions result in the formation of radical cations which may be studied by electron spin resonance (ESR) techniques.¹¹⁻¹⁹ The radical cations are, thus, sensitive probes of the surface of the model system and of the changes it undergoes with the various treatments.

In this paper we report ESR results which extend earlier measurements on the radical ions formed on the surface of molybdena-alumina.^{14,15} A carefully selected series of aromatic and heteroaromatic molecules was used to probe the surface characteristics of a $Mo-\eta Al_2O_3$ system. The molecules contained one, two, or three aromatic rings with greatly varying structural characteristics and ionization potentials. The ESR study of these species allows us not only to systematically investigate their electron-transfer reactions with the surface but also to assess the structural and dynamical aspects of the resulting adsorbed cations. The Mo(V) ESR spectra of the substrate have also been monitored, thus allowing for a more definitive assessment of the electron-transfer processes between probe molecules and catalytic surfaces. The precise ESR spectral parameters of the radical ions, obtained from computer fitting of the experimental spectra, are compared to the corresponding parameters of the solution species.

II. Experimental Section

A. Preparation of Samples. The experimental procedures used have been described earlier in detail.²⁰ Batches of 9% (by weight) Mo- ηAl_2O_3 were prepared, pelletized, and sieved to 20–40 mesh size. The solid-state and surface characteristics of this model catalytic system were investigated by monitoring the structure and dynamical behavior of certain aromatics and heteroaromatics ("probes") adsorbed on the catalyst surface. Fifteen different one-, two-, or three-ring aromatic hydrocarbons, some of which contained N, O, or S heteroatoms, were investigated (Figure 1). Solutions 10^{-2} M of the aromatic or heteroaromatic in cyclohexane were added to the catalyst. On



Figure 1. Molecular structures and ionization potentials of aromatic and heteroaromatic molecules ("probes") added to the surface.

occasion, only cyclohexane was added to the surface ("cyclohexane only" runs), or neither probe nor solvent was added ("blank" runs). Samples were prepared by one of three thermal treatments described below.

(1) Two-Hour Evacuation and Calcination (2-h EC). A 0.3-g sample of 9% Mo- η Al₂O₃ was weighed, placed in a reaction tube, and heated to 500 °C in a vacuum of about 10⁻³ Pa (10⁻⁵ torr). After 2 h at 500 °C, the reaction tube was removed from the vacuum line and heater, opened to the air, and cooled to 200 °C. The probe solution (2 mL) was added and the reaction tube immediately closed off from the air. The reaction tube was shaken for ca. 0.5 min to ensure adequate mixing. The sample was evacuated for 0.5 h after it appeared to be dry. While still under vacuum, the sample was transferred to a Pyrex ESR side-arm tube, which was sealed off and stored in the dark. Sufficient quantities of sample were prepared so that the ESR sample tube was filled well beyond the ends of the ESR spectrometer cavity.

(2) Four-Hour Evacuation and Calcination (4-h EC). As in the previous procedure, samples prepared by this technique were heated for 2 h at 500 °C under vacuum. However, the 4-h EC samples were heated for an additional 2 h at 500 °C in air. The rest of this procedure is the same as the one outlined above.

(3) Two-Hour Hydrogen Reduction (2-h H_2 Red.). These samples were heated for 2 h at 500 °C in dried, flowing H_2 . The rest of this procedure is the same as in (1), above.

B. ESR Spectra. A Varian ESR spectrometer (Model V-4600) operating at 9.5 GHz with 100-kHz field modulation and a 12-in. magnet was used to obtain spectra for the determination of g values. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used for calibration. A dual-cavity Varian ESR spectrometer (Model V-4500) with 400-Hz and 100-kHz cavities and a 9-in. magnet was used to obtain spectra for the determination of absolute intensities. An ash sample was used as reference. Signal intensities were determined by the "cut-and-weigh method". The first derivative of the absorption signal was recorded in all cases. All ESR measurements were made at room temperature.

A Fortran program was used to simulate ESR spectra.²¹ The program requires input parameters which describe the

TABLE I:	Physical	Characterization	of $\eta Al_2 O_3$
and 9% Mo-	$-\eta Al_2O_3$		• •

	total pore vol, cm³/g	pore radius, nm	surface area, m²/g
ηAl_2O_3 (powder)	0.30	3.0	201
$\eta Al_2 O_3 (20-40 \text{ mesh})$	0.32	3.0	211
9% Mo-Al ₂ O ₃ (20-40 mesh)			
thermally untreated	0.24	2.9	165
2-h EC	0.24	2.8	173
4-h EC	0.24	2.9	170
$2 \cdot h H_2 \text{ Red.}$	0.24	2.9	164

microwave frequency, magnetic field, signal height, choice of the line shape (Gaussian or Lorentzian), and suggested g values and line widths. Line shapes, g values, and line widths were varied until the best fit was obtained. The goodness of fit was determined by superposition of simulated and experimental spectra.

C. Other Characterization Techniques. X-ray diffraction (Picker powder X-ray diffractometer) was used to investigate the molybdena-alumina phase of several samples. Scanning electron microscopy and X-ray emission analysis (Jeol JSM-U3) were used to examine the distribution of molybdenum in variously treated samples. A nitrogen adsorption technique (BET) was used to determine the total pore volume, average pore radius, and surface area of Al_2O_3 and 9% Mo- ηAl_2O_3 samples.

III. Results and Discussion

A. General Characterization of Samples. Several 9% $M_0-\eta Al_2O_3$ samples were investigated by X-ray diffraction. The samples used were (a) thermally untreated 9% Mo- ηAl_2O_3 , (b) 2-h evacuation and calcination (2-h EC) followed by the adsorption of xanthene, and (c) 2-h H_2 -reduced (H₂ Red.) "blank". An analysis of the results confirmed the presence of the ηAl_2O_3 phase in each sample; however, the molybdenum phase could not be so readily identified. The observed molybdenum phase was found not to correspond to the spectra of known molybdenum oxide compounds. Although the presence of a heteroaromatic (xanthene) was not found to have any noticeable effect on the molybdenum or alumina species, the method of sample preparation was shown to have a significant effect. The intensities of the spectral peaks corresponding to the alumina and molybdenum oxide species were noticeably smaller in the spectrum of the hydrogen-reduced (H₂ Red.) sample compared to those of either the evacuation and calcination (EC) sample or the 9% $Mo-\eta Al_2O_3$ sample with no thermal treatment. The smaller signal intensities indicate a different crystalline arrangement of molybdenum and alumina in the hydrogen-reduced samples.

Two "solvent (cyclohexane) only" samples of 9% Mo- ηAl_2O_3 were analyzed by scanning electron microscopy and X-ray emission analysis. Microphotographs of the catalyst surface at 500× and 1000× show no significant differences between the evacuated-and-calcined (4-h EC) and the reduced (2-h H₂ Red.) samples. Both samples appear to be inhomogeneous, but X-ray emission analysis indicates that both have a very homogeneous distribution of molybde-num (Figure 2).

Results from the surface area and pore size distribution analyses of a powdered ηAl_2O_3 sample, a 20–40 mesh size ηAl_2O_3 sample, and several 20–40 mesh size 9% Mo– ηAl_2O_3 samples are shown in Table I. The total pore volume of the 20–40 mesh size alumina was 0.32 cm³/g, and the average pore radius and BET surface area were 3.0 nm and 211 m²/g, respectively. Four 9% Mo– ηAl_2O_3 samples were Radical Cations Formed on Mo-Al₂O₃ Surfaces

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Figure 2. Scanning electron microscope photographs of a 4-h evacuation and calcination $9\% \text{ Mo}-\eta \text{Al}_2\text{O}_3$ sample with adsorbed cyclohexane: (a) catalyst at 1000X; (b) molybdenum distribution of this sample.

also analyzed: a thermally untreated sample and samples prepared by each of the three thermal treatments (2-h EC, 4-h EC, and 2-h H₂ Red.). None of the thermal treatments was found to significantly affect the physical characteristics of the 9% Mo– η Al₂O₃ samples. The total pore volume was determined to be $0.24 \text{ cm}^3/\text{g}$ for both thermally untreated and thermally treated samples. The average pore radius was 2.8 or 2.9 nm for the four samples studied, and the pore volume distribution as a function of pore radii was not found to vary with thermal treatment. The BET surface area was 164 m^2/g in the thermally untreated 9% $Mo-\eta Al_2O_3$ sample and ranged from 165 to 173 m²/g in the thermally treated samples. Thus, incorporation of the molybdenum lowers the surface area of the substrate by 20% (regardless of the treatment). Also, the total pore volume is lowered by about 25%, whereas the pore radius remains unaffected.

In order to better understand the interactions which may be occurring on the surface, the size of the various probes added to the catalyst should be considered. Molecular sizes were determined by simple calculations by using densities and molecular weights and assuming a spherical molecular shape. For example, the radius of anthracene was calculated to be about 0.4 nm. Comparison of this dimension with the pore radii distribution of the catalysts shows that the probe molecules are much smaller than most of the catalyst pores.

Similar calculations can also be used to estimate the surface area covered by the aromatics or heteroaromatics added to the surface. If anthracene is used again as an example, about 11% of the 9% Mo– η Al₂O₃ surface area is calculated to be covered by these molecules. Similar

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small fractions of the surface area are expected to be covered by the other molecules used in this study. The radical cation signal intensities reported in the next section show that the maximum conversion of probe molecules to radical ions was about 37%. Thus, at the very most, 4% of the catalyst surface was covered by radical cations.

It was interesting to note that catalyst samples prepared by 2-h H_2 reduction were always brown in color, regardless of the presence or absence of probe and solvent. The evacuation and calcination samples were occasionally lighter in color, and, in contrast to the H_2 -reduced samples, the catalyst color was sometimes determined by the adsorbed species.

B. ESR of the Adsorbed Radical Cations and of the Mo(V) Species. In most of the systems studied, ESR detected two paramagnetic species. These signals, located at $g_{\rm av} \simeq 1.93$ and $g_{\rm av} \simeq 2.00$, were assigned to the Mo(V) species and the radical cation of the adsorbed species, respectively. In this section, we present the general features of the two ESR signals observed. A systematic investigation has been made of the dependence of these signals on the support and thermal treatment.

(1) Unsupported MoO_2 or MoO_3 . Thermally untreated MoO_2 and MoO_3 samples were analyzed by ESR. Various thermally treated MoO_3 samples were also investigated, including one where 2 mL of 10^{-2} M phenothiazine in cyclohexane was added to an EC MoO_3 sample. Neither the radical cation nor the Mo(V) species was observed in the ESR spectra of any of these samples.

(2) Thermally Untreated 9% $Mo-\eta Al_2O_3$ Samples. Two thermally untreated 9% $Mo-\eta Al_2O_3$ samples were prepared by evacuating for 0.5 h at room temperature. One sample was analyzed by ESR at this point. Phenothiazine (2 mL of a 10^{-2} M solution) was added to the other, the solvent was removed by evacuation, and the sample was then analyzed by ESR. Neither radical cation nor Mo(V) signals were observed in the ESR spectrum of the first sample. However, both signals were detected in the spectrum of the sample containing phenothiazine. Signal intensity measurements showed that an unusual, large cation signal and a very small Mo(V) signal were formed. The ratio of cation to Mo(V) signal intensities was 60.

(3) Thermally Treated 9% $Mo-\eta Al_2O_3$ Samples. (a) "Blank" Samples. As reported earlier in this paper, samples of 9% $Mo-\eta Al_2O_3$ were prepared by all three thermal treatments where no probes or solvents were added. ESR analysis detected the Mo(V) species in samples prepared by all three thermal treatments.

(b) "Solvent Only" Samples. Other thermally treated 9% Mo- η Al₂O₃ samples were prepared where only the solvent, cyclohexane, was added. Again, the Mo(V) signal was observed in samples prepared by all three thermal treatments, and extremely small cation signals (0.02 \times 10^{18} -0.04 × 10^{18} spins/g of catalyst) were detected in the The radical cation signal was EC samples (Table II). located at g = 2.00317 in the 2-h EC sample and at g =2.00112 in the 4-h EC samples. Since "cyclohexane only" samples had either no cation signals or barely detectable ones, and since cyclohexane has a relatively high ionization potential compared to the molecular probe (IP(cyclohexane) = 9.8 eV, it is assumed that cation signals resulting from the addition of probe molecules in cyclohexane solution are due entirely to ionization of the probes. It follows from this assumption that the spectral parameters of the cation signal, especially the g values, should be consistent with other spectral parameters reported for these systems from solution spectra. This is indeed the case (vide infra).

TABLE II:	Average ESR Signa	l Intensities of Mo(V)	and Cation Signals in	9% Mo-Al ₂ O ₃ Samples
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	2-h	EC	4-h	EC	2-h H	2 red.	
	cation spins	Mo(V) spins	cation spins	Mo(V) spins	cation spins	Mo(V) spins	
blank		2.5		0.5		3.7	
cyclohexane only	0.04	3.9	0.02	1.4		3.7	
toluene only	NA^{b}	NA^b	0.1	4.1		3.8	
toluene	NA^b	NA^{b}	0.03	1.7		3.7	
naphthalene	0.2	4.2	0.7	2.2	0.02	3.3	
anthracene	3.2	4.5	3.7	2.9	0.02	3.5	
phenanthrene	0.3	4.1	1.2	3.4		4.1	
azulene	0.6	5.4	0.6	4.1	0.7	2.9	
phenazine	0.04	4.0	0.03	2.5	0.3	3.2	
phenothiazine	4.5	2.4	14.7	0.4	0.4	3.8	
phenoxanthin	3.1	3.9	14.2	1.7		4.3	
phenoxazine	6.2	2.6	11.2	0.4	0.7	4.4	
thianthrene	1.9	5.2	3.0	4.7		3.6	
thiophene	0.06	2.8	0.05	2.3	0.005	3.7	
2,3-benzothiophene	0.2	5.7	0.6	3.5	0.01	3.5	
dibenzothiophene	0.06	4.4	0.4	2.6		3.5	
acridan	0.03	5.3	NA^{b}	NA ^b		3.3	
acridine		3.4	NA^{b}	NA^{b}		3.7	
xanthene	0.06	6.4	NA^{b}	NA^{b}		3.3	

^a ($\times 10^{18}$ spins/g of catalyst). Signed intensities represent average from up to four different samples. Maximum and minimum absolute errors are, respectively, 1.4×10^{18} and 0.01×10^{18} spins/g of catalyst. ^b NA = not available.

(c) Samples with "Probes" (Adsorbed Species). When samples of 9% $Mo-\eta Al_2O_3$ were thermally treated by evacuation and calcination and a probe solution was added, radical cation and Mo(V) signals were always detected by ESR. Depending on the probe added, the EC cation signal intensities ranged from 0.04×10^{18} to 6.2×10^{18} spins/g of catalyst for the 4-h samples (Table II). In similar samples prepared by H_2 reduction, the Mo(V) species was always detected although the cation signal intensity was often very small or altogether absent. Cation signal intensities in H₂-reduced samples ranged from about 0.005 $\times 10^{18}$ to 0.7 $\times 10^{18}$ spins/g of catalyst (Table II). Our results are consistent with those of other workers who report in general small cation signal intensities in H₂-reduced samples. Naccache and co-workers²² found that when perylene was added to H_2 -reduced $Mo-\eta Al_2O_3$ samples, radical cations were not formed, in contrast to the results obtained when the samples were prepared by evacuation and calcination. Similar findings were reported by Fogo²³ and Hall²⁴ in their studies of polynuclear aromatics added to silica alumina catalysts. When the catalyst was heated in flowing H₂, the cation signal intensity was always smaller than when the catalyst was simply calcined. Sometimes the decrease in signal intensity was by nearly an order of magnitude.²⁴

The cation signal intensity in our sample was also found to be affected by the length of thermal treatment and by the nature of the adsorbed species. A comparison of similarly treated samples to which probes had been added (2-h EC and 4-h EC) showed that the latter procedure usually produced samples with an increased cation signal intensity and a decreased Mo(V) signal intensity (Table II). It should be recalled that the sample is exposed to the atmosphere for the final 2 h in the latter procedure. A comparison of the 2-h and 4-h EC data also shows that the effect of a particular aromatic or heteroaromatic was roughly the same in both procedures. For example, an added probe which formed a large cation signal in the 2-h EC case also produced a relatively large cation signal in the 4-h case. Similarly, if the addition of a particular probe produced an intense Mo(V) ESR signal in the 2-h sample, the corresponding 4-h sample would also have a relatively intense Mo(V) signal.

C. Relation between Radical Cation and Mo(V) ESR Signal Intensities. It is expected that the overall elec-



Figure 3. Variation of the radical cation signal intensity of various 9% Mo $-\eta$ Al₂O₃ 4-h evacuation and calcination samples as a function of the first ionization potential of the added aromatic or heteroaromatic ("probe").

tron-transfer process between an adsorbed species and a surface will be determined by the ionization potential of the probe and the electron affinity of the surface. If, as in this case, the surface is the same for all experiments, then the propensity of a series of related molecules to form radical cations would be controlled primarily by the ionization potential of the probe. Richardson¹² has investigated the radical cations of a number of aromatic hydrocarbons adsorbed on synthetic faujasite that was ion exchanged with various metal ions. He showed that the degree of ionization of anthracene, pyrene, and naphthalene (but not of perylene) was related to the difference between their ionization energy and the electron affinity of the corresponding cation.

In our work, we found that the intensities of the cation signals from evacuated and calcined 9% Mo $-\eta Al_2O_3$ samples varied over three orders of magnitude. The higher

Radical Cations Formed on Mo-Al₂O₃ Surfaces



Figure 4. Variation of the ratio of radical cation and Mo(V) signal intensities of various 9% Mo $-\eta$ Al₂O₃ 4-h evacuation and calcination samples as a function of the first ionization potential of the added aromatic or heteroaromatic ("probe").

the first ionization potential of the probe molecule, the lower the ESR signal intensity. Figure 3 shows the plot of the log of the absolute cation concentration vs. the ionization potential of the probes for the 4-h EC samples. The ionization potentials of the probes varied from 7.13 eV for phenothiazine and phenoxazine to 8.87 eV for thiophene. A reasonably good linear relationship was observed for all probes except azulene.

A least-squares regression analysis was used to evaluate this linear relationship. All experimental data were included except for experiments where azulene or "cyclohexane only" were used. "Cyclohexane only" experiments were omitted because of the nonaromaticity of cyclohexane. Azulene was not included because it consistently and significantly deviated from the trend established by the other probe molecules (Figure 3). This deviation could be due to errors in the reported ionization potentials, but this is rather unlikely. Another possible explanation for the low signal intensity of azulene is that its radical cations may undergo some structural rearrangements which would result in partial quenching of the paramagnetic signal. Although inclusion of the azulene results would not negate the observed correlation, regression analysis yielded improved R^2 values when these results were omitted. Correlation coefficients of $R^2 = 0.89$ and $R^2 = 0.84$ were generated by the regression analysis to describe the variation of cation signal intensity as a function of ionization potential in the 2-h and 4-h EC cases, respectively. An even better fit of the 4-h EC data was obtained when the log of the ratio of the cation and Mo(V) signal intensities was graphed against the ionization potential of the adsorbed species. The correlation coefficient describing this relationship remained the same in the 2-h case $(R^2 = 0.89)$ but increased to $R^2 = 0.91$ in the 4-h case (Figure 4). This improved fit lends greater credence to the hypothesis that the relative propensity of the surface to accept an electron can be a significant factor in the electron-transfer process. We had observed earlier that EC treatments yield surfaces of somewhat greater variability. The plotting of the cation/Mo(V) signal ratio would take this variability into account and yield improved correlations as observed. In-



Figure 5. Comparison of experimental and simulated values of the cation/Mo(V) ratio for 9% Mo– η Al₂O₃ 4-h evacuation and calcination samples.

deed the improvement is greatest with the 4-h EC treatment which had the largest variation in Mo(V) signal intensities (Table II).

These linear variations of signal intensities as a function of the ionization potential of the probes may be described by the following general expression

$$y = c_1 \exp[c_2(\mathrm{IP}/kT)]$$

where c_1 and c_2 are constants generated in the regression analysis, y is the cation signal intensity or the ratio of cation and the Mo(V) signal intensities, IP is the ionization potential of the probe in eV, T is the temperature in K, and k is the Boltzmann constant in eV/K. The expression describing the variation of the 4-h EC signal intensity ratio as a function of the ionization potential of the adsorbed species is then

$$y = (1.61 \times 10^{16}) \exp[-0.122(\text{IP}/kT)]$$

and the analogous expression for the 2-h case is

$$y = (4.37 \times 10^{10}) \exp[-0.085(\text{IP}/kT)]$$

A comparison of the simulated and experimental values of the cation and Mo(V) ratios is shown in Figure 5 for the 4-h evacuation and calcination case.

The signal intensities of the radical cations generated on H₂-reduced surfaces were considerably smaller or even nonexistent. The maximum cation signal observed was that of azulene with a concentration of 0.7×10^{18} spins/g and an uncertainty of $\pm 70\%$ (Table II). Thus, these fewer data which have a greater uncertainty do not allow the opportunity to establish a meaningful correlation with ionization potential.

D. Quantification of the Radical Cation and Mo(V)ESR Signal Intensities. In order to better quantify the relationship between the electron-transfer reaction and the electron-accepting capabilities of the molybdena-alumina surface, the interaction of one specific probe, anthracene, with the catalyst was studied in greater detail by varying





Figure 6. Variation of the anthracene radical cation signal intensity as a function of the amount of anthracene probe incorporated on both 5% and 9% $Mo-\eta Al_2O_3$ systems.

TABLE III: Average ESR Intensities of Mo(V) and Anthracene Racial Cation Signals in 5% and 9% $Mo-\eta Al_2O_3$

total anthracene incorporated, 10 ⁵ mol	Mo(V) intensity, 10 ⁻¹⁸ spins/ g of cat.	cation intensity, 10 ⁻¹⁸ spins/ g of cat.	cation intensity, 10 ⁻¹⁹ spins/ g of Mo
	5% Mo-n A	Al.O.	
0	0.68 ± 0.04	2-3	
0.5	0.79 ± 0.05	0.42 ± 0.04	0.84 ± 0.08
1.0	1.26 ± 0.14	0.77 ± 0.13	1.54 ± 0.26
2.0	1.60 ± 0.22	0.08 ± 0.08	2.16 ± 0.16
4.0	1.34 ± 0.22	1.05 ± 0.10	2.10 ± 0.20
	9% Mo-nA	Al.O.	
0	2.46 ± 0.02	2 - 5	
1.0	3.94 ± 0.20	2.56 ± 0.13	2.84 ± 0.15
2.0	4.52 ± 0.02	3.24 ± 0.03	3.60 ± 0.03
4.0	5.44 ± 0.14	3.82 ± 0.14	4.24 ± 0.16
8.0	6.15 ± 0.40	4.28 ± 0.12	4.76 ± 0.13

both the amount of probe material used and the percentage of molybdenum in the surface species. All samples were treated according to the 2-h EC procedure. Both 5% and 9% Mo catalysts were used. The amount of anthracene allowed to come into contact with the surface was varied from 0.5×10^{-5} to 8.0×10^{-5} mol.

The absolute number of anthracene radical cation and Mo(V) spins per gram of sample for both 5% and 9% systems is given in Table III and shown in Figure 6. The number of radical cation spins initially increases and then levels off as the amount of probe material is increased. There is a concomitant decrease in the percent conversion to radical cations. This is to be expected since there is a finite number of active sites present on the surface. It should be noted that the plateau region occurs sooner for the 5% catalyst. This result is not unexpected, if the amount of molybdenum is to be correlated with the number of active sites. Indeed, the absolute number of radical cation spins produced on the 9% Mo catalyst was found

 TABLE IV:
 Comparison of Mo(V) and Anthracene

 Radical Cation ESR Signal Intensities

to	tal	anthracene	~		
1	ncc 1	orporated, 0 ⁵ mol	% (cation/ total probe)	% (Mo(V)/ total Mo)	cation/ Mo(V)
	~~~~		5% Mo-n	Al.O.	
		0	0,0110	$0.22 \pm 0.01$	
		0.5	$14.0 \pm 1.3$	$0.25 \pm 0.02$	$0.53 \pm 0.09$
		1.0	$12.8 \pm 2.2$	$0.40 \pm 0.05$	$0.61 \pm 0.19$
		2.0	$9.0 \pm 0.0$ $4.4 \pm 0.4$	$0.51 \pm 0.07$ 0.43 + 0.07	$0.08 \pm 0.10$ 0.78 ± 0.25
		1.0	9% Mo-n	AL O	0.10 ~ 0.20
		0	070 MO 17.	$0.44 \pm 0.01$	
		1.0	$42.5 \pm 2.2$	$0.70 \pm 0.04$	$0.65 \pm 0.07$
		2.0	$26.9 \pm 0.3$	$0.80 \pm 0.01$	$0.72 \pm 0.01$
		4.0	$15.9 \pm 0.5$	$0.96 \pm 0.03$	$0.70 \pm 0.05$
		8.0	$8.9 \pm 0.3$	$1.09 \pm 0.07$	$0.70 \pm 0.06$
	6.4				/R ² = 0.99
	6.0	-			X
	5.6	F		Y	
	5.2	-		ĺ	
ST)	4.8	_			
TALY	4.4	-		/×	
9 CA	4.0	L			
/SNI	3.6	Ļ	/	/	
018 SF	3.2	-	/		
Ξ	2.8	-	/		
ENS				χ 9∞ Mo ⊕ 5% Mo	-ηΑΙ ₂ Ο3 -ηΑΙ ₂ Ο3
INT	2.4	-	R ² = 0.95	5	,
INAL	2.0	$\vdash$	//		
/1 SIC	1.6	- 19			
Mol	1.2	⊢ /∮ [€]	I		
	.8				
	<u>,</u> 4	1			
				<b> </b>	
	4	0.4.8	1.2 1.6 2.0 2.4	2.8 3.2 3.6	4.0 4.4 4.8 5.2
		ANINRA	ITO'S SPINS	GATALYST	-110111

Figure 7. Variation of the Mo(V) signal intensity as a function of anthracene radical cation intensity for both 5% and 9%  $Mo-\eta Al_2O_3$  systems.

to be greater than that produced on the 5% catalyst for every quantity of probe studied. This concurs with similar results previously reported by Petrakis and Seshadri²⁵ and Naccache et al.²²

A more quantitative relationship between the radical cation and the Mo(V) spins can be obtained by calculating the ratio of the signal intensities as a function of total probe utilized (Table IV). The mean intensity ratio is constant at  $0.69 \pm 0.03$  and  $0.65 \pm 0.11$  for the 9% and 5% catalysts, respectively.

The most striking evidence for a relationship between these two species is shown in Figure 7 where the absolute Mo(V) intensity is plotted against the absolute radical cation intensity. This figure includes data points for all values of total probe studied. A definite linear relationship exists for both 9% and 5% catalysts as attested by the correlation factors of 0.99 and 0.95, respectively. The ratio of Mo(V) to radical cation spins is found to be 1.30 and 1.04 for the 9% and 5% systems, respectively. The smaller ratio of the 5% catalyst should not be construed as evi-

TABLE V:	ESR Catio	n Signals:	Line Width
$(\Delta H_{pp})$ in G	auss ^a		

			2-h	
	2-h EC	4-h EC	$H_2$ red.	
 blank	10.3			
cyclohexane only	11.6	19.3		
toluene only	NA	$\mathbf{N}\mathbf{A}$		
toluene	NA	11.9		
naphthalene	8.4	7.1	9.3	
anthracene	10.6	NA		
phenanthrene	8.8	8.3		
azulene	9.0	9.6	10.5	
phenazine	NA	11.6	23.1	
phenothiazine	19.0	20.3	17.1	
phenoxanthin	10.4	11.0		
phenoxazine	22.2	23.9	19.9	
thianthrene	17.1	NA		
thiophene	9.5	8.4		
2.3-benzothiophene	8.8	7.7	5.1	
dibenzothiophene	10.3	8.9		
acridan	8.0	NA		
acridine	0.0	NA		
xanthene	8.0	NA		

 $^{a} \Delta H_{pp}$  is defined as the distance in gauss between slope extrema.  $\Delta H_{pp}$  represents the average value from up to four different samples. Absolute errors ranged from 0.1 to 1.3 G, with typical relative errors of 1-6%. NA = not available.

dence for greater activity in this system. As shown in Table III, the absolute number of radical cations per gram of total Mo is always greater for the 9% system. This again substantiates previous work showing the 9% system to have the greater electron-accepting capabilities. The difference in the intensity ratio could possibly be attributed to differences in the manner in which the molybdenum is incorporated into the two catalyst systems. The fact that such a difference may exist is reflected in the greater ease with which the Mo is reduced to the +5 oxidation state in the 9% catalyst (Table IV). This is true even when no probe is utilized.

In summary, the experimental results show that a greater number of Mo(V) and radical cations are formed on the 9% Mo catalyst than on the 5%. A comparison of radical cation signal intensity with the total molybdenum present indicates that the 9% system has a greater electron-accepting capacity. This is confirmed by the more rapid saturation and therefore lower radical cation conversion on the 5% catalyst. The thermal treatment prior to adsorption of the probe principally determines the amount of Mo(V) formed and the capacity of the surface to enter into the electron-transfer reaction. The addition of the probe material is a secondary factor in Mo(V) formation. The existence of a quantitative relationship between the Mo(V) and the radical cation indicates that the capacity for radical cation formation is clearly related to the Mo(V).

E. Analyses of the ESR Spectra of the Radical Cations. (1) Experimental Spectral Parameters. The experimental line widths  $(\Delta H_{\rm pp})$  of the radical cation signals are summarized in Table V. The experimental line width is defined as the distance in Gauss between the maximum and minimum points of the first-derivative spectrum. This procedure was followed even for obviously anisotropic spectra and for spectra containing hyperfine splittings (vide infra). The values in Table V represent the average of  $\Delta H_{\rm pp}$  values from up to three different samples. The maximum absolute error was  $\pm 1.3$  G, but absolute errors were usually on the order of  $\pm 0.1-0.5$  G. The relative errors for these  $\Delta H_{\rm pp}$  values typically ranged from 1% to 6%.

TABLE VI: g Values o	<b>Radical</b> Cation	ESR Signals ^{$a$}
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			2-
	2-h EC	4-h EC	H ₂ red.
blank	2.00309		
cyclohexane only	2.00317	2.00112	
toluene only	NA	2.00261	
toluene	NA	2.00256	
naphthalene	2.00258	2.00249	2.00351
anthracene	2.00271	2.00256	NA
phenanthrene	2.00274	2.00254	
azulene	2.00259	2.00252	2.00302
phenazine	NA	2.00255	2.00303
phenothiazine	2.00547	2.00526	2.00526
phenoxanthin	2.00643	2.00635	
phenoxazine	2.00339	2.00286	2.00350
thianthrene	2.00778	2.00769	
thiophene	2.00282	2.00281	
2,3-benzothiophene	2.00356	2.00414	2.00300
dibenzothiophene	2.00472	2.00520	
acridan	2.00293	NA	
acridine		NA	
xanthene	2.00305	NA	

^a A g value is defined as the point halfway between slope extrema. Averages of values from up to four separate samples are presented. Absolute errors ranged from 0.00001 to 0.00014 with typical absolute errors of 0.00005. NA = data not available.

Although the line widths of the Mo(V) ESR signals varied considerably from one thermal treatment to another, the  $\Delta H_{\rm pp}$  values for a particular cation appeared to be much less affected by the particular thermal treatment. For example, when phenothiazine was added to thermally treated samples,  $\Delta H_{\rm pp}$  of the Mo(V) signal ranged from 21.1 G (4-h EC) to 50.3 G (2-h EC) to 76.0 G (2-h H₂ Red.). However, the line width of the corresponding radical cation signal was 19 G in the 2-h EC sample, 20 G in the 4-h EC sample, and 17 G in the 2-h H₂ Red. sample.

The total signal spread of the radical cation signals was also measured. This quantity was defined as the distance in gauss covered by the first-derivative spectrum of the cation signal. In all cases the experimental spectra are sufficiently broadened that all hyperfine splittings could be accommodated within the observed spectral pattern. Also the fact that the observed spectra have total widths far in excess of what would be expected for solution spectra is a clear indication that strong anisotropic effects exist.

The nitrogen hyperfine splitting of some of the nitrogen-containing species (phenazine, phenothiazine, phenoxazine) was sufficiently large that it could be resolved in the ESR spectrum. The phenazine radical cation spectrum obtained in this work is comparable in line width, shape, and hyperfine structure to that obtained by Seshadri and Petrakis²⁶ when phenazine was adsorbed on a silica-alumina surface. They calculated  $g_{av}$  to be 2.0024, which can be compared with  $g_{av} = 2.00299$  obtained in this work. The spectrum of phenothiazine on 9%  $Mo-\eta Al_2O_3$  is also quite similar to the spectrum of phenothiazine on alumina reported by Khulbe and co-workers.²⁷ Although acridan and acridine have nitrogen and proton hyperfine splittings which are comparable in magnitude to splittings in phenazine, phenothiazine, and phenoxazine, no hyperfine structure was observed.

The g values of radical cations from each thermal treatment are listed in Table VI. The numbers in this table represent the average of g values from up to three different samples. Although the uncertainty in the Mo(V) g values was quite large because of the broad ESR signals, the cation signals were much narrower and more sharply defined. The maximum absolute error of the cation g values was  $\pm 0.00049$ , but typical absolute errors were on

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Figure 8. Comparison of the g values of radical cations adsorbed on 9% Mo- $\eta$ Al₂O₃ samples with g values of the cations in solution.

the order of  $\pm 0.00005$ . The minimum absolute error was  $\pm 0.00001$ . Note that the g values of the cations from the corresponding 2-h and 4-h evacuation and calcination experiments were especially close. This indicates that the cations prepared by these EC thermal treatments must have very similar environments on the 9%  $Mo-\eta Al_2O_3$  surface.

A search of the recent literature yielded the g values for many of these cations in solution, usually in  $H_2SO_4$ . Figure 8 shows that the g value of a radical cation on the surface of 9% Mo- $\eta$ Al₂O₃ (which was prepared by EC or H₂ Red. thermal treatments) corresponds quite well with the g value of that cation in solution. For example, the g value of anthracene in solution was determined to be 2.002565. This can be compared with the g values of anthracene on variously treated 9% Mo- $\eta$ Al₂O₃ surfaces: 2.00256 for the 2-h EC sample, 2.00271 for the 4-h EC sample, and 2.00351 for the 2-h H₂ Red. sample. The similarity of these g values from two radically different environments indicates (1) that this cation must be rather loosely held on the molybdena alumina surface and (2) that the structure of the cation on the catalytic surface is not significantly modified compared to the structure of the cation in solution.

(2) Simulated Spectral Parameters. The spectra of nine different radical cations, chosen to avoid large nitrogen and proton hyperfine splittings, were simulated by using the ESR spectral simulation program. The absence of complicating hyperfine structures allowed anisotropic g values to be accurately determined. One factor influencing the cation spectra which could not be eliminated was the presence of the Mo(V) signal occurring at a higher magnetic field (lower g value) than the cation signal. The Mo(V) signal is often a comparatively large signal, and the cation signal often appears superimposed on the low-field wing of the Mo(V) spectrum. (This resulted in a sloping baseline for the radical cation signal.) All simulations were of radical cations from EC samples since the EC samples always had much larger cation signals than the corresponding H₂ Red. samples. Data on experimental and simulated g values, line widths, and line shapes are compiled in Table VII and in Figures 9-12.

F. Conclusions on the Effect of the Support and Thermal Treatment on Radical Cation Formation. (1)

TABLE VII:	Simulated and	Experimental ESF	. Spectral	l Parameters of Radical Cations	
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	parameters for "best fit"				
radical cation	line shape	line width, G	g tensor components	g _{av}	$\operatorname{exptl}^a g_{\mathbf{av}}$
azulene	Lorentzian Gaussian	7.65 5.3	2.00300, 2.00300, 2.00300 2.00300, 2.00300, 2.00300	2.00300 2.00300	2.00258
naphthalene	Lorentzian Gaussian	6.2 4.28	2.00230, 2.00230, 2.00230 2.00225, 2.00225, 2.00225	2.00230 2.00225	2.00248
anthracene	Lorentzian Gaussian	7.5 5.5	2.00360, 2.00360, 2.00360 2.00360, 2.00360, 1.99935	2.00223 2.00218	2.00274
phenanthrene	Lorentzian Gaussian	$\substack{\textbf{4.5}\\\textbf{4.2}}$	2.00485, 2.00225, 1.99970 2.00485, 2.00225, 1.99990	$2.00227 \\ 2.00233$	2.00252
2,3-benzothiophene	Lorentzian Gaussian	$6.5 \\ 4.5$	2.00370, 2.00370, 2.00370 2.00365, 2.00365, 2.00365	$2.00370 \\ 2.00365$	2.00410
dibenzothiophene	Lorentzian Gaussian	6.2 5.2	2.00705, 2.00500, 2.00290 2.00500, 2.00500, 2.00500	$2.00498 \\ 2.00500$	2.00520
thianthrene	Lorentzian Gaussian	4.0 3.2	2.01277, 2.00812, 2.00207 2.01305, 2.00805, 2.00209	2.00765 2.00773	2.00787
phenoxanthin	Lorentzian Gaussian	5.0 $4.1$	2.00918, 1.00735, 2.00253 2.00930, 2.00730, 2.00193	2.00635 2.00618	2.00640

^a Defined as the point halfway between slope extrema.





**Figure 9.** Comparison of experimental and simulated spectra of the naphthalene radical cation adsorbed on a 9% Mo $-\eta$ Al₂O₃ evacuation and calcination sample.

Support Effects. It appears that the support is critical in determining not only the distribution of molybdenum valences but also the formation of radical cations. ESR did not detect any evidence for the Mo(V) or radical cation species in unsupported molybdena samples of MoO₂ or MoO₃. Thermal treatments of the unsupported MoO₃ samples and the addition of probe molecules did not change this result.

(2) Thermal Treatment of 9%  $Mo-\eta Al_2O_3$ . Thermal treatments have dramatic effects on both of the paramagnetic species (Mo(V) and the radical cation) in the 9%  $Mo-\eta Al_2O_3$  catalyst. In thermally untreated 9%  $Mo-\eta Al_2O_3$  sample to which phenothiazine had been added, a very large cation signal and a very small Mo(V) signal were observed by ESR. In general, the effect of any of the three thermal treatments was to produce larger Mo(V) signals and smaller cation signals than those observed in the

**Figure 10.** Comparison of experimental and simulated spectra of the phenanthrene radical cation adsorbed on a 9%  $Mo-\eta Al_2O_3$  evacuation and calcination sample.

thermally untreated samples.

(3) Types of Thermal Treatment. The types of thermal treatment had quite different effects upon the cation and Mo(V) signal intensities. The H₂-reduced samples tended to have a rather constant Mo(V) formation and little or no cation formation. Evacuated and calcined samples, on the other hand, always had radical cation formation with a range of signal intensities over four orders of magnitude. Generally, the 4-h EC treatment produced larger cation signals than the 2-h treatment. The maximum amount of probe molecules undergoing electron transfer to form radical cations was 37%. The propensity of the probe molecules to form radical cations increased logarithmically as the first ionization potential decreased. An even better fit of the data is obtained if one considers the ratio of the cation and Mo(V) concentrations. This indicates that the thermal treatments modify somewhat the ability of the 1038 The Journal of Physical Chemistry, Vol. 84, No. 9, 1980



Flaure 11. Comparison of experimental and simulated spectra of the thianthrene radical cation adsorbed on a 9% Mo-nAl₂O₃ evacuation and calcination sample.



Figure 12. Comparison of experimental and simulated g values of radical cations adsorbed on 9% Mo- $\eta$ Al₂O₃ evacuation and calcination samples.

surface to accept an electron from the probe, although the overall electron-transfer reaction is controlled primarily by the ionization potential of the probe.

(4) ESR Spectral Features of Radical Cations. Various spectral features including signal spreads, line widths, g values, and line shapes were examined in order to determine the environment of the radial cation. The consistency of  $\Delta H_{\rm pp}$  and  $g_{\rm av}$  values of cations from samples prepared by any of the three thermal treatments shows that the cations are not greatly affected by the different surfaces.

Several factors appear to influence the g tensor of radical cations adsorbed on the 9%  $M_0-\eta Al_2O_3$  catalyst surface. One factor is the radical cation size. Each of the two-ring cations (azulene, naphthalene, and 2,3-benzothiophene) can be simulated by using an isotropic **g** tensor  $(g_x = g_y)$  $= g_z$ ), whereas all of the three-ring radical cations require an anisotropic tensor  $(g_x = g_y \neq g_z \text{ or } g_x \neq g_y \neq g_z)$ . It may be expected that the smaller radical cations would be freely tumbling on the catalyst surface while the larger, bulkier molecules may have some preferential orientation on the surface. The second factor influencing the g value tensor is the shape of the radical cation. Although anthracene and phenanthrene are isomers, anthracene requires only axially symmetric g values whereas the bent phenanthrene radical cation needs totally anisotropic g values for a good fit. And, although thianthrene and phenoxanthin have structural arrangements like anthracene, a third factor, the presence of heteroatoms, may be responsible for their totally asymmetric g tensors. Perhaps the heteroatoms of these large aromatic compounds provide a site where interaction with the catalyst surface occurs. This would lead to restricted motion of the heteroaromatic radical cation and, therefore, give rise to anisotropic g tensors.

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