JOURNAL OF CATALYSIS **25**, 334-341 (1972)

An Electron Spin Resonance Study of Cation Radicals on the Surface of MoO_3–Al_2O_3 and MoO_3–SiO_2 Catalysts

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Received May 19, 1971

ESR spectra of polynuclear aromatic hydrocarbons adsorbed on MoO_3–Al_2O_3 and MoO_3–SiO_2 have been recorded. Formation of the corresponding cation radicals indicates the presence of strong electron-deficient sites on the surface of these catalysts. The effect of activation temperature on radical forming ability of these solids has been studied. In the electron transfer reaction, Mo^{6+} is reduced to Mo^{5+}. Molybdenum is therefore directly involved in the electron transfer process. The radical concentration was dependent upon the molybdenum content and its oxidation state. The effect of oxygen on radical-ion formation has also been studied.

INTRODUCTION

The catalytic activity of molybdenum oxide in the pure form or on high surface area supports has been correlated with the molybdenum content. In the case of mild oxidation reactions, the formation of a surface complex involving electron transfer has been postulated. The adsorption complex may be a hybrid between $C_4H_7^-Mo^{6+}$ and $C_4H_7Mo^{5+}$ (*1*). Krylov and Margolis (*2*) suggested for the mechanism of oxidation of olefins the formation of a π-complex between the hexavalent molybdenum ion and butene, $Mo^{6+} + C_3H_6 \rightarrow Mo^{5+}C_3H_6^+$ and/or the formation of an allyl complex: $Mo^{6+} + O^{2-} + C_3H_6 \rightarrow Mo^{5+}C_3H_5 + OH^-$. Although these species have not been isolated, several results seem to be in agreement with these schemes. Evidence that the surface of these catalysts may donate electrons has been demonstrated by the formation of O_2^- radicals during the adsorption of oxygen (*2, 3*). The present paper provides evidence for the formation of positive radicals on the surface of MoO_3–Al_2O_3 and MoO_3–SiO_2 catalysts. ESR has previously been used to investigate the nature of electron acceptor sites, their number, and their strength in the case of alumina, silica–alumina, and zeolites (*4–7*).

EXPERIMENTAL METHODS

MoO_3–Al_2O_3 and MoO_3–SiO_2 were prepared by impregnation of the carriers with a solution of ammonium paramolybdate containing the required amount of molybdenum. The solids were dried at 110°C and then heated in a stream of air at 500°C. Samples contained between 2 and 17 wt % Mo. Data for the catalysts have been given in a previous publication (*8*). The supports used were gamma and eta alumina, and silica. X-Ray analysis, except for MoO_3–SiO_2 and for MoO_3–Al_2O_3 containing more than 12% Mo, gave no lines attributable to MoO_3 (*8*).

Adsorption of polynuclear aromatics. Samples were heated *in vacuo* at the required temperature between 100 and 600°C. Above 600°C, evaporation of molybdenum occurred. Some samples were dehydrated in a stream of oxygen or reduced in hydrogen at 500°C, and then evacuated at the same temperature. Solutions of the polynuclear hydrocarbons perylene, anthracene, benzidine, and 1,1-diphenylethylene in benzene

TABLE 1
Effect of the Activation Temperature on the Formation of Mo^{5+} for MoO_3–ηAl_2O_3 (5.4% Mo)

T (°C) of desorption	Mo^{5+} ESR intensity (relative)
200	0.4
300	1.1
400	2.2
500	3.9
600	6.3

were carefully degassed by repeated freezing and pumping to eliminate dissolved oxygen. Adsorption was achieved by the procedure proposed by Porter and Hall (*5*). ESR measurements were made with a Varian X-band spectrometer using low microwave power. Radical concentrations were measured by comparison with a standard sample of DDPH.

Results

MoO_3–γAl_2O_3 containing less than 10% Mo and treated *in vacuo* at 100–600°C gave no ESR signals. On the other hand MoO_3–ηAl_2O_3 and MoO_3–SiO_2 under the same conditions give an asymmetric ESR signal at $g = 1.93$ assigned to Mo^{5+} ions (*2, 3, 8, 9*). The integrated intensity of the ESR signal increases with the temperature of calcination (Table 1) and with the Mo content (Fig. 1).

The adsorption of perylene on MoO_3–Al_2O_3 and MoO_3–SiO_2 samples produced colored solids. Simultaneously a strong ESR signal was observed similar to that obtained by adsorption of perylene on silica-alumina catalysts (*4–6*). Spectra obtained for MoO_3–γAl_2O_3 (2% Mo) and (12% Mo) are shown in Fig. 2. These spectra can be attributed to the perylene positive radical, Pn^+. The nine equally spaced hyperfine lines are well resolved in the case of samples of low Mo content. At higher concentration of Mo, the resolution is much poorer. Under vacuum, the Pn^+ radical was stable for long periods.

The effect of the activation temperature of the solids upon the Pn^+ concentration is shown in Fig. 3.

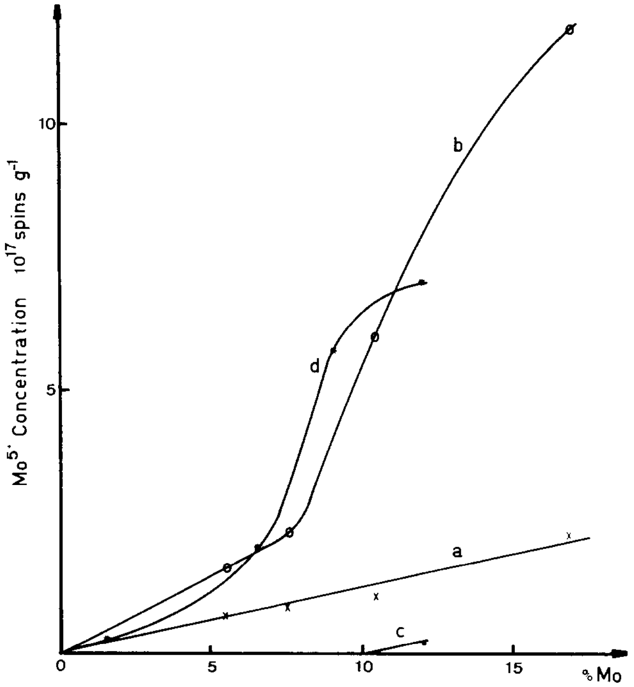

Fig. 1. Dependence of integrated Mo^{5+} ESR signal intensity on total molybdenum content: (a, b) MoO_3–ηAl_2O_3; (c, d) MoO_3–γAl_2O_3; (a and c) before perylene adsorption; (b and d) after perylene adsorption.

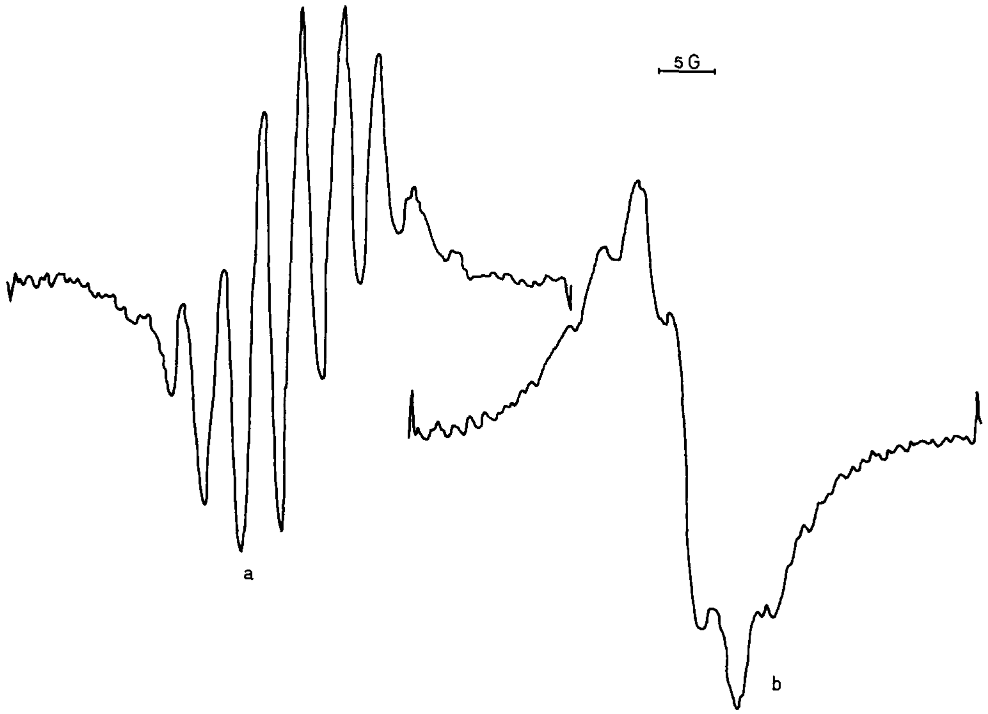

FIG. 2. ESR spectra of the perylene positive radical: (a) on MoO_3–γAl_2O_3 (1.5% Mo); (b) MoO_3–γAl_2O_3 (12.1% Mo).

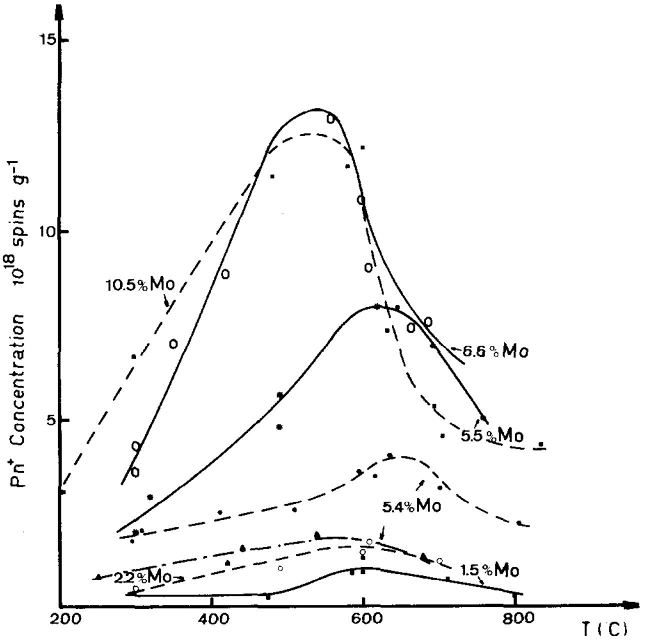

FIG. 3. Effect of activation temperature on the relative concentration of Pn^+ radicals: (—) MoO_3–γAl_2O_3; (— —) MoO_3–ηAl_2O_3; (— - —) MoO_3–SiO_2.

Maximum oxidizing activity with perylene is obtained at about 600°C. Figure 3 also shows the increase in Pn^+ concentration with the total molybdenum content for a given carrier. Figure 4 shows the dependence of integrated Pn^+ signal intensity on the total Mo content for MoO_3–SiO_2 samples activated at 600°C under vacuum. The generation of perylene ions on supported molybdenum oxide is strongly dependent on the nature of the carrier. Figure 3 shows that, for the same molybdenum content and the same activation temperature, silica gives a less active catalyst than alumina. Moreover eta and gamma alumina are not equally effective. The formation of Pn^+ is accompanied by an increase in the Mo^{5+} signal in all the samples. This is connected with reduction of the hexavalent molybdenum. The increase of the number of Mo^{5+} ions during perylene adsorption on MoO_3–Al_2O_3 activated at 600°C is shown in Fig. 1. As hexavalent molybdenum ions appeared to be involved in the oxidation of perylene, the properties of the reduced catalysts were examined. The molybdenum catalysts were dehydrated at 600°C under vacuum, reduced in a flow of hydrogen at 300°C, and evacuated at the same temperature. All the samples gave a strong ESR signal at $g = 1.93$. The reduced samples were then allowed to react with perylene. These reduced samples were incapable of removing an electron from the aromatic to form the positive radical ion. In contrast to this, samples activated at 600°C in a stream of oxygen and then degassed under vacuum gave the same results as those obtained with samples activated under vacuum in the absence of oxygen. To obtain some light on the nature of the electrophilic sites, the effect of water and pyridine adsorption on the generation of positive radical ions was examined. The catalysts were evacuated overnight at 600°C and rehydrated at room temperature. The samples were then degassed under vacuum at 25–600°C in order that all physically adsorbed water was desorbed. The results (Table 2) indicate a substantial decrease in the oxidizing properties of the samples by rehydration. As chemisorption of pyridine at high temperature (100–200°C) resulted in reduction of molybdenum, the poisoning effect of pyridine was studied at room temperature. The catalysts were activated overnight at 600°C and then equilibrated overnight with a benzene solution of pyridine containing a known amount of the nitrogen base. The solvent was then removed and the pyridine-catalyst sample was allowed to react with perylene. The

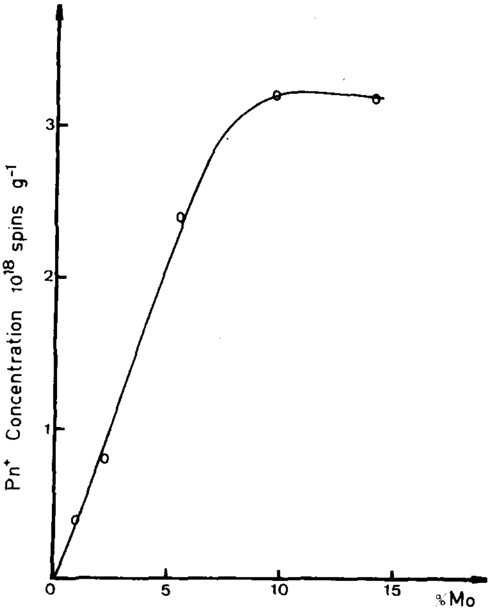

FIG. 4. Influence of the Mo content on the relative concentration of Pn^+ radicals formed on MoO_3–SiO_2 (samples activated at 600°C).

TABLE 2
EFFECT OF REHYDRATION ON THE OXIDIZING PROPERTIES OF MoO_3–Al_2O_3 CATALYSTS ACTIVATED AT 600°C

T (°C) of desorption after rehydration	5.4% MoO_3–ηAl_2O_3 (10^{18} Pn^+ spins/g)	6.6% MoO_3–γAl_2O_3 (10^{18} Pn^+ spins/g)
25	0	0
300	0.7	3.7
405	1.1	6.6
490	2.8	8.8
600	4.0	10.8
Sample nonrehydrated	3.7	10.3

results are shown in Table 3. No linear relation between the amount of pyridine added and the Pn^+ concentration was obtained. However, these results suggest that pyridine is adsorbed on the oxidizing sites.

The effect of oxygen on the number of perylene ions formed on the surface of molybdenum catalysts was also examined. The Mo catalysts were activated at 600°C under vacuum, perylene was adsorbed, solvent was removed, and oxygen was admitted to the sample. Figure 5 shows the effect of oxygen pressure on the concentration of perylene radical ions for, respectively MoO_3–γAl_2O_3 (5.5% Mo) and MoO_3–SiO_2 (5.5% Mo). The effect of oxygen on molybdenum–silica catalysts was completely reversible. The initial spectra were restored when the oxygen was pumped off. On the other hand in the case of molybdenum–alumina catalysts an increase in Pn^+ concentration was observed after the oxygen had been removed. Alumina containing more than 10% Mo showed only a reversible effect with oxygen as with MoO_3–SiO_2 catalysts.

The strength of the sites responsible for the formation of cation radicals was studied by adsorbing polynuclear aromatics of different ionization potential. Samples containing different amounts of Mo were degassed (under vacuum) at 600°C and allowed to react with perylene (*IP*, 7.0 eV), anthracene (*IP*, 7.5 eV), benzidine (*IP*, 8.6 eV), and 1,1-diphenylethylene. The number of positive radical ions formed versus the molybdenum content is shown in Figs. 6 and 7 for gamma and eta alumina carrier, respectively. As pointed out by Richardson (*10*), the dependence of the spin concentration on the ionization potential of the donor molecule is evident from these figures. It is clear also that increasing the Mo content results simultaneously in an increase in the number of electrophilic sites and an increase in their oxidizing strength.

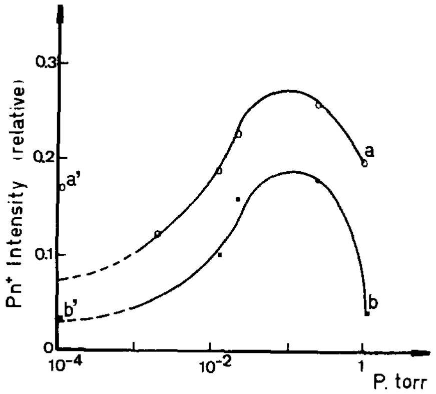

FIG. 5. Effect of oxygen pressure on the peak height of the perylene radical-ion spectrum: (a) MoO_3–γAl_2O_3 (5.5% Mo) activated at 600°C (a') O_2 pumped off; (b) MoO_3–SiO_2 (5.5% Mo) activated at 600°C (b') O_2 pumped off.

TABLE 3

POISONING EFFECT OF ADSORBED PYRIDINE ON RADICAL-ION GENERATION FOR CATALYST SAMPLES ACTIVATED AT 600°C[a]

6.6% MoO_3–γAl_2O_3		5.4% MoO_3–ηAl_2O_3		5.4% MnO_3–SiO_2	
Pyridine adsorbed ($\times 10^{18}$ molecules/g)	Pn^+ (spins/g $\times 10^{18}$)	Pyridine adsorbed ($\times 10^{18}$ molecules/g)	Pn^+ (spins/g $\times 10^{18}$)	Pyridine adsorbed ($\times 10^{18}$ molecules/g)	Pn^+ (spins/g $\times 10^{18}$)
0	10.8	0	5.3	0	3.6
2.2	10.7	20.3	0.5	3.6	0.7
12	7.0	86.7	0.5	20.7	0.6
45	6.6	193	0.4	248	0.3
100	5.3	Saturated	0	Saturated	0
Saturated	0				

[a] These results were reproducible with 10% error.

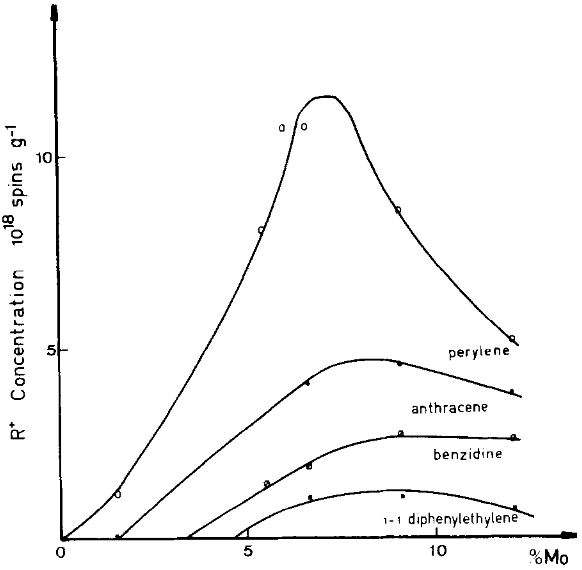

FIG. 6. Dependence of oxidizing strength of MoO_3–γAl_2O_3 on the Mo content (activation temp, 600°C).

DISCUSSION

The spectrum of perylene adsorbed on the molybdenum catalysts leaves no doubt that the molecule has lost one electron and has become the corresponding positive radical ion, indicating that sites with strong electron affinity are present on the surface. Silica–alumina and decationated zeolites behave in a similar manner. In these cases, the sites responsible for the electron transfer have been identified either as trigonal aluminum ions (Lewis sites) (*4*, *5*, *7*, *11*) or as Brønsted sites catalyzed by molecular oxygen (*12*). The results reported in this paper exclude Brønsted sites for the formation of positive radical ions. In fact the radical forming activity increases with increasing dehydration tem-

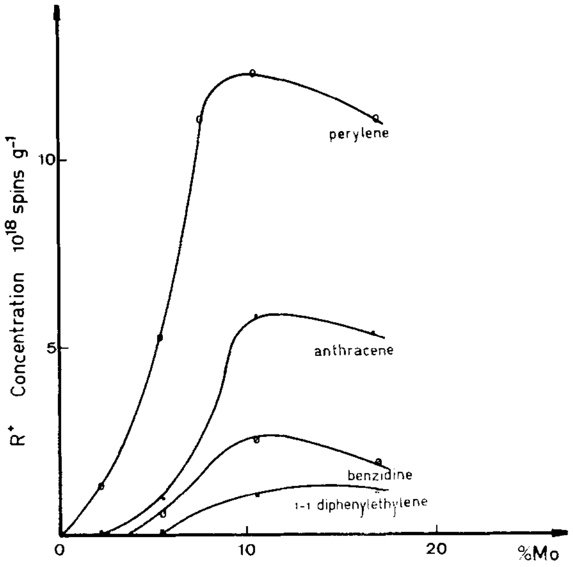

FIG. 7. Dependence of oxidizing strength of MoO_3–ηAl_2O_3 on the Mo content (activation temp, 600°C).

perature, i.e., as the proton concentration decreases. This view is supported by the observed decrease in the number of perylene ions when the concentration of protons is increased by rehydration. Silica alone is ineffective for ionizing perylene, while alumina has radical forming activity only in the presence of molecular oxygen (*13*). Flockhart *et al.* (*13*) suggested that, for alumina catalysts, the aromatics are adsorbed on the trigonal aluminum ions. The electron affinity of this Lewis site is not sufficiently great to abstract one electron from the aromatic molecule. Only a weak charge transfer complex is formed. However, when oxygen is adsorbed on this site, O_2 acts as acceptor and the perylene is ionized. On silica–alumina catalysts, the active site is the trigonal aluminum and the SiO_4 residue, the electron acceptor. As MoO_3–Al_2O_3 catalysts are active for radical ion formation in the absence of molecular oxygen, it is possible that the aromatic is adsorbed on the trigonal aluminum and the electron is captured by hexavalent molybdenum which plays a similar role to that of molecular oxygen or SiO_4. The fact that during Pn^+ formation Mo^{5+} ions are formed, provides powerful evidence for this hypothesis. It appears that electron transfer from the adsorbed aromatic to Mo^{6+} operates through the lattice. Such a transfer has already been suggested by Krylov and Margolis (*2*) in their studies on the formation of O_2^- ions on the surface of MoO_3–MgO and MoO_3–Al_2O_3. Silica–molybdena catalysts also show powerful electron deficient sites which are capable of forming aromatic radical ions. The suggestion of Flockhart *et al.* (*13*) does not apply to this catalyst, if one supposes SiO_4 is the electron acceptor. As a matter of fact the increase in the number of Mo^{5+} ions observed during the formation of the positive radical ions indicates that for these catalysts the electron acceptor is also hexavalent molybdenum. For these reasons, it can be argued that, on silica–molybdena catalysts, trigonal silicon ions are formed which would be the adsorption sites for the aromatics, hexavalent molybdenum acting again as the acceptor.

X-Ray analysis has shown (*8*) that with alumina as support no free MoO_3 was detectable while this oxide is present on silica even at a low Mo content. The mechanism of the interaction between the molybdenum compound and the carriers was explained by the reaction of the hydroxyl groups with molybdic acid. This difference between alumina and silica is possibly explained by a difference in the basicity of the carrier surface hydroxyl groups. The hydroxyl groups of alumina have a more basic character compared to the hydroxyl groups of silica and therefore are capable of forming more readily a salt with the molybdic acid. Thus with alumina as carrier practically all the molybdenum is combined to form Mo–O–Al– groups which are the active sites in radical ion generation. With the less basic hydroxyl groups of silica, only a fraction of the molybdenum forms Mo–O–Si– groups, the greater part being present as MoO_3. As MoO_3 is inactive for the formation of positive radical ions, for the same molybdenum content, alumina should have more ionizing sites than silica and should give a greater number of positive radicals, in agreement with the present data. The poisoning effect of pyridine on the oxidizing properties of these catalysts indicates that the active sites are acidic in character. The reversible increase in the radical concentration after addition of oxygen to the system perylene–silica–molybdena can be accounted for by a change in the saturation level and not necessarily by a real increase in the number of positive radical ions. The addition of an excess of oxygen leads to a reversible broadening of the signal and subsequently to a decrease in the signal intensity. These catalysts possess only strong electrophilic centers in contrast to silica–alumina catalysts. In the case of alumina, the irreversible effect of oxygen decreases as the molybdenum content increases and for 10% Mo content only a reversible effect is observed. At low molybdenum contents, two types of sites may be present on the surface of the catalyst, trigonal aluminum atoms characterized by a low electron affinity and which require oxygen to generate positive radical ions and Mo–O–Al sites which have strong oxidizing properties, hexavalent molybdenum acting as the electron acceptor. The number of Mo–O–Al sites increases with molybdenum content and simultaneously the number of Al–O–Al sites decreases. Therefore, the oxygen effect is less pronounced at higher Mo concentration and disappears completely for complete coverage of the surface with Mo–O–Al groups.

The principal conclusion is that catalysts obtained by impregnation of alumina or silica with a molybdate solution behave like silica–alumina in the formation of positive radical ions. The mechanism by which these ions are formed on the surface of the solids involves the adsorption of the aromatic molecule on a Lewis acid site to form a weak charge transfer complex with subsequent transfer of an electron to hexavalent molybdenum through the lattice.

ACKNOWLEDGMENTS

The authors are grateful to Dr. B. Imelik and to Dr. R. C. Pink, the Queen's University of Belfast, for valuable suggestions and comments.

REFERENCES

1. BATIST, P. A., LIPPENS, B. C., AND SCHUIT, G. C. A., *J. Catal.* **5**, 55 (1966).
2. KRYLOV, O. V., AND MARGOLIS, L. Y., *Kinet. Katal.* **11**, 432 (1970).
3. DUFAUX, M., CHE, M., AND NACCACHE, C., *C. R. Acad. Sci. Ser. C* **268**, 2255 (1969).
4. ROONEY, J. J., AND PINK, R. C., *Trans. Faraday Soc.* **58**, 1632 (1962).
5. PORTER, R. P., AND HALL, W. K., *J. Catal.* **5**, 366 (1966).
6. FLOCKHART, B. D., AND PINK, R. C., *J. Catal.* **4**, 90 (1965).
7. STAMIRES, D. N., AND TURKEVICH, J., *J. Amer. Chem. Soc.* **86**, 749 (1964).
8. DUFAUX, M., CHE, M., AND NACCACHE, C., *J. Chim. Phys.* **67**, 527 (1970).
9. SESHADRI, K. S., AND PETRAKIS, L., *J. Phys. Chem.* **74**, 4102 (1970).
10. RICHARDSON, J. T., *J. Catal.* **9**, 172 (1967).
11. DOLLISH, F. R., AND HALL, W. K., *J. Phys. Chem.* **71**, 1005 (1967).
12. HIRSCHLER, A. E., AND HUDSON, J. O., *J. Catal.* **3**, 239 (1964); HIRSCHLER, A. E., *J. Catal.* **5**, 196 (1966).
13. FLOCKHART, B. D., SCOTT, J. A. N., AND PINK, R. C., *Trans. Faraday Soc.* **62**, 730 (1966).