JOURNAL OF CATALYSIS 43, 339–345 (1976)

Electron Spin Resonance Studies of Donor and Acceptor Properties of Alumina, Silica, Alumina–Palladium and Silica–Palladium Catalysts

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Received December 17, 1975

Electron donor and acceptor properties of γ-alumina, silica and γ-alumina and silica supported palladium oxide have been studied. It was observed that while γ-alumina had both electron acceptor and donor properties, silica had only electron acceptor characteristics. γ-Alumina supported palladium oxide showed better acceptor properties than donor properties. Silica supported palladium oxide showed only electron acceptor properties. The effects of electron donor and acceptor compounds and different solvents on the radical formed by acetylene over Al_2O_3 and SiO_2 supported PdO_2 were studied. It is concluded that the structure of Al_2O_3–PdO_2–C_2H_2 complex is radically different from that of SiO_2–PdO_2–C_2H_2 complex. Possible mechanisms for the reactions are discussed.

INTRODUCTION

The formation of anion and cation radicals by compounds adsorbed on the surface of catalysts is indicative of electron donor and acceptor properties of the catalysts. Thus, the formation of the anion radicals of tetracyanoethylene (TCNE), or trinitrobenzene (TNB) adsorbed on the surface of Al_2O_3–TiO_2 or MgO requires a charge transfer from the catalyst to the electron acceptor compounds (*1–4*). The formation of radicals of acetylene on the surface of alumina–PdO_2 (*5*) catalysts, and the change in the intensity of the ESR signal in the presence of added oxygen, solvents, and electron donor and acceptor compounds also demonstrates the dual nature of the alumina–PdO_2 surface. In this work, we report the results of our ESR studies regarding the donor and acceptor properties of pure Al_2O_3, pure SiO_2, and Al_2O_3 and SiO_2 supported PdO_2 catalysts, and the influence of a variety of donor and acceptor compounds and solvents on the ESR signals. The relative donor and acceptor properties of a system have been inferred by the intensity of the ESR signals, all with respect to the intensity of the ESR spectra of TCNE and thiodiphenylamine (TDPA) supported on a similar catalyst.

EXPERIMENTAL METHODS

a. Reactants. While cylinder oxygen (Linde 99.99% O_2) was used as such, reagent grade acetylene (Matheson Co.) and dimethylacetylene (K and K Lab.) were further purified by vacuum distillation. Silica (Cab-O-Sil) and alumina supplied by Cabot Corp. and Fisher Co. were used. All other chemicals were high purity analytical grade reagents and were obtained from Fisher or K and K laboratories.

b. Catalysts. A paste of silica powder was made in water, dried at 60°C and calcined at 500°C for 15 hr. The calcined silica powder was ground and sieved. A 40–60

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mesh silica was used. Alumina of 40–60 mesh size was prepared in a similar way from 8–10 mesh active alumina. Silica or alumina supported PdO catalysts (1.5 and 3% Pd) were prepared by the impregnation of the support material with the calculated amounts of $(NH_4)_2$ $PdCl_6$ solution. The impregnated catalyst was evaporated to dryness at 60°C and calcined at 500°C for 15 hr. Unsupported PdO_2 catalyst was prepared by calcining $(NH_4)_2$ $PdCl_6$ at 500°C for 15 hr. The weight of the catalyst in the ESR tube was always about 0.2000 g.

c. ESR measurements. The ESR measurements were carried out using a Bruker 416 spectrometer operating on the *X*-band. All measurements were made at room temperature. The relative intensities of the signals were measured by integrating the area covered by the signals. The "*g*" values were calculated by comparing the *g* values of the free radical D.P.P.H. (2.003). The ESR tube was connected to a three-way stopcock. One side of the stopcock was connected by a ball joint to a conventional vacuum apparatus (*6*). The other side of the stopcock was joined to a glass cup from which liquid reactants or solvents could be introduced into the tube. The ESR tube along with the three-way stopcock could be easily detached or connected to the vacuum apparatus. The required amounts of the acetylenes or oxygen were admitted to the ESR tube from the storage vessel.

RESULTS AND DISCUSSION

Alumina (Al_2O_3) system

The addition of a solution of tetracyanoethylene (TCNE) in benzene (0.1 *M*) to Al_2O_3 at room temperature produced a brown coloration. The ESR spectrum was composed of 11 lines and was identified by comparison as the TCNE anion radical (*7*). When the solvent was a 1:1 mixture of benzene and acetic acid the intensity of the signal of TCNE anion radical was very much reduced. The addition of methanol to the solution of TCNE led to an almost total disappearance of the ESR signal.

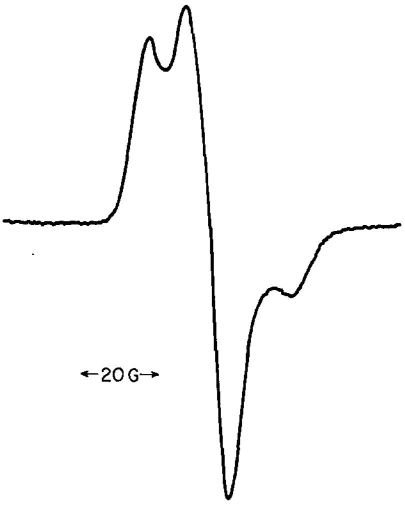
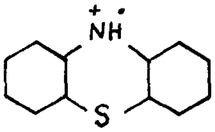


FIG. 1. ESR spectra of TDPA on γ-alumina.

The addition of a solution of phenothiazine (TDPA) in benzene to alumina produced a spectrum (Fig. 1) which was identified as the cation radical of TDPA (*8*):

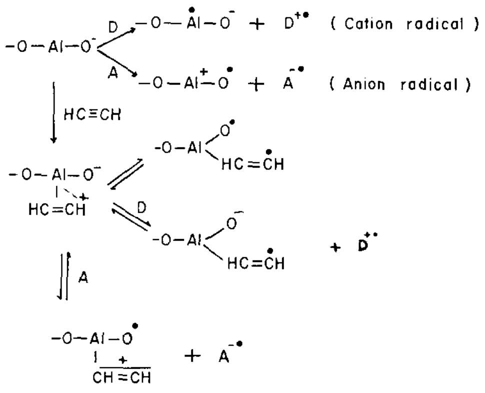


The formation of a paramagnetic species (PMS) was observed when other electron donor compounds, viz, benzidine in benzene, carbon tetrachloride or a mixture of benzene and acetic acid were added to alumina. The signals are attributed to cation radical of benzidine.

Alumina activated by heating at 360°C and in the presence of oxygen for 1 hr formed very small amounts of the PMS (*g* = 2.00), line width 3.5 G with acetylene adsorbed (at 360°C) on its surface. It gave a very weak ESR signal. Similar results were obtained by heating acetylene with alumina supported copper oxide (*9*) or group VIII transition metals (*5*). The addition of TCNE in benzene to the system acetylene–alumina lead to a greatly enhanced (more than 120 times) ESR signal. The ESR spectra observed corresponded to an overlapping of the signals of acetylene–alumina and the TCNE anion radical. When TDPA in benzene was added to the acetylene–alumina, the intensity of the ESR signal increased sharply (more than 60 times).

X-ray analysis confirmed the alumina to be of γ-type. γ-Alumina has a very complex structure. Important catalytic properties of γ-alumina are associated with the acid sites created on the surface during the removal of hydroxyl groups at 400°C. However, surface OH groups are not completely eliminated, even by drying under vacuum between 800 and 1000°C (*10*). The Bronsted and Lewis acid sites have always been looked upon as the active catalytic centers in alumina. Recently Hightower (*11*) reported that γ-alumina possessed many types of active sites. Perhaps this complexity is responsible for making alumina such a versatile catalyst for a wide variety of reactions. The electron donating characteristics of the alumina surface has been reported by Flockhart *et al.* (*4*) who showed that the electron spin resonance spectrum of TCNE adsorbed on alumina indicated the presence of a radical anion. However, when alumina is preheated above 500°C, the radical anion could no longer be observed. At higher temperatures the electron deficient character of alumina is dominant. In the present investigations the γ-alumina which was preheated at 500°C was quite active to give TCNE anion radical. This indicated the presence of active sites different from those that were present in Flockhart's preheated alumina (*4*). The number of various types of sites present on the alumina surfaces appear to be completely dependent on the method of preparation.

Infrared studies of acetylenic compounds on several metals and alumina has revealed (*13–17*) that the acetylenic molecule interacts with the surface using either the –C≡C– triple bond or C–H single bond. Associatively bonded acetylene has also been proposed on the basis of volumetric studies (*18*). According to the present observations we suggest that the principal mode of the interaction of acetylene with Al_2O_3 or alumina supported Pd is by means of –C≡C– triple bond. The following mechanism is therefore possible for the electron donor and acceptor nature of alumina and alumina–acetylene system:



MECHANISM 1

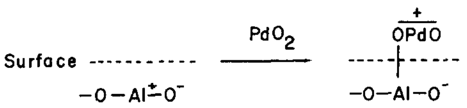
PdO_2–*Alumina System*

Palladium oxide alone did not give any ESR signal either with acetylene (at 360°C) or with the electron donor and acceptor compounds. The lack of results on pure PdO_2 imply that it has no electron donor or acceptor characteristics under experimental conditions.

Alumina supported palladium oxide (1.5–3% wt Pd) decreased noticeably the intensity of the ESR signal for both donor and acceptor compounds. However, the donor and acceptor properties did not decrease in equal proportions. Alumina supported palladium oxide showed better acceptor properties than donor properties. This behavior was opposite to the one observed with alumina where the donor properties were superior. For example, while with alumina, the ratio of the PMS in TCNE and TDPA was 3.9, it was 0.3 for PdO_2–alumina. There are growing evidences that the support may not be really inert as assumed hitherto, but may influence the catalytic activity in any of the several ways. (a) It may interact chemically with the metal therby modifying the properties of the latter (*19*). (b) The support may exert an influence on the actual structure of the metal, although such effects may be difficult to separate from the chemical effects. (c) The support may act either as a source of reactive intermediate or as a seat of reactions, through the migration of adsorbed species between metal and support (*20*).

X-Ray analysis did not reveal the existence of any detectable amount of free palladium or oxides of palladium in the alumina supported palladium (before and after interaction with acetylene). All the palladium in the supported catalyst is possibly present in the form of Pd–O–Al groups which are active sites for the generation of radicals. Schwab and Kral (*21*) suggested that doped alumina could have both the electron donor and electron accepting sites. This is confirmed by the present investigations since alumina supported palladium oxide gave TCNE and TDPA, anion and cation radicals, respectively.

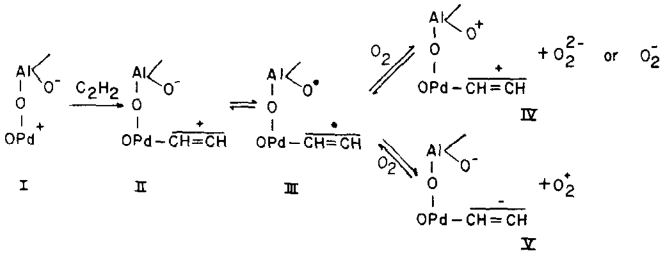
The difference in the donor and acceptor behavior between pure alumina and alumina supported palladium oxide may be explained in terms of the difference in the polarity of Al–O bond in Al_2O_3 and Pd–O bond in Al_2–PdO_2. The relatively greater decrease in the donor properties in PdO_2–alumina suggest that palladium oxide interferes with the basic center, Al^+–O^- in the alumina as follows:



MECHANISM 2

Active PdO_2–alumina (activated by heating at 360°C in 200 mm O_2 for 2 hr was fairly active to give PMS with acetylene (*5, 9*) at 360°C. Active PdO_2–alumina did not give any PMS with acetylene at room temperature. The addition of oxygen at 20°C to the evacuated acetylene–PdO_2–alumina led to a complete removal of ESR signal of PMS formed by acetylene with PdO_2–alumina at 360°C. The effect of O_2 was reversible (*5*). When electron acceptor compounds such as TCNE in benzene, $SnCl_4$, $SbCl_5$, etc., were added to the oxygen treated sample, there was a very sharp increase in the intensity of the ESR signal, 10 to 500 times in comparison to the original (not oxygen treated). A considerable increase in the intensity over the oxygen treated sample was observed when nonpolar solvents such as benzene, CCl_4, etc. were added. However, the ESR intensity decreased when solvents like methyl alcohol, water, acetic acid, which have the property to solvate the ions, were added. In some cases, the ESR signal decreased to almost zero. Ernst *et al.* (*22*) observed that on the addition of benzene to a freshly prepared platinum oxide–pyrene mixture, there was an initial enhancement of the ESR intensity. They suggested that this was partly due to the displacement of oxygen or water from the surface. The enhancement of the ESR intensity may also be due to an increased mobility of solute surfaces not involved initially in the oxide–organic contact, including inner surfaces. They have also reported that the addition of ethyl alcohol to a solid mixture resulted in the immediate disappearance of paramagnetism.

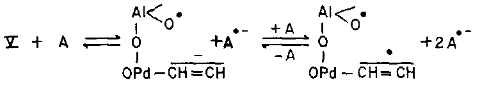
Sokolova *et al.* (*23*) studied the adsorbed species of acetylene–Pd–alumina by ir between −78 and 400°C. They reported that the palladium alumina–acetylene surface compounds were stable up to ≤400°C. [^{14}C]Acetylene studies (*24*) on the metals demonstrated the existence of acetylene on the surface after evacuation at 150°C which gives the PMS (*9*) with PdO_2–alumina. Acetylene is associatively adsorbed on the surface of metals (*13–17*). The formation of PMS radical and the effect of oxygen can be visualized as taking place according to the following mechanism:



Mechanism 3

The ESR spectra of paramagnetic species of oxygen (*25*, *26*) could not be observed either due to the low concentration of their species (*27*) or due to the experimental conditions (*26*). Nonpolar solvents will shift the equilibrium from II, IV, and V towards III (radical species are more stable in nonpolar solvents). The reverse is true in case of the polar solvents.

The electron acceptor compounds (A) may influence these radicals in the following way:



Mechanism 4

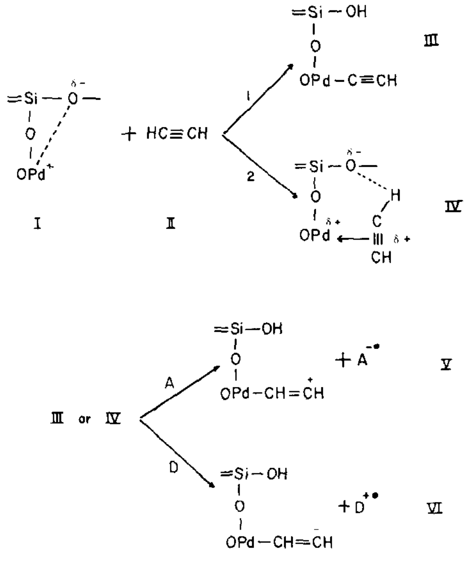
SiO_2 System

The ESR characteristics of SiO_2 and SiO_2–PdO_2 alone or treated with TCNE and TDPA in the absence or presence of acetylene were investigated. Table 1 shows the results obtained on SiO_2 and palladium supported SiO_2.

While alumina gave ESR signals, pure silica, and SiO_2–PdO_2 did not give any signals either alone or when treated with C_2H_2. Also no signals were observed when SiO_2–PdO_2 was treated with TCNE. From catalytic studies, it has been long established that alumina has a much more reactive surface than silica. Since both surfaces contain hydroxyl groups, the lesser activity of silica is attributed to the presence of an acid site, different from that which exists in alumina.

Silica supported PdO_2 gave a signal with electron donor compounds such as TDPA, 3,3′-dimethyl benzidine in benzene. When TDPA or TCNE were added to the acetylene treated PdO_2–SiO_2, ESR signals were observed. These signals can be attributed to TDPA cation and TCNE anion radicals.

The results imply that the structure of SiO_2–PdO_2–C_2H_2 complex is radically different from that of Al_2O_3–PdO_2–C_2H_2 complex. It appears that the principal mode of interaction of acetylene molecule with SiO_2 and SiO_2–PdO_2 is by means of a C–H bond (Path 1). The present results suggest that the interaction of C_2H_2 with SiO_2 or SiO_2–PdO_2 may be "halted" with the formation of a π complex (Path 2). No paramagnetic intermediates are generated by either of the pathways (Paths 1 or 2):



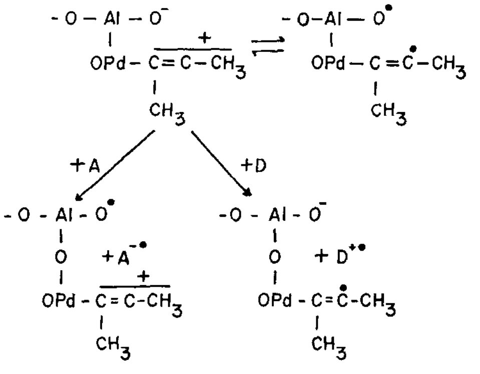
Mechanism 5

TABLE 1

Signals with SiO_2 and SiO_2–PdO_2

Sample	Reactant	ESR results
SiO_2	—	No signal
$SiO_2 + PdO_2$	—	No signal
$SiO_2 + PdO_2$	C_2H_2 (at 360°C)	No signal
$SiO_2 + PdO_2$	TCNE	No signal
$SiO_2 + PdO_2$	TDPA	Signal
$SiO_2 + PdO_2$	C_2H_2 + TDPA	Signal but less than with TDPA alone
$SiO_2 + PdO_2$	C_2H_2 + TCNE	Very weak signal

In another experiment dimethylacetylene was treated with activated PdO_2/alumina and activated PdO_2/silica at 360°C. It was observed that the spin concentrations of TDPA cation radicals and the PMS formed by dimethylacetylene were approximately the same over PdO_2/alumina. However, the presence of the PMS formed by the reaction of dimethylacetylene over PdO_2/alumina surface enhanced the interaction of TDPA and TCNE nearly 100 times and yielded TDPA cation radical and TCNE anion radical. The interaction of TDPA and TCNE on dimethylacetylene can be treated as follows:



Mechanism 6

Under analogous conditions there were neither observable interaction between dimethylacetylene and PdO_2–SiO_2 nor a ESR signal was found when either TCNE or TDPA was added to the dimethylacetylene treated PdO_2–SiO_2. It can be concluded that dimethylacetylene with PdO_2–SiO_2 is not strongly adsorbed on the surface of the catalyst. This observation is in full agreement with the schemes proposed earlier where the quantitative influence of steric hinderance on π complex formation in Path 1 has been known (Mechanism 5).

ACKNOWLEDGMENTS

The authors are grateful to the National Research Council for financial support (A-1125) and to the Canada Council for the award of a fellowship (to I.B.).

REFERENCES

1. Che, M., Naccache, C., and Imelik, B., *J. Catal.* **24**, 328 (1972).
2. Flockhart, B. D., Naccache, C., Scott, J. A. N., and Pink, R. C., *Chem. Commun.* 238 (1965).
3. Naccache, C., Kodratoff, Y., Pink, R. C., and Imelik, B., *J. Chim. Phys.* **63**, 341 (1966).
4. Flockhart, B. D., Leith, I. R., and Pink, R. C., *Trans. Faraday Soc.* **65**, 542 (1969).
5. Khulbe K. C., Bodrikov, I. V., and Mann R. S., *Reaction Kinet. Catal. Lett.*, in press.
6. Mann, R. S., and Khulbe, K. C., *Canad. J. Chem.* **46**, 623 (1968).
7. Stamires, D. N., and Turkevich, J., *J. Amer. Chem. Soc.* **85**, 2557 (1963).
8. Lagercrantz, C., *Acta Chem. Scand.* **15**, 1545 (1961).
9. Mann, R. S., and Khulbe, K. C., *J. Catal.* **42**, 115 (1976).
10. Pen, J. B., and Hannan, R. B., *J. Phys. Chem.* **64**, 1526 (1960).
11. Higtower, J. W., *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.* **18**, 263 (1973).
12. Hair, M. L., and Chapman, I. D., *J. Phys. Chem.* **69**, 3949 (1965).
13. Yates, D. J. C., and Lucchesi, P. J., *J. Chem. Phys.* **35**, 243 (1961).
14. Little, L. H., Sheppard, N., and Yates, D. J. C., *Proc. Roy Soc., Ser.* A **259**, 242 (1960).
15. Nash, C. P., and Desieno, R. P., *J. Phys. Chem.* **4**, 312 (1964).
16. Erschens, R. P., and Pliskin, W. A., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komarewsky, and P. B. Weisz, Eds.), Vol. 10, p. 1, Academic Press, New York, 1958.
17. Pliskin, W. A., and Eischens, R. P., *J. Phys. Chem.* **60**, 482 (1956).
18. McKee, D. W., *J. Amer. Chem. Soc.* **84**, 1109 (1962).

19. Thomson, S. J., and Harvey, G. A., *J. Catal.* **22**, 359 (1971).
20. Webb, C., Surface Defect Properties Solids **3**, 184 (1974).
21. Schwab, C. M. and Kral, H., *Proc. Int. Congr. Catal., 3rd, 1964* **1**, 433 (1965).
22. Ernest, I. T., Garnett, J. L., and Sollich-Baumgarner, W. A., *Aust. J. Chem.* **19**, 529 (1966).
23. Sokolova, N. P., Kazakova, L. A., and Borisenko, L. A., *Zh. Fiz. Khim,* **44**, 2657 (1970).
24. Inoue, Y., and Yasumon, I., *J. Phys. Chem.* **73**, 1618 (1969).
25. Meistrich, M. L., *J. Phys. Chem. Solids* **29**, 111 (1968).
26. Iyenger, R. D., Codell, M., Karra, J., and Turkevich, J., *J. Amer. Chem. Soc.* **88**, 5055 (1966).
27. Schlegel, J., *J. Amer. Chem. Soc.* **97**, 683 (1975).