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Formation of Thianthrene Radical Cations on Molybdena–Alumina Surfaces

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The radical ion of thianthrene was generated on molybdena-modified alumina under a variety of experimental conditions. Two resonance signals, one due to the cation and the other due to Mo(V), were observed and their absolute concentration was measured. The absolute intensities depend on the amount of molybdena incorporated in the catalysts and their pretreatment. The role of molybdenum in the electron transfer reaction is discussed, and a mechanism is presented that accounts for the varying intensities.

INTRODUCTION

The characteristics of molybdenum-modified alumina have received considerable attention in recent years with both the surface acidity and oxidizing properties of Al_2O_3 being affected by MoO_3 (*1–3*). Radical-forming activity, for example, has been observed in molybdenum-modified alumina even in the absence of molecular oxygen (*2a*).

In previous papers (*1,3*), we showed the considerable changes that the molybdena, when incorporated into alumina, can impart to the host material. The surface acidity is changed, both as to the nature and distribution of acid sites. Too, the capacity of the surface to enter into electron transfer reaction is dramatically changed when molybdena is incorporated into alumina. We have also shown that the number of paramagnetic centers formed during the electron transfer reaction upon the adsorption of thianthrene on molybdenum–alumina depends significantly on the pretreatment of the substrate. So does the anisotropy of the site occupied by the Mo(V) centers.

We have examined the surface characteristics of MoO_3–Al_2O_3 by generating the thianthrene radical cation under a variety of experimental conditions and measuring its absolute spin concentration. In addition, we have measured the spin concentration of Mo(V) which is formed in the process. In a previous paper (*3*), we presented the activated analysis of the spectrum of this radical cation on SiO_2–Al_2O_3 and MoO_3–Al_2O_3. In this study our main concern was the formation of the cation and the electron transfer process itself.

EXPERIMENTAL METHODS

The experiments were carried out as discussed earlier (*1b*). A dual sample cavity, operating at 9.5 GHz and employing 100-kHz magnetic field modulation, was used for intensity measurements. A solution of diphenyl picryl hydrazyl (DPPH) in benzene and Cu(II) in Y-type Na-zeolite were intensity standards for measuring the absolute concentration of thianthrene radical ion and Mo(V), respectively. Spectra, collected in digital form through a PDP 8/S, were double-integrated by a Gaussian quadrature formula for the first integration and Simpson's one-third rule for the subsequent integration. Additional details of intensity measurements are described elsewhere (*1b*).

Molybdena–alumina samples were prepared by impregnating η-Al_2O_3 with ammonium paramolybdate solution, followed by drying at 100°C for 2 hr with subsequent calcination at 500°C in a current of air for about 18 hr. The catalysts were used in 20–40 mesh pellet form. Thianthrene, supplied by Aldrich, was boiled in acetone over charcoal and further purified by crystallization from hot acetone; its purity was checked by differential scanning calorimetry. The solvents used were purified by distillation.

Each catalyst was activated at 500°C for 4 hr and thianthrene in solution was brought into contact with the catalyst as it was cooling below 200°C in air, unless the whole activation process was carried out entirely in vacuum. The sample was shaken for 1 min and the excess solvent was removed by pumping for 0.5 hr at room temperature. The catalyst was then transferred to a side ESR tube (Pyrex; 4 mm o.d., 2 mm i.d.) and sealed. Activation was done in a current of air, oxygen, hydrogen or vacuum.

RESULTS AND DISCUSSION

Thianthrene, when adsorbed from a benzene solution on η-Al_2O_3 which had been activated in air or vacuum, gave no evidence of resonance absorption. But, when adsorbed on silica–alumina or molybdena–alumina, a pink-colored solid appeared, which gave a three-component ESR spectrum along with a broad signal in the case of molybdena–alumina assigned to Mo(V). Several arguments have been presented to show that the three-component spectrum is due to a single species and the triplet structure is the result of complete *g* anisotropy (*3*).

Supported hexavalent molybdenum is reduced to some extent to the pentavalent state upon calcination at elevated temperatures (500°C) in air, oxygen or vacuum. The concentration of Mo(V) formed is about 10^{18} spins/g. When the activation is carried out in hydrogen, there is a further increase in the level of Mo(V) observed. Reduction is therefore presumed to proceed via oxygen abstraction from the lattice.

Radical cations were generated on an MoO_3–Al_2O_3 (9% by wt Mo) surface after hydrogen reduction and on samples similarly activated in vacuum, air or in a current of oxygen. The concentration of Mo (V) and of the radical cation generated under these activation conditions is shown in Fig. 1 along with the level of Mo(V) formed when a hydrogen-reduced sample is treated with benzene only. The level of pentavalent molybdenum produced is maximum in the hydrogen-reduced sample and least in the air and oxygen activated samples, while in the evacuated sample, it is intermediate. But, the radical cation concentration is inversely related to the level of Mo(V). The radical cation was generated also in a series of MoO_3–Al_2O_3 samples with increasing total molybdenum concentration activated in a current of air, and the spin concentration of the two species was measured (Fig. 2). The concentration of Mo(V) and of radical cation has an identical dependence on the total molybdenum incorporated into the support; the intensity of both passes through a maximum at about 9% by weight of total molybdenum. In Fig. 2, several data points

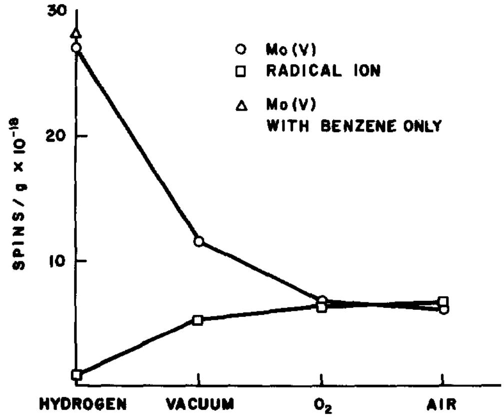

FIG. 1. Absolute intensity of ESR signals of Mo(V) and thianthrene radical cation generated under various conditions.

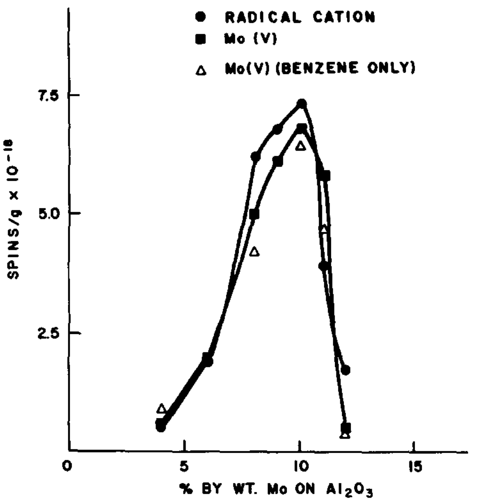

FIG. 2. Absolute intensity of Mo(V) and thianthrene radical cation on a series of MoO_3–Al_2O catalysts activated in air at 500°F.

are given which give the level of Mo(V) produced when the catalyst is treated with benzene alone. The amount of Mo(V) produced in hydrogen-reduced molybdena-alumina behaves similarly; i.e., it increases with total molybdenum content up to about 9% by weight Mo and then decreases.

There are sufficient experiments reported that account for the behavior of Mo(V) with amount of molybdenum incorporated (Fig. 2). Mo(V) is known to require stabilization by a host material and it cannot be formed in bulk MoO_3. Thus, in the rising part of the curve, up to about 9% molybdena, the increased amount of Mo(V) simply reflects the increasing amounts of MoO_3 initially incorporated. However, beyond that level multilayers and clusters probably occur; i.e., there is formation of "bulk" MoO_3. This would preclude the formation of additional Mo(V) and would predict at least a leveling off of the amount of Mo(V) formed. However, it is also known (*4*) that reduction at these high levels favors Mo(IV) formation. This formation can occur both at the expense of Mo(VI) and Mo(V), resulting in the observed decrease of Mo(V).

The reduction of hexavalent molybdenum to the pentavalent state by several hydrocarbons has also been observed by ESR. The formation of Mo(V) in this case has been explained assuming the formation of charge transfer complexes (*5*). Although Mo(V) has been observed by ESR, the signal due to the radical cation of the corresponding hydrocarbon has not been detected in the room temperature studies. The mechanism proposed (*6*) to explain the formation of Mo(V) in propane-treated mixed oxide catalysts containing MoO_3 includes the following. Propane adsorbs on a molybdenum site, interacts with O^{2-} releasing an electron, which is accepted by an adjoining Mo(VI), resulting in pentavalent molybdenum. But, the corresponding O^- or OH^- that is produced during this reaction has not been observed by ESR. The mechanism proposed by Peacock *et al.* (*6*) for Mo(V) formation is consistent with our results also. At no time did we observe the benzene radical cation, although this species is known to exist, for example, as stabilized on hydrogen zeolon (*7*). Since the Mo(V) and the radical cation concentration correlate well over the entire concentration of molybdenum in alumina (Fig. 2), it is tempting to write the following simple reaction:

$$\mathrm{Mo(VI)} + \mathrm{Th} \rightarrow \mathrm{Th}^{\cdot +} + \mathrm{Mo(V)}. \quad (1)$$

In view of the fact that Mo(VI) is a good electron trap and the ionization potential of thianthrene is rather low, this scheme would not be unreasonable. However, this simple equation for the electron transfer reaction is not sustained upon closer scrutiny.

If the situation were described by Eq. (1), we would predict that: (a) as we increase the Mo content of the catalyst, we would increase both the cation and Mo(V) concentration, and (b) the Mo(V) level observed would correspond quantitatively to the cation concentration, or if there were initially some Mo(V) present, cation formation would entail further enhancement of the Mo(V) level equal to the number of cations formed. Figures 1 and 2 show that we obtain the quantitative correlation between the two species, but they also show that the level of Mo(V) is the same regardless whether the catalyst has been treated with benzene only or benzene-thianthrene solution. The way out of this apparent paradox, we feel, is the following scheme, quite analogous to the observations of Naccache, Bandiera and Dufaux (*2a*) in their study of polyacene radical cations on MoO_3–Al_2O_3.

The rising portion of the curve suggests that hexavalent molybdenum is the electrophillic sites and the number of these sites increases with total Mo concentration, with a corresponding increase in the concentration of radical cations also. Flockhart, Scott and Pink (*8*) have established that the electron affinity of Lewis acid sites on Al_2O_3 are not sufficiently strong to abstract electrons from adsorbed polyacene molecules and the presence of molecular oxygen is necessary to effect electron transfer. But, radical cations can be generated on MoO_3–Al_2O_3 surface in air and also in vacuum. By analogy, Naccache, Bandiera and Dufaux (*2a*) have concluded that Mo plays a similar role as molecular oxygen.

The initial pretreatment history determines the distribution of Mo in its various valences. In addition, the number of sites that can enter into electron transfer reactions is determined. Cation formation can proceed in accordance with the experimental observations if we simply assume then that reduction of Mo(VI) to Mo(IV) is strongly favored. The thianthrene neutral molecules, upon being adsorbed, lose an electron which is captured by hexavalent molybdenum atoms. These eventually are reduced to the +4 state. Formally we may write

$$\mathrm{ThO^{2-} \rightarrow Th^{+} \cdot O^{2-} + e,}$$
$$\mathrm{Mo(VI) + 2e \rightarrow Mo(IV).}$$

This mechanism would explain the inverse relationship between the amounts of Mo(V) and thianthrene radical cation as well as the fact that there is no difference in the level of Mo(V) with benzene only or benzene plus thianthrene.

As the amount of MoO_3 incorporated into alumina increases, the more Mo(VI) sites are available for electron capture to produce eventually Mo(IV) and $Th\cdot^+$. Thus, in the rising part of the curve (Fig. 2), we expect the Mo(V) concentration to remain constant even after the $Th\cdot^+$ generation for a given percentage of molybdena initially introduced into the substrate. In addition, we expect an increase of $Th\cdot^+$ concentration, this concentration of the cation closely paralleling the Mo(V) concentration. The reason for this is that at the lower levels of molybdena incorporated, there is little Mo(IV) and, therefore, the Mo(V) reflects, also by difference, the number of Mo(VI) sites. In addition, this scheme of things would be consistent with the inverse relationship (Fig. 1) between Mo(V) and $Th\cdot^+$ concentration. Let us compare, for example, the hydrogen-reduced and air-calcined situations, both with the same amount of MoO_3 incorporated (9%). Upon hydrogen reduction, there is a large formation of Mo(V) and proportionally a smaller number of Mo(VI) sites remain for electron capture to produce Mo(IV) and $Th\cdot^+$ formation. Thus, generally, the more you reduce initially the Mo(VI) to Mo(V), the less the cation concentration will be when thianthrene is adsorbed.

To complete the scheme of things, we need some quenching mechanism to account for the lower levels of Mo(V) and cation radical beyond 9% of molybdena in alumina. We have already indicated that the Mo(V) decreases during the pretreatment for, multilayers and clusters being in essence bulk MoO_3, favor Mo(IV) formation. Thus, to start with, there are fewer Mo(VI) sites which can participate in the cation formation. Additionally, the reverse reaction could become important, namely,

$$\mathrm{Mo(IV)} + 2\mathrm{Th}^+\ \mathrm{O}^{2-} \rightarrow \mathrm{Mo(VI)} + 2\ \mathrm{ThO}^{2-},$$

since we have such a high preponderance of Mo(IV) sites.

In conclusion, the amount of MoO_3 initially incorporated into the lattice and the treatment of the catalyst prior to thianthrene adsorption determine the eventual concentration of both paramagnetic species present. The amount of Mo(V) is fixed during pretreatment and remains unchanged during the oxidation of thianthrene. Yet, Mo(V) determines the thianthrene cation concentration for it controls the number of sites that are available for electron transfer. This situation obtains for the entire range of percentage of MoO_3 incorporated into the lattice. This mechanism explains the formation of radical cation and its intricate dependence on total molybdenum content and pretreatment of samples. It is also in agreement with the observation that in supported MoO_3 (*1b*), Mo(V) is an intermediate in the reduction of Mo(VI) to Mo(IV).

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