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Electron Spin Resonance Studies of Adsorption of Alkynes and Allene over Alumina Supported Copper Oxide

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The formation of an interesting new type of paramagnetic species ($g = 2.00$, width 3.5 G) is observed over alumina supported copper oxide catalyst by alkynes and allene at 360°C. Alkenes and alkanes do not give paramagnetic species (PMS) under experimental conditions. Alumina supported copper oxide contains at least two types of active sites. While one has electron acceptor property (thiodiphenylamine cation radical formation) the other, Cu^{2+}, has the property to give PMS with alkynes and allene. The affinity of the studied hydrocarbons for the formation of PMS were in the following sequence: acetylene > methylacetylene > allene > ethylacetylene > dimethylacetylene. The intensity of ESR signals dropped drastically as soon as PMS came into contact with air or oxygen. However, on removing the oxygen from O_2 adsorbed PMS either by evacuating or passing CO, CO_2, H_2, D_2, N_2 or acetylene over Cu–alumina at room temperature, the ESR signal reappeared to almost original shape and intensity. A possible mechanism for the formation of these radicals and the effect of oxygen on these is discussed on the basis of charge transfer and an equilibrium shift between PMS and oxygen.

INTRODUCTION

Electron spin resonance technique have previously been used for the investigation of charge transfer complexes (*1–5*), whereas few ESR studies of the generation of paramagnetism in systems of catalytic interest are available (*6*, *7*). An interesting new class of radicals or paramagnetic species (PMS) were obtained on the surface of the active alumina supported copper oxide (5% wt Cu) by heating alkynes and allene with the catalyst. Oxygen effect was also studied over these species.

EXPERIMENTAL METHODS

Reagents

Linde's 99.99% oxygen was used. Hydrogen, nitrogen, carbon monoxide, carbon dioxide and deuterium were obtained from Matheson Co. Alkynes, allene (Matheson Co.) and dimethylacetylene (K and K Laboratory) were further purified by vacuum distillation. All other reagents and materials used were either from Fisher Co. (high quality grade) or from K and K Laboratory.

Catalysts

Active alumina (Fisher Co.) of 8–10 mesh size was ground until it passed a 40–60 mesh size seive. Only 40–60 mesh size alumina granules were used for catalyst purposes. Alumina supported copper oxide (5% Cu) was prepared by the impregnation of the supported material with the calculated amount of cupric nitrate. The mixture was evaporated to dryness at 60°C and calcined at 500°C for 15 hr. Pure alumina catalyst was prepared in a similar

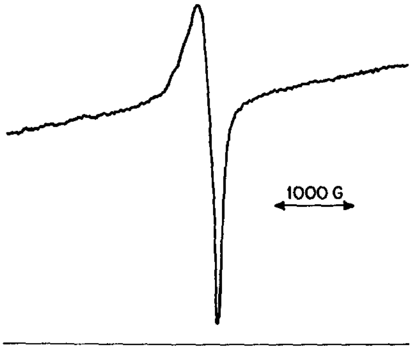


FIG. 1. ESR spectra of Cu–alumina.

way by treating alumina with water. All catalysts were heated and evacuated for 2 hr in the ESR tube prior to use. The weight of the catalyst in the ESR tube was always ~0.25 g.

ESR Measurements

The ESR measurements were carried out using a Bruker 416 spectrometer operating at *X*-band. All measurements were made at room temperature. The relative intensities of the ESR signals were measured by integrating the area covered by the signals. The *g* values were calculated by comparing the *g* value of DPPH (2.003). The ESR tube (Wilmad Glass Co., stopcock joint and sample tube) was connected by a ball joint to a conventional vacuum apparatus (*8*) which was maintained at 10^{-3} mm Hg pressure. The tube along with the stopcock could be easily detached or connected to the vacuum apparatus. There was also a heating arrangement for the ESR tube in the conventional vacuum apparatus.

A special type of ESR glass tube was made to observe the effect of H_2, D_2, N_2, CO, CO_2 and acetylene on the oxygen treated paramagnetic species.

X-Ray Diffraction Studies

A Phillips diffractometer was used. The measurements were carried out by the Debye-Scherrer method at room temperature using a cobalt target and iron filter. X-Ray analysis showed that the alumina used was of γ-type. No free Cu, CuO or CuO_2 was detected in the used and unused CuO supported alumina catalyst.

The products of the reaction of methylacetylene and allene with Cu–alumina were analyzed by gas chromatography using a dimethylsulfolane column.

RESULTS

The ESR spectrum of the oxidized catalyst containing 5% Cu on alumina is shown in Fig. 1. The observed spectra are due to Cu^{2+} (*9*). The lack of HFS indicates that for polycrystalline or amorphous material, the crystallites or molecules are randomly oriented in the field and the ESR spectra are the sum of the resonances of either crystallites or molecules in all orientations. No appreciable effect was observed on heating and evacuating the sample for 2 hr at 360°C under experimental conditions.

When Cu–alumina was treated with a solution of thiodiphenylamine in benzene (TDPA) a new peak was observed including the Cu^{2+} under same conditions as with Cu–alumina (Fig. 2). The new peak was from TDPA cation radical (*10*). This cation radical was formed by donating an electron which was accepted by Cu–alumina. On

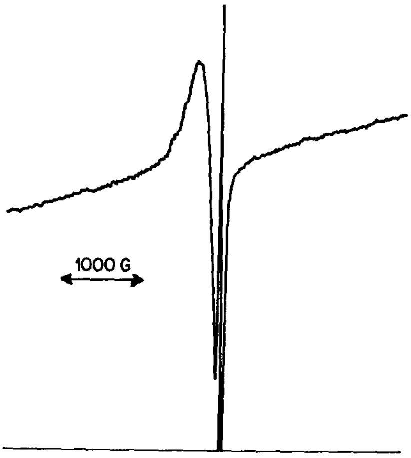


FIG. 2. ESR spectra of Cu–alumina/TDPA in benzene.

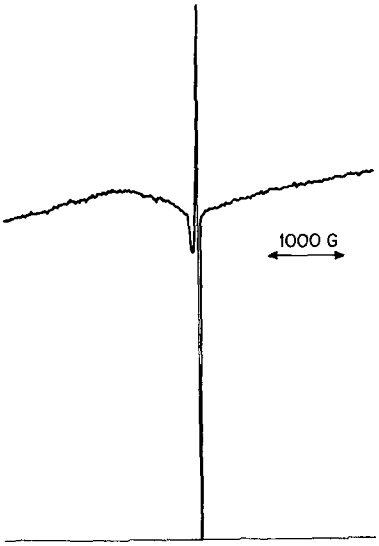


FIG. 3. ESR spectra of Cu-alumina/acetylene.

the other hand, no new band was observed for tetracyanoethylene (TNCE), anion radical (*11*) when the Cu-alumina catalyst was treated with TNCE in benzene.

When Cu-alumina was treated with acetylene, methyl-, ethyl-, dimethylacetylene and allene at room temperature, no appreciable effect was observed in the ESR spectra of Cu^{2+} ion. But the spectra changed (Fig. 3) when these gases were admitted into the tube at 360°C after activating the catalyst by heating and evacuating at 360°C for 2 hr. The color of the catalyst changed from green to dark pitch black depending on the hydrocarbon admitted. While it was dark pitch black for acetylene, it was gray for dimethylacetylene. It also depended on the interaction time. A new line was observed in the spectra at $g = 2.00$. The Cu^{2+} concentration decreased drastically. It seems that Cu^{2+} ion interacted with adsorbed gases and gave paramagnetic species. No such effect was observed with pure alumina under experimental conditions. Figure 4 shows the spectra of the paramagnetic species formed by acetylene over Cu-alumina. The width of the line was ~3.5 G and slightly nonisotropic. Similar behavior was observed when other alkynes and allene were used instead of acetylene. The characteristics of the present spectra are similar to those obtained from carbon chars. But the present spectra is not from carbon due to the following reasons:

i. X-Ray analysis of the treated catalyst (after reaction) did not show any traces of free carbon, though the color of the catalyst (treated) was dark pitch black.

ii. Negative results for free carbon tests were obtained when the treated catalyst was heated with melted $KClO_3$ (*12*) or burned in excess of air (*12*).

iii. While the width of the coke samples reported in the literature is ~8 ± 2 G (*13*), the width of the present spectra is ~3.5 G and slightly nonisotropic.

iv. While the coke samples reported in the literature are obtained at >500°C (*13*), the present sample was obtained at 360°C.

Sokolova *et al.* (*14*) also reported that alumina supported palladium oxide formed a complex with acetylene which was stable at ⩾400°C. Alkanes and alkenes do not give paramagnetic species under experimental conditions. The observed paramagnetic species are attributed to a low lying thermally populated, triplet state of charge transfer complex (*6*, *15*, *16*).

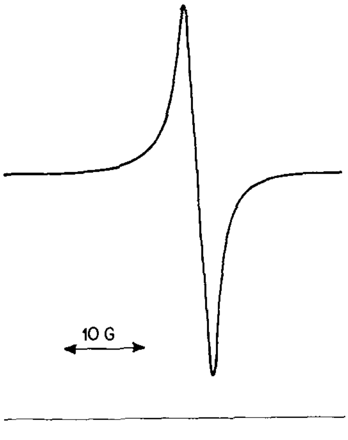


FIG. 4. ESR spectra of PMS from acetylene on Cu-alumina.

TABLE 1

Results of the Cu–Alumina/Alkanes and Allene Interaction

Hydrocarbon	Pressure drop[a]	No. of spins ($\times 10^{15}$)
Acetylene	43	6.8
Methylacetylene	25	2.6
Ethylacetylene	20	1.5
Dimethylacetylene	13	1.0
Allene	18	2.3

[a] Initial pressure of hydrocarbon = 100 mm and interaction time = 10 min.

The results of present investigations are given in Table 1. The concentration of the paramagnetic species were calculated by comparing the area covered by the signals to the area covered by a coke sample containing 10^{14} spins. These radicals were very stable and could not be destroyed either by heating or evacuating continuously at 360°C for several hours.

Figure 5 shows the increase in ESR signal intensity as a function of time for the system Cu–alumina/acetylene as a solid mixture. The intense resonance, obtained almost immediately on mixing, was not an equilibrium value, but increased with time, becoming substantially at equilibrium within 10 min. Cu^{2+} concentration decreased with the increase in paramagnetic species. The equilibrium value depends on the nature of the reactant used. Subsequent decay was almost imperceptible over several hours even when the Cu–alumina/hydrocarbon was heated and evacuated for 26 hr at 360°C. Similar results were obtained with $PtO_2 \cdot 2H_2O$/chrysene as a solid mixture in the presence of benzene (*6*). When oxygen or air was admitted into the evacuated Cu–alumina/hydrocarbon, the intensity of the ESR signal decreased drastically. No effect on Cu^{2+} concentration was observed. The signal of paramagnetic species reappeared with original intensity and shape when oxygen was evacuated either at room temperature or at 360°C continuously for 10 min.

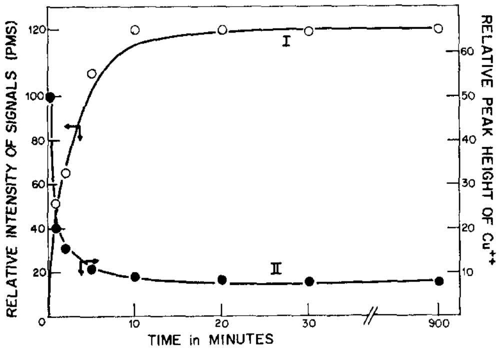


Fig. 5. Relative intensities of PMS and Cu^{2+} with respect to reaction time.

In another experiment the catalyst was heated at 360°C for 1 hr. in the special tube. Acetylene was passed over the catalyst for 10 min. The spectrum was similar to that shown in Fig. 4. On passing oxygen over this sample only for 2 min at room temperature, the intensity of the spectrum decreased and the line width increased. When carbon monoxide was passed over this sample for 5 min at room temperature, the spectrum reappeared with almost original signal intensity and shape. Similar effect was observed when D_2, H_2, N_2, CO_2 and acetylene were passed over oxygen treated paramagnetic species. While the affinity to remove O_2 from the paramagnetic species for CO and D_2 was the maximum it was minimum for nitrogen and acetylene. This effect was also observed over oxygen treated paramagnetic species formed by other alkynes and allene. It seems that either oxygen is very weakly adsorbed and bonded with paramagnetic species or is due to the shifting in the equilibrium between the paramagnetic species and nonparamagnetic species, discussed below.

An analysis of the products of the treated methylacetylene and allene suggests that the polymerization, self-hydrogenation and cracking processes occurred together. However, no detailed study has been made.

DISCUSSION

The ESR spectrum of Cu–alumina (Fig. 2) is due to Cu^{2+} ions (*9, 17*). The lack of HFS suggests an exchange narrowed orthorhombic spectrum. This type of spectra is observed whenever a spin-exchange interaction between paramagnetic centers takes place and the spinexchange frequency is larger than the hyperfine separations (*18*).

X-Ray analysis confirmed the alumina to be of γ-type. The structure of γ-alumina is a very complex one. No detectable amounts of free Cu, CuO and CuO_2 was found in γ-alumina supported copper oxide (before and after the interaction with the hydrocarbons). Some of the surface hydroxyl groups of alumina (basic group) are very difficult to remove. The hydroxyl groups of alumina are capable of forming a salt with the cupric acid. Thus with alumina as a carrier, copper is combined to form Cu–O–Al groups, which are active sites for the generation of the radicals.

On comparing the spectra of Cu–alumina, Cu–alumina/TDPA and Cu–alumina/acetylene systems (Figs. 1, 2, and 3) it appears that Cu–alumina contains at least two types of active sites. While one has electron acceptor property (TDPA cation radical formation) (*10*), the other, Cu^{2+} has the property of interacting with alkynes and allene to give paramagnetic species. As there was no appreciable effect of TNCE in benzene (electron acceptor compound to give TNCE anion radical) (*11*), it seems that electron donor properties of Cu–alumina were poisoned. Pure alumina has more electron donor property than electron acceptor (*19*). Schwab and Kral (*20*) also have suggested the possibility of both electron donor and electron acceptor sites being present on the surface of doped aluminas. A comparison of the concentrations of Cu^{2+} in Cu–alumina and Cu–alumina/TDPA (Figs. 2 and 3) suggests that the Cu^{2+} ion concentration is the same in both the cases. The ESR spectra confirmed that γ-alumina supported copper oxide has at least two active sites. While one site serves as an electron acceptor, the other one acts to form paramagnetic species with alkynes and allene in Cu^{2+}.

It was observed that the relative intensity of a series of acetylenic compounds to form a bridge between catalytic centers is in the order: acetylene > methylacetylene > allene > ethylacetylene > dimethylacetylene.

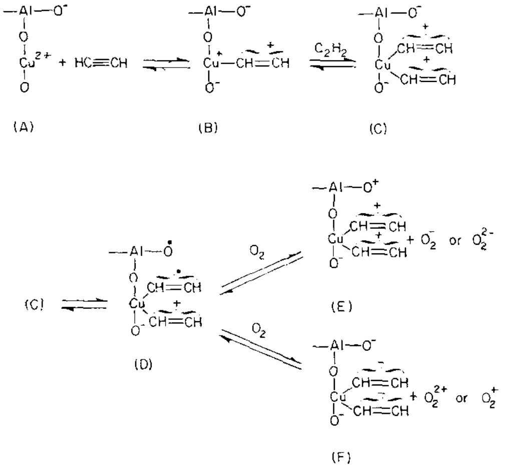
The data reported in Table 1 indicate that the effects involve steric factors. Besides this, other reasons are also possible. For a particular hydrocarbon the amounts of each adsorbed species vary from metal to metal. Also the amounts of adsorbed species for a particular metal depends on the structure of the metal surface. ^{14}C acetylenic adsorption studies on metals (*21*) demonstrate the existence of four types of adsorbed acetylene: (A) which undergoes desorption on evacuation; (B) which is removed from the surface during hydrogenation; (C) which is not removed during hydrogenation, but is removed by treatment with hydrogen at 150°C and (D) which remains on the surface even after evacuation at 150°C. It is possible that this last type of adsorbed acetylene and other hydrocarbons give the paramagnetic species.

It was observed that while alkynes and allene interact with Cu–alumina to give paramagnetic species, alkanes and alkenes do not. The common structure of electrons bonding, i.e., *sp* hybridized orbital, may be responsible for the formation of paramagnetic species. The electrons of π bonding interacts with the electrons of the *d* orbitals of the metal (*22*) and give paramagnetic complex.

The results of the present investigation suggest that the principle mode of interaction between acetylenic hydrocarbons with Cu–alumina is by means of $-C\equiv C-$, triple bond and in allene, $=C=C-$bond (*23–26*). It may be possible that paramagnetic species formation from allene is due to the methylacetylene formed by the isomerization of allene (*28*).

From the present published data it appears that the role played by oxygen in the ESR investigations of catalysts is still controversial. Whereas Hirota *et al.* (*29*) and Leftin (*30*) have reported that oxygen severely diminishes the ESR signal intensity arising from the interaction of hydrocarbons with silica–alumina, Fogo (*31*) found the signal intensity increased. Scott *et al.* (*32*) have investigated the one electron oxidation of perylene on alumina dehydrated above 400°C. They found that molecular oxygen was important in the process, since while no ESR spectrum was obtained when alumina was subjected to prolonged evacuation prior to hydrocarbon addition, it appeared on subsequent admissions of oxygen. In the present investigations though oxygen reduced the signal intensity severely, the ESR spectra reappeared with almost original intensity and shape on evacuation of oxygen (in some cases evacuating at higher temperatures up to 200°C. Dollish and Hall (*33*) carefully examined the effects of the diphenylethylene–silica–alumina and established that adsorbates, such as H_2, N_2 and Ar functioned only in a physical manner, influencing the signal intensity without altering the actual spin concentrations and that the behavior of more active adsorbates such as H_2O and oxygen was greatly complex. In the present investigations O_2 could be easily removed by passing CO, CO_2, D_2, N_2, H_2 and acetylene over oxygen treated paramagnetic species at room temperature and the ESR spectra reappeared with original intensity and shape. It seems either oxygen interacted with the paramagnetic species with a very weak bond and formed a nonparamagnetic complex or it was adsorbed physically resulting in a shift in the equilibrium between the paramagnetic and nonparamagnetic species.

The following mechanisms are postulated for the paramagnetic species formation and the oxygen effect which are based on shift in the equilibrium between paramagnetic and nonparamagnetic species.



The ESR spectra of the paramagnetic species of O_2 (*34*, *35*) could not be observed due to the low concentration of these species (*36*).

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