An Electron Spin Resonance Study of the Interactions of Olefins with Na and K Molybdates

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The ESR spectra and the catalytic activity of sodium and potassium molybdates have been investigated. In agreement with the structural analogies with the bismuth molybdate catalysts active in olefin oxidation, formation of the Mo(V) ESR signal is observed when they are placed in contact with 1-butene or propene. However, the catalytic activity was almost nil. The catalytic inactivity has been explained as due to the difficulty of reoxidation by gaseous oxygen. The failure of a partner with red-ox properties, such as Bi(III) or Fe(III), and the higher stability of the reduced centers have been suggested to be responsible for the difficulty of reoxidation.

INTRODUCTION

Bismuth molybdates are well known catalysts for the selective oxidation of olefins (1, 2). Some authors have advanced that bismuth molybdates present structural analogies either with $Na_2Mo_2O_7$ (3, 4) or with $K_2Mo_3O_{10}$ (5). Both these compounds have molybdenum–oxygen double bonds as shown by their i.r. spectra (3, 5). According to previous suggestions (6–8), this type of bond is typical for the molybdates active in olefin oxidation. Moreover, $K_2Mo_3O_{10}$ is known to possess edge-sharing octahedra and tetragonal pyramids (9), a structure which was suggested as the surface active center for the catalytic activity in the bismuth molybdates (5).

In this work, the catalytic activity and the ESR spectra observed after reduction of these compounds have been investigated.

EXPERIMENTAL

$Na_2Mo_2O_7$ and $K_2Mo_3O_{10}$ were prepared following the procedures reported respectively in refs. (3 and 5). MoO_3 was Riedel

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de Haen reagent grade. All the catalysts were characterized by X-ray and ir spectroscopy. Calcination of the catalysts was carried out at 450°C for 2 hr.

ESR spectra were obtained with a Varian V 4502 X-band spectrometer. The sample probe, directly inserted in the ESR resonance cavity, was connected to a vacuum line set immediately above the resonance cavity. Sample heating was achieved by using a modified heater coil analogous to that described by Sancier et al. (10) in order to obtain temperatures up to 450°C. The power for the heating was controlled by a Variac. The temperature was measured by a copper–constantan thermocouple. Excessive heating of the cavity was avoided by means of a fan.

The reproducibility of the ESR spectra was within 5–10%.

On $Na_2Mo_2O_7$ and $K_2Mo_3O_{10}$, oxidation runs of 1-butene, 1% in air, with 1.5 gm of catalyst and a flow rate of 60 cc/min, were carried out in a Pyrex flow microreactor, over the temperature range 300–450°C. Oxidation runs on the same catalysts in a batch reactor of the type described in ref. (11) were carried out at 380°C for 10 min with 5% 1-butene in air, and with 3 gm of catalyst.

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RESULTS

ESR Results

When reduced under vacuum, in hydrogen, propene, or 1-butene, $Na_2Mo_2O_7$ shows in previously reported reduced Bi/Mo the well-known molybdenum (V) axially symmetric spectrum ($g_\parallel = 1.894$, $g_\perp = 1.932$, $g_{av} = 1.919$, Fig. 1, spectrum A), which behaves similarly to that observed catalysts (*10, 12–15*). The signal is very easily obtained even by simple evacuation at moderate temperature (about 200°C). $K_2Mo_3O_{10}$, in contrast, gives a rhombic spectrum with three g-values ($g_1 = 1.936$, $g_2 = 1.921$, $g_3 = 1.904$, $g_{av} = 1.920$, Fig. 2). With respect to the sodium dimolybdate, the potassium compound is much less reducible, a spectrum being observed only by reduction with 1-butene at temperatures above 300°C. MoO_3 is almost as reducible as $K_2Mo_3O_{10}$. All these results are in contrast with the unsupported Bi_2MoO_6 catalyst which is known to give no Mo(V) ESR signal in analogous conditions (*15, 16*). Figure 3 summarizes the ESR signal intensity of the three samples investigated as a function of the time of reduction with propene.

Other signals, in addition to the Mo(V) signal, are also observed. In $Na_2Mo_2O_7$, a sharp and symmetrical signal centered at $g = 2.003$ (Fig. 1, spectrum B), when reduced with propene, is identical to that previously described on 1/1, 2/3, and 6/1 Bi/Mo catalysts supported on silica with various catalyst/support ratios (*10, 12*). In the present paper this signal will not be further discussed. Further details of this signal on other molybdenum catalysts will be published elsewhere (*17*). A broad signal ($g = 2.35$) is also observed particularly on $Na_2Mo_2O_7$, which narrows with increasing temperature (Fig. 1, spectrum C). A similar spectrum has been investigated by Schuit and co-workers on bismuth molybdates and on other catalysts (*18*). We do not further investigate this signal.

Upon readmission of oxygen at elevated temperatures ($\simeq$450°C), for a few minutes, all samples are reoxidized and the color turns to white. After reoxidation and evacuation, no ESR Mo(V) signal can be detected either at 450°C or at room tem-
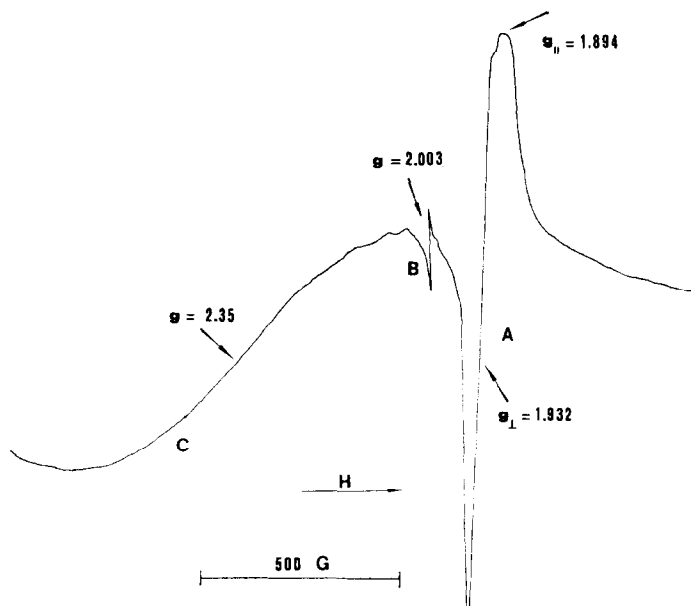

FIG. 1. ESR signal from $Na_2Mo_2O_7$ reduced with propene (100 mm Hg) at 350°C. Temperature of registration: 23°C. For spectrum A, B, and C, see text.
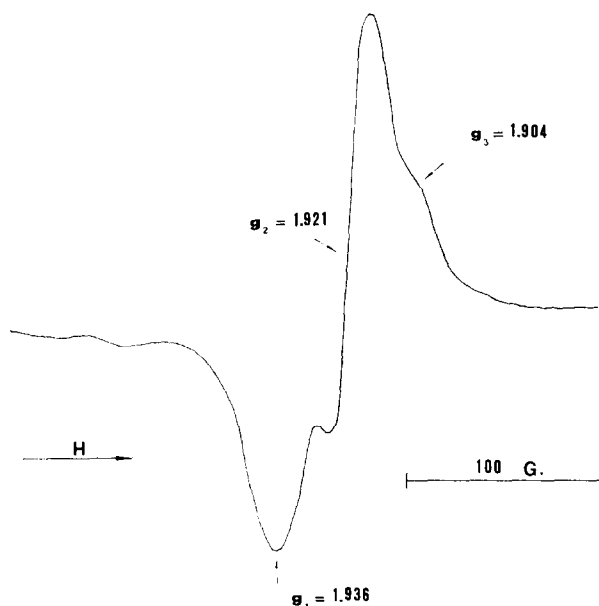
FIG. 2. ESR spectrum from $K_2Mo_3O_{10}$ reduced with propene (100 torr) at 400°C. Temperature of registration: 23°C.

perature. However, there are large differences in the case of reoxidation with increasing temperature. From Fig. 4, the following order of reoxidizability can be deduced: $MoO_3 \gg Na_2Mo_2O_7 \simeq K_2Mo_3O_{10}$.

Adsorbed oxygen at room temperature does not influence appreciably the intensity of the Mo(V) signal for all three catalysts.

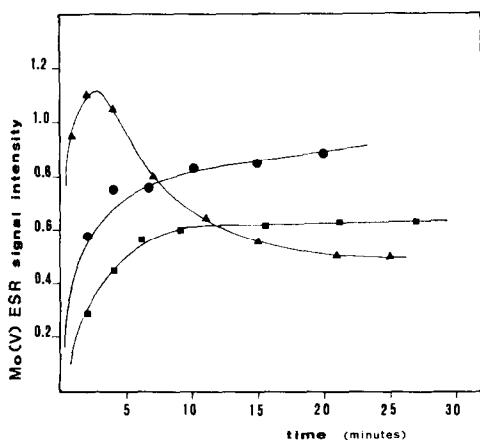FIG. 3. Mo(V) ESR signal intensity against time of reduction with 1-butene (100 torr) at 350°C; ▲, $Na_2Mo_2O_7$; ●, MoO_3; ■, $K_2Mo_3O_{10}$. Temperature of registration: 350°C.

Measurements of Activity

$Na_2Mo_2O_7$ and $K_2Mo_3O_{10}$ were inactive in the oxidation of 1-butene in a flow reactor over the entire temperature range investigated. In the batch reactor, sodium dimolybdate gave traces of butadiene and no carbon oxides were detected. No butadiene and carbon oxides has been observed with the potassium trimolybdate.

The color of the two molybdates after the oxidation runs of 1-butene was, in both reactors, blue-black, while the starting materials were white.

DISCUSSION

Mo(V) ions symmetrically coordinated have very short spin-lattice relaxation times, with the result that the ESR signals are undetectable even at liquid nitrogen temperature. A square pyramidal coordination with C_{4v} symmetry has been proposed for the Mo(V) ions giving an ESR signal with two g-values obtained from molybdenum catalysts after reduction (12, 13). Bond parameter calculations support this assumption (13). This reduced form of Mo(V) must be associated with lattice
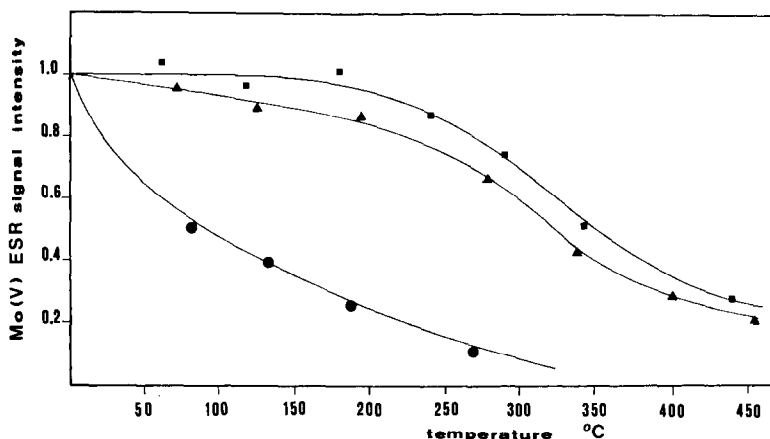
Fig. 4. Reoxidation rate against temperature of oxygen admission (500 mm Hg, 2 min) as evaluated from the decrease of the Mo(V) ESR signal: ▲, $Na_2Mo_2O_7$; ●, MoO_3; ■, $K_2Mo_3O_{10}$. All ESR measurements are taken at room temperature.

defects or oxygen vacancies in order to account for the required axial symmetry. We suggest however, that the degree of reduction is much stronger than indicated by the Mo(V) signal intensity, since part of the Mo(V) sites can be almost symmetrically coordinated.

Sodium dimolybdate shows an ESR signal with almost the same ESR parameters, thereby suggesting the same coordination for the Mo(V) ions. The crystal structure of $Na_2Mo_2O_7$ presents a chain structure formed by MoO_4 tetrahedra, each sharing two oxygen atoms with a chain of MoO_6 octahedra (19). From the ESR parameters, it is conceivable that the reduced centers responsible for the signal arise from the MoO_6 octahedra, while tetrahedral molybdenum is either unreduced or reduced to almost symmetrical Mo(V) or to Mo(IV), which are both undetectable by ESR.

The crystal structure of $K_2Mo_3O_{10}$ consists of infinite chains of edge-shared MoO_6 octahedra and MoO_5 square pyramids (9). Both octahedra and square pyramids are strongly distorted both in the Mo–O bond distances and in the bond angles. The observed three g-factor spectrum can be due to Mo(V) ions in the square pyramids or in the strongly distorted octahedra, independently of the presence of oxygen vacancies. Similar ESR spectra have been previously observed for Mo(V) in an

octahedral field with strong rhombic distortion when Mo(V) replaces +4 ions in a rutile-type crystal (20).

We shall now discuss the effect of molecular oxygen adsorbed on the surface. As previously discussed (12), the triplet state unpaired electrons in the O_2 molecule establish a dipole–dipole interaction with nearby unpaired spins. As a consequence, adsorption of oxygen at room temperature on the reduced catalysts broadens the ESR spectra which derive from surface centers, while it does not affect the bulk centers. The Mo(V) signals for the three catalysts investigated in this work are not appreciably influenced by the adsorbed oxygen in contrast with the Bi/Mo oxides and MoO_3 supported on silica (12). On the contrary, the sharp signal at $g = 2.003$ is broadened out by exposure at a few millimeters Hg oxygen pressure. From this observation we can deduce that most of the reduced Mo(V) centers in the sodium and potassium compounds are located in the bulk. The mechanism of initial olefin oxidation at the expense of the lattice oxygen through a catalyst reduction, therefore, seems the same as in the active bismuth molybdates.

The formation of Mo(V) in the interaction of propene with $Na_2Mo_2O_7$ and $K_2Mo_3O_{10}$, and the formation of butadiene in the interaction between 1-butene and

$Na_2Mo_2O_7$ in the batch reactor, are a direct proof of the existence of oxidizing sites at the surface of the investigated molybdates. However, despite the presence of oxidizing sites and also of a certain mobility of oxygen in the lattice, as can be deduced from the existence of bulk $Mo(V)$, $Na_2Mo_2O_7$ and $K_2Mo_3O_{10}$ are inactive in the flow reactor towards olefin oxidation. The main difference between active and inactive catalysts can therefore be identified as the difficulty of the reoxidation of the latter. Indeed, Bi_2MoO_6, which is the most active catalyst (21), is known to be reoxidized to the extent of 95% within 1 min at ~200°C (22). From Fig. 4, it is possible to deduce that $Mo(V)$ oxidation on MoO_3 reaches ~80% at ~200°C within 2 min of 500 mm Hg oxygen contact, while for the sodium and potassium compounds, $Mo(V)$ is barely reoxidized even at 400°C. Moreover, activation energies for the oxygen diffusion of 13 kcal/mole for Bi_2MoO_6 (23) of 22 kcal/mole for the MoO_3 reduction with butene (24) have been reported, which show a big difference in the oxygen mobility in different oxides.

The difficulty of reoxidation of the sodium and potassium compounds can be attributed to various factors. The first, and perhaps the most important, is the absence of a partner such as $Bi(III)$ or $Fe(III)$ in the active bismuth and iron molybdates, which is able to reoxidize the $Mo(V)$ via lattice interaction and be successively reoxidized by gaseous oxygen (25, 26). It is therefore probable that the interaction of oxygen with the reduced centers is the same in potassium and sodium molybdates as in MoO_3. These sites can obviously be $Mo(V)$ and/or $Mo(IV)$. However, from Fig. 4, it is possible to deduce that the reduced sites are more stable in $K_2Mo_3O_{10}$ and $Na_2Mo_2O_7$ than in MoO_3. The structural differences between MoO_3, which has only MoO_6 octahedra, and $Na_2Mo_2O_7$ (octahedral and tetrahedral coordination) or $K_2Mo_3O_{10}$ (octahedral and square pyramidal coordination) may well explain the different reoxidation rate for the three catalysts.

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