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The Role of O^- Ions in the Oxidative Dehydrogenation of Ethane over Molybdenum Oxide Supported on Silica Gel

In an earlier paper the role of N_2O in the oxidative dehydrogenation (OXD) of ethane over supported molybdenum oxide was reported; however, it was not possible to obtain steady-state kinetic data in the recirculating reactor which was employed (*1*). Nevertheless, the results of the previous study suggested that O^- ions, formed by the surface decomposition of N_2O, initiated the catalytic process via a hydrogen abstraction reaction. Stoichiometric reactions between ethane and O^- ions on MgO and on supported molybdenum result in the formation of ethylene as the principal hydrocarbon product (*1*, *2*).

Electron paramagnetic resonance (EPR) studies have demonstrated that O^- ions may be formed on partially reduced MoO_3/SiO_2 under mild conditions (25–100°C) from N_2O but not from O_2 (*3*, *4*). Adsorption of oxygen results in the formation of O_2^- (*4*, *5*). In an attempt to further evaluate the role of O^- in the OXD reaction we have compared N_2O and O_2 as oxidants. A single-pass flow reactor was used so that steady-state kinetic data could be obtained.

Catalysts containing from 2 to 20% molybdenum by weight were prepared from silica gel (40–60 mesh) and ammonium paramolybdate as described previously (*1*). Prior to use the oxidized catalysts were reduced for 3 hr at 480°C using carbon monoxide and degassed at the same temperature. An initial concentration of O^- ions was generated by heating the partially reduced catalyst in N_2O for 16 hr at 90°C. Mixtures of C_2H_6 and either N_2O or O_2 were passed through 3.1 g of catalyst in a cylindrical flow reactor. When necessary helium was used as a diluent in order to maintain a constant total flow rate. In one series of experiments N_2O and O_2 were simultaneously present in the reaction mixture. The system was treated as a differential reactor since the conversion of ethane was normally less than 10%.

Upon passing the reactants over a catalyst containing 6.6% by weight molybdenum the products C_2H_4, CO_2, and H_2O were detected by gas chromatography. A trace of CH_4 (<0.01%) was also formed at reaction temperatures above 400°C, but no other hydrocarbon products were detected. The C_2H_4 production was transformed into a steady-state process for reaction times greater than about 30 min. The rates of formation as a function of temperature are shown in Fig. 1 for a gas mixture of 112 Torr C_2H_6 and 648 Torr N_2O. Here, a rate of 1.0 μmole min^{-1} g-Mo^{-1} for the formation of ethylene corresponds to a conversion of 0.6% based on ethane. The selectivity to ethylene (defined as mole ethylene/mole ethylene + $\frac{1}{2}$ mole CO_2) was 84% at 350°C and 64% at 425°C. Although not evident in the figure, the formation rate at 475°C was 12.6 and 13.9 μmole min^{-1} g-Mo^{-1} for C_2H_4 and CO_2, respectively. From

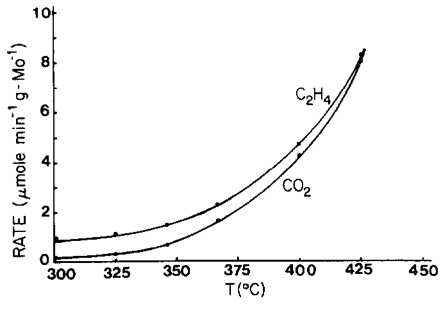

FIG. 1. Rate of formation of C_2H_4 and CO_2 as a function of the temperature of reaction between N_2O and C_2H_6 over 6.6 wt% Mo/SiO_2.

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plots of the logarithm of rates versus reciprocal absolute temperatures the apparent activation energies for the formation of C_2H_4 and CO_2 were 18.4 ± 0.6 and 28.7 ± 0.9 kcal/mole, respectively. The different activation energies suggest that different mechanisms are responsible for the two products.

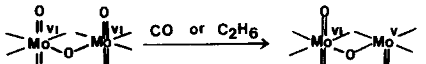
The rates of formation for both C_2H_4 and CO_2 were first order with respect to N_2O and C_2H_6 over the range of temperatures from 350 to 450°C and the range of pressures from 76 to 380 Torr for both reactants. At each temperature the selectivity to C_2H_4 was essentially independent of partial pressures of N_2O and C_2H_6.

With O_2 as the oxidant the reaction rate as a function of temperature is described in Fig. 2. Except for the substitution of O_2 for N_2O all of the experimental conditions were the same as those used to obtain the data of Fig. 1. With O_2 the apparent activation energy for the formation of CO_2 was 27.2 ± 0.8 kcal/mole which is not significantly different from the activation energy for the formation of CO_2 from N_2O. For the formation of C_2H_4 the apparent activation energy was 23.3 ± 0.7 kcal/mole. The rate of formation of both C_2H_4 and CO_2 was zero order with respect to O_2, but first order with respect to C_2H_6 over the temperature range from 350 to 450°C and the pressure range from 76 to 380 Torr for each reactant.

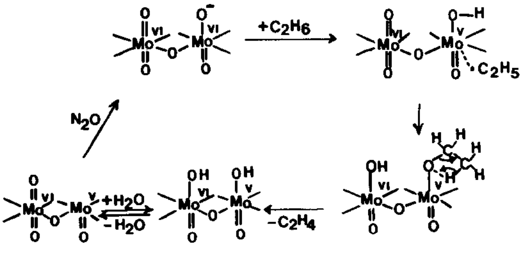
Upon comparing the rates of formation of C_2H_4 for reactions of N_2O–C_2H_6 and O_2–C_2H_6 over supported molybdenum catalysts, as depicted in Figs. 1 and 2, it is evident that at moderate temperatures N_2O is much more effective than O_2. For example, the rates of formation of C_2H_4 were in the ratio 7: 1 at 375°C. Even at 450°C the ratio of rates was 3.7: 1, although it is evident that the ratio decreased with increasing temperature.

Blank experiments in which only silica was present in the reactor demonstrated that at 400°C with N_2O as the oxidant approximately 10% of the C_2H_4 and CO_2 was derived from support and gas-phase reactions. By comparison, with O_2 as the oxidant 14% of the C_2H_4 and 75% of the CO_2 were derived from support and gas-phase reactions.

Differences in activation energies and orders of reaction indicate that the mechanisms are not the same for N_2O and O_2. Although the mechanism involving O_2 is unknown at this time, a mechanism for the formation of C_2H_4 via the reactive O^- intermediate enables one to understand the role of N_2O as an oxidant. The reaction mechanism may be described as:



(1)



(2)

Here we favor the incorporation of at least two Mo atoms in the active site since our results demonstrated that the catalyst with 10% by weight Mo had a maximum activity and selectivity for the formation of ethylene. At this loading, it is probable that

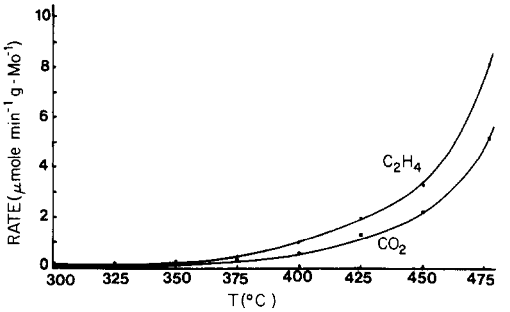


FIG. 2. Rate of formation of C_2H_4 and CO_2 as a function of the temperature of reaction between O_2 and C_2H_6 over 6.6 wt% Mo/SiO_2.

surface species with two adjacent molybdenum atoms, bridged by an oxygen atom, may exist in a considerable amount on the silica gel.

After the initial reduction step this mechanism would predict 100% selectivity for the formation of C_2H_4, which, of course, was not observed. Since O^- is a transient species which may also be destroyed by the interaction with an electron to form O^{2-} with the concomitant oxidation of Mo^V to Mo^{VI}, it is apparent that the surface must be subsequently reduced to produce Mo^V. It has been demonstrated that ethane is capable of promoting this reduction (*1*), and since the mechanism for the reduction of Mo^{VI} is not clear, we will describe it by the stoichiometric reaction:

$$14Mo^{VI} + 7O^{2-} + C_2H_6(g) \rightarrow 14Mo^V + 2CO_2(g) + 3H_2O(g). \quad (3)$$

The reaction rate law and the selectivities for the formation of C_2H_4 using N_2O may be rationalized if one assumes that the rates for the reaction

$$Mo^V + N_2O(g) \rightarrow Mo^{VI} - O^- + N_2(g) \quad (4)$$

and the reduction of Mo^{VI} according to reaction (3) are comparable. If such were the case, the overall steady-state rate would be first order with respect to both N_2O and C_2H_6. Since reactions (2) and (3) probably have different activation energies, it is not surprising that the selectivities for the formation of ethylene varied somewhat with temperature.

According to the mechanism proposed above $CH_3\dot{C}H_2$ radicals are present as intermediates. As pointed out by Benson (*6*) R · radicals react with O_2 molecules by one of two pathways:

$$CH_3\dot{C}H_2 + O_2 \begin{cases} \xrightarrow{\text{low temp.}} CH_3CH_2O_2\cdot & (5) \\ \xrightarrow[\text{high temp.}]{} CH_2 = CH_2 + HO_2\cdot & (6) \end{cases}$$

The low-temperature path leads to the formation of peroxides and hydroperoxides together with their decomposition products, while the high-temperature path leads to olefin formation. Equation (5) is also favored by high oxygen pressures, and Benson (*6*) has calculated gas-phase equilibrium constants for this reaction.

As a test for the presence of ethyl radicals on the surface, experiments were carried out in which both N_2O and O_2 were present in the reactant mixture, while the flow rate was kept constant at 71 ml/min. The N_2O served as the source of $CH_3\dot{C}H_2$ radicals via the O^- ion, and O_2 reacted with the radicals according to Eqs. (5) or (6). From Table 1 it is apparent that the rate of formation of C_2H_4 reached a maximum at O_2 partial pressures of 14 to 26 Torr. This maximum rate was 2.5 and 20 times greater, respectively, than the rates observed with only N_2O and only O_2 as oxidants. Further increases in oxygen partial pressure altered the direction of the reaction toward the formation of peroxides which resulted in nonselective oxidation to CO_2. It is interesting in Table 1 to compare the $(C_2H_5O_2\cdot)/(C_2H_5\cdot)$ ratios, obtained from gas-phase equilibrium data as a zero-order approximation, with the change in selectivity.

TABLE 1

Reactions of C_2H_6 with Mixtures of N_2O–O_2[a]

P_{O_2}	Formation rate (μmole/min/g Mo)		Selectivity to C_2H_4 (%)	$\frac{(RO_2\cdot)_{eq}}{(R\cdot)_{eq}}$[b]
	C_2H_4	CO_2		
0	8.5	6.0	74	—
12	19.0	14.1	73	1.25
14	21.0	13.0	76	1.45
26	21.0	14.0	75	2.70
32	19.0	18.0	68	3.33
40	17.0	20.0	63	4.16
68	14.0	21.0	57	7.07
103	12.5	26.0	49	10.70

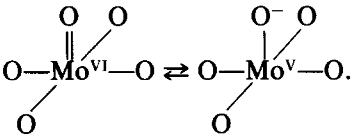
[a] $P_{N_2O} = 207$ Torr, $P_{C_2H_2} = 258$ Torr, $T = 400°C$.

[b] $R\cdot = C62H_5\cdot$. Estimated values for the gas-phase association $R\cdot + O_2 \rightleftarrows RO_2\cdot$ at 400°C with $K_{eq}\cdot$ derived from S. W. Benson, *J. Amer. Chem. Soc.* **87**, 972 (1965).

Clearly, the selectivity to ethylene was greatly decreased when the ratio of peroxy radicals to alkyl radicals became large.

A similar role of oxygen in promoting nonselective reactions has been suggested for the stoichiometric reactions of O_3^- with ethane on MgO (*7*). Here, as well, ethyl radicals were proposed as surface intermediates. In the presence of O_2 it was observed that the selectivity for olefin formation greatly decreased, due to the formation ethylperoxy radicals. It should be pointed out that the initial reactions on MgO were carried out at 25°C, and the formation of peroxy radicals would be favored at this lower temperature. The effects of O_2 in both the low-temperature and the high-temperature reactions support the formation of ethyl radicals on the surface during the oxidative dehydrogenation of ethane.

Although the O^- ions generated in the experiments described here appear to be derived mainly from N_2O, one may speculate that at sufficiently high temperatures O^- may be formed spontaneously by the reaction



(7)

Direct experimental evidence for this thermal reaction is lacking; however, Balistreri and Howe (*8*) have found that Mo^V and H· may be photochemically produced by irradiation of MoO_3/SiO_2 at 370 nm in the presence of H_2. The irradiation, which corresponds in energy to 3.35 eV or 77 kcal/mole, is believed to produce Mo^VO^- as an intermediate complex. Moreover, theoretical studies by Surratt and Kunz (*9*) and by Klein (*10*) have shown that the O^- ion is a *stable* species when associated with cation vacancies in the transition metal oxides NiO and CoO. According to the theoretical results these O^- ions could account for the dissociative chemisorption of hydrogen. These results also suggest that O^- ions may be formed more readily from oxide ions on unsupported metal oxides where cation vacancies exist. According to this model O_2 would only serve to replenish the oxygen ions which were removed during reaction.

On the basis of the experimental evidence presented here we suggest that the O^- ion may be responsible for hydrogen atom abstraction in a variety of catalytic reactions over metal oxides, e.g., the OXD of alkanes, alkenes, and alcohols.

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REFERENCES

1. Ward, M. G., Lin, M. J., and Lunsford, J. H., *J. Catal.* **50**, 306 (1977).
2. Aika, K., and Lunsford, J. H., *J. Phys. Chem.* **81**, 1393 (1977).
3. Ben Taarit, Y., and Lunsford, J. H., *Chem. Phys. Lett.* **19**, 348 (1973).
4. Shevets, V. A., and Kazansky, V. B., *J. Catal.* **25**, 123 (1972).

5. Ben Taarit, Y., and Lunsford, J. H., *J. Phys. Chem.* **77**, 780 (1973).
6. Benson, S. W., *J. Amer. Chem. Soc.* **87**, 972 (1965).
7. Takita, Y., and Lunsford, J. H., *J. Phys. Chem.* **83**, 683 (1979).
8. Balistreri, S., and Howe, R. F., 2nd International Symposium on Magnetic Resonance in Colloid and Interface Sci., Menton, France, 1979.
9. Surratt, G. T., and Kunz, A. B., *Phys. Rev. Lett.* **40**, 347 (1978).
10. Klein, D. L., Ph.D. Thesis, University of Illinois, 1978.

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