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The Oxidative Dehydrogenation of Ethane by Nitrous Oxide over Molybdenum Oxide Supported on Silica Gel

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The oxidative dehydrogenation of ethane over partially reduced MoO_3 supported on silica has been investigated using nitrous oxide as the oxidant at temperatures of 280–350°C. Ethylene typically comprised 80% of the product gases for 100 min of reaction. Although the initial rate for the formation of C_2H_4 on a fresh catalyst was high, the reaction was inhibited by coke and OH^-, and eventually a steady state was observed at 280°C. Whereas the rate of formation of C_2H_4 became essentially constant, the mole fraction of CO_2 continued to increase with time. It was found that the conversion was dependent on the extent of reduction of the molybdena and increased significantly for small levels of reduction. On the basis of electron paramagnetic resonance (EPR) and electron spectroscopy for chemical analysis (ESCA) studies, it appears that a fraction of the Mo^{5+} ions formed during reduction were active catalytic sites. In a separate experiment the decomposition of N_2O over the partially reduced MoO_3/SiO_2 resulted in the formation of O^- ions which reacted rapidly with ethane to produce C_2H_4 in amounts comparable to the original O^- concentrations. The maximum concentrations of O^- that could be obtained at 90°C were of the same order of magnitude as the amount of C_2H_4 produced initially in the reactions of N_2O–C_2H_6 mixtures at 280°C. Moreover, the ethylene formed from the reaction of O^- and C_2H_6 completely desorbed at less than 300°C, which is consistent with the C_2H_4 produced via the reaction of N_2O–C_2H_6 mixtures. These facts support the role of O^- as the active form of oxygen in the dehydrogenation reaction.

INTRODUCTION

The selective conversion of alkanes into alkenes is an important reaction both in fundamental and in industrial catalysis. Although the process of oxidative dehydrogenation (OXD) has been widely implemented to solve the problem of an unfavorable equilibrium, high reaction temperatures are usually necessary and poor selectivities to the alkene have often resulted. Consequently, studies of the OXD of alkanes have been initiated in order to investigate the fundamental properties of various catalysts and oxidants that may be used.

The catalysts employed for OXD reactions have generally consisted of supported or unsupported transition metal oxides. In particular, binary oxide catalysts have achieved great prominence (*1–3*). In a majority of these reactions, oxygen or air has been used as the oxidant because it is cheap and readily available; however, selectivities are often poor and reaction temperatures are high when oxygen is used. Substantial gains in process efficiency may be realized by consideration of less conventional oxidants.

The patent literature discloses a number of reactions where SO_2 has been used as the oxidant. Over chromia–alumina catalysts, SO_2 has been used as the oxidant to produce isobutylene from isobutane (*4*), whereas, over a supported copper catalyst,

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SO_2 was employed to form butadiene from butene (*5*). Two advantages of SO_2 as an oxidant are its ease of handling and the endothermic nature of the dehydrogenation reaction. Most important, selectivities using SO_2 have been found to be higher than for O_2 and the reaction temperatures are lower (*6*).

Another oxidant that has been successfully employed is carbonyl sulfide. This molecule has been shown to be one of the most selective oxidants for hydrocarbons having less than four carbons in a chain (*7, 8*). Haag and Miale (*9*) have reported high conversions and selectivities using COS with such catalysts as MoO_3/SiO_2 and MgO at about 600°C. In fact, the high selectivity of COS for the formation of alkenes has been found to be unmatched by O_2 or SO_2. Higher reaction temperatures and flammability are disadvantages of using COS as an oxidant.

One oxidant that has been neglected in studies of OXD is nitrous oxide. The literature suggests that N_2O has been used as an oxidant in the oxidation of CO (*10*), as well as in numerous photocatalytic studies (*11*), but little information is available concerning the use of N_2O in OXD reactions. This lack of interest in N_2O as an oxidant may be a result of the supposed similarity between the reactivities of N_2O and O_2, which is indeed the case over some catalysts at elevated temperatures. Nevertheless, the two oxidants may have extremely different reactivities, as well as selectivities, at lower temperatures on a particular catalyst. For practical reasons it is interesting to note that large quantities of N_2O are produced as a by-product of adipic acid synthesis.

The reactivity and selectivity of the oxidant can be significantly affected by the nature of the intermediate oxygen species formed. The N_2O molecule decomposes over several metal oxides, including partially reduced MoO_3/SiO_2, to form the highly reactive O^- ion (*12, 13*). It has also been reported (*12, 14*) that O_2 forms O^-, in addition to O_2^-, on V_2O_5/SiO_2 catalysts, but there is no evidence to indicate that O^- may be formed directly from O_2 on MoO_3/SiO_2 catalysts.

The exact forms of the reactive species of oxygen in hydrocarbon oxidation, including OXD, have not been convincingly established. However, the O^- ion has been suggested as an intermediate in the OXD of butene over $MgFe_2SO_4$ (*15*) and has been proven to be extremely reactive toward molecules such as CO, CO_2, C_2H_4, and CH_3OH (*16–19*). The surface intermediates from these latter reactions were observed at moderate to low temperatures by the electron paramagnetic resonance (EPR) technique. In high temperature reactions, it is reasonable to expect that the products will ultimately desorb, but, until recently, there had been little effort expended in analyzing the gas-phase products. In this laboratory it has been shown that surface reactions occur between C_1 to C_4 alkanes and O^- on MgO at minimum temperatures approaching the normal boiling points of the alkanes (*20*). The corresponding alkenes were observed in the gas phase when the reactions were carried out at 25°C, but the conversion reached a maximum when the sample was heated above 300°C. In particular, ethylene was observed from the reaction of O^- and C_2H_6, and a stoichiometry of one C_2H_4 molecule per one O^- ion was determined.

Since O^- can be formed from N_2O on partially reduced MoO_3/SiO_2 and the ion has been shown to be the active form of oxygen in the stoichiometric OXD of simple alkanes on MgO, it was of interest to study the catalytic OXD of ethane over supported molybdena using nitrous oxide as the oxidant. The specific objectives of this research were (a) to study the nature of the active site, (b) to determine the active form of oxygen, and (c) to propose a plausible mechanism consistent with the experimental data for the OXD of ethane.

EXPERIMENTAL METHODS

A catalyst containing 6.6% molybdenum by weight was prepared by evaporating to dryness a solution containing silica gel and ammonium paramolybdate. The catalyst was first heated at 110°C for 1 hr in air and then for 16 hr at 500°C to decompose the ammonium paramolybdate. In the pretreatment procedure, a 3.0-g sample of catalyst was calcined in O_2 for 1.5 hr at 480°C and degassed *in vacuo* at the same temperature. The total BET surface area of this catalyst was determined to be 311 m^2/g. The sample was reduced for a predetermined amount of time at 480°C using carbon monoxide, and the amount of CO_2 produced was measured by gas chromatography. The CO_2 concentration was then used to calculate an extent of reduction parameter, χ, defined as

$$\chi = (CO_2)_{\mathrm{produced}}/(O)_{\mathrm{total}} \times 3, \qquad (1)$$

where the catalyst has the stoichiometry $MoO_{3-\chi}$. The term $(O)_{\mathrm{total}}$ is the total amount of oxygen in the original molybdena. The sample was again degassed after reduction at 480°C until a residual pressure of less than 2×10^{-5} Torr was obtained (1 Torr = 133.3 $N\ m^{-2}$).

The gases used were obtained from commercial sources and were of the following purities: 99% C_2H_6; 98% N_2O; 99% CO; and 99% O_2. The C_2H_6 and N_2O gases were purified further by a freeze-pump technique at −196°C.

The experimental apparatus used to study the reactions of N_2O–C_2H_6 mixtures over the catalyst consisted of a glass recirculating system having a total volume of 492 cm^3. The gases to be analyzed were sampled through a 2.0 cm^3 sample loop and introduced to a Porapak Q column, which served to separate CH_4, C_2H_4, C_2H_6, C_3H_6, N_2O, and CO_2; bisethoxyethyladipate and 5A molecular-sieve columns were employed to analyze for any C_4 hydrocarbons and CO_2 respectively. Typical errors for the chromatographic system are estimated to have been ±5%.

For EPR studies, a Vycor reactor with a quartz side arm was used. Both Varian E-6S and E-3 X-band spectrometers were employed to obtain the EPR spectra of the O^- and Mo^{5+} ions. The g-values were evaluated using a phosphorus-doped silicon standard having a g value of 1.9987. The concentrations of O^- and Mo^{5+} were obtained by double integration of the EPR spectra using the same standard. Errors for the determination of spin concentration are estimated to have been ±10%.

For experiments involving N_2O–C_2H_6 mixtures, the catalyst was pretreated, and a suitable mixture of N_2O and C_2H_6 was introduced into the recirculating system at a specific temperature. Samples were then taken at predetermined times to monitor the progress of the reaction. The water produced from the reaction was removed by an in-line trap cooled to −78°C. The vapor pressure of H_2O at this temperature is 5.6×10^{-4} Torr.

In EPR experiments designed to determine the ratio of the amount of O^- reacted to the C_2H_6 produced, a 3.0-g sample of catalyst was pretreated and a known amount of N_2O (ca. 65 μmol/g of catalyst) was introduced. The reactor was heated at 90°C for 16 hr to generate the O^- ion (*24*), and the EPR spectrum was recorded with the sample at −196°C. After evacuation for several minutes at temperatures ranging from 25 to 200°C, the spectrum was again recorded. The catalyst containing the O^- ion was subsequently exposed to C_2H_6 (3 μmol/g of catalyst), and the products were desorbed by heating the sample at 350°C for 1 hr. The gases were collected in a special sampler and injected into a Carle AGC-311 gas chromatograph with both thermal conductivity and flame ionization detectors.

The Mo^{5+} concentrations were also obtained by EPR. In this case, a 0.2-g sample was reduced for a period of time, and the CO_2 produced was measured. After evacuating the CO for 10 min at 480°C, the Mo^{5+} spectrum was recorded. Subsequently, more CO was introduced, and the procedure was continued until several values of x and the corresponding Mo^{5+} concentrations had been obtained.

The concentrations of Mo^{6+}, Mo^{5+}, and Mo^{4+} as a function of time of reduction were obtained by photoelectron spectroscopy using a Hewlett–Packard Model 5950A ESCA (electron spectroscopy for chemical analysis) spectrometer. The instrument utilized monochromatic Al$K\alpha_{1,2}$ X irradiation (1486.6 eV) to obtain the photoelectron spectra. The MoO_3/SiO_2 was pressed into a thin film and placed on a sample plate. The samples were oxidized, dehydrated, and reduced under the previously stated conditions in the sample preparation chamber of the spectrometer. A lamp heater located in the chamber was used to heat the sample to temperatures in excess of 300°C. Typical collecting times were 1 hr for Mo 4*d* peaks, and 10 min for the O 1*s* peak. Binding energies were referenced to a gold spot which was deposited on the sample. The $4f_{7/2}$ level of Au was assigned a binding energy of 84.0 eV. Charge compensation was achieved by flooding the sample with nearly zero kinetic-energy electrons. Measured binding energies were reproducible to ±0.1 eV for Mo and O peaks. The data points of the ESCA spectra were smoothed by a simple 5-point program, and the spectra were deconvoluted using a DuPont 310 curve resolver.

Thermal desorption experiments were carried out in a separate recirculating system having a volume of 50 ml. After pretreatment of a 3.0-g sample, O^- ions were produced by heating the catalyst with N_2O for 12 hr at 90°C. The N_2O was briefly evacuated, and a 1% mixture of C_2H_6 contained in helium was introduced. After circulating the mixture through the catalyst for 30 min, the excess C_2H_6 was trapped at −196°C and removed. The products were then thermally desorbed according to a temperature program of 25, 150, 300, 400, and 450°C each for 0.5 hr and 500°C for 1 hr. At each temperature and time interval the desorbed products were collected and analyzed using the Carle GC. The same temperature program and sampling techniques were used to analyze the products of C_2H_5OH decomposition and C_2H_4 desorption. Both of these gases were introduced from 1% mixtures and contacted with the reduced catalyst. In the case of ethylene, the excess gas phase and the weakly adsorbed molecules that remained after 30 min of initial contact with the catalyst were removed by evacuation at 25°C, and the program was subsequently started.

RESULTS

Reactions of N_2O–C_2H_6 Mixtures over Supported Molybdena

The major products from the reaction of the N_2O–C_2H_6 mixtures were C_2H_4, CO_2, and H_2O. Smaller amounts of CH_4 and propylene were also formed. Ethylene typically comprised about 80% of the gaseous products at 280°C for 100 min of reaction. After an initial reaction rate of approximately 15 μmol/min/g of Mo, the C_2H_4 production was transformed into a steady-state process for reaction times greater than about 30 min. The steady-state rate for C_2H_4 production was ca. 0.3 μmol/min/g of Mo. The CO_2 also was produced rapidly for short times of reaction (ca. 2.5 μmol/min/g of Mo), and the reaction rate at intermediate reaction times varied between 0.1 and 0.3 μmol/min/g of Mo, depending on the pressure of N_2O. After many hours of reaction, however, the CO_2 became the predominant gaseous product. Accurate initial rate data could not be obtained with the recirculating

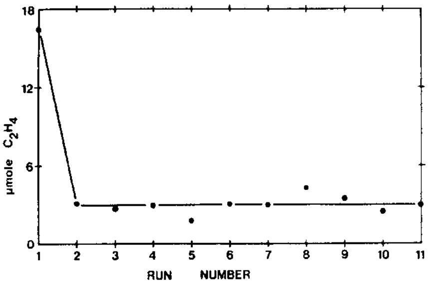

FIG. 1. The decrease and subsequent stabilization of the activity for C_2H_4 production at 280°C: 16-hr runs with conversion measured after 100 min of reaction for each run; 30-min evacuation between runs at 300°C; $P_{N_2O} = 51.0$ Torr, $P_{C_2H_6} = 47.0$ Torr; $\chi = 0.20$.

reactor because of an approximate 1-min delay in the introduction of gases.

The decrease and partial regeneration in activity of the catalyst for C_2H_4 formation were investigated in several experiments. It was generally observed that the initial activity could be partially regenerated by evacuation of the catalyst at elevated temperatures. In each experiment, the amount of products was determined after 100 min of reaction, although the duration of each run was 16 hr. Between runs, the catalyst was evacuated for 30 min at 300°C. As shown in Fig. 1, the catalyst reached a stable level of activity which remained constant for 11 runs. The observation is in agreement with the previous rate experiments. A total of 263 μmol of C_2H_4 was produced on the catalyst during 11 runs. Following the last run and subsequent evacuation, the catalyst was treated with O_2 at 480°C to determine whether any form of carbon had accumulated on the surface. An analysis revealed that 126 μmole of CO_2 were produced. The carbonaceous surface material could not be removed by degassing at 480°C, but the original activity could be restored by an oxidation–reduction cycle at 480°C. Because a significant amount of carbonaceous material was formed on the catalyst surface, the selectivity based on the amount of C_2H_6 reacted was not determined. The product distribution was calculated on the basis of mole percentages of gas phase products.

In order to determine whether the reaction was inhibited by its products, C_2H_4, CH_4, CO_2, and H_2O were each added in separate experiments to a mixture of N_2O and C_2H_6. Neither C_2H_4, CO_2, nor CH_4 significantly altered the conversion to C_2H_4 for 100 min of reaction, but exposure of the catalyst to 25 Torr of H_2O resulted in an 80% loss of conversion at 280°C. The conversion was not affected to a great extent by the presence of smaller amounts of H_2O, similar to the quantities produced during the course of the reaction at 280°C; however, it is likely that these smaller amounts were distributed between the silica gel and the molybdena. It was also

TABLE 1

Effect of Evacuation and Temperature on the Activity for C_2H_4 Formation[a]

Temperature (°C)	C_2H_4 produced (μmol)	
	One run, 150-min total	Five runs, 150-min total
280	27.1	33.6
300	Expt not performed	62.8
350	96.0	207.0

[a] Recirculating system; 3.0 g of catalyst; pretreatment: $\chi = 0.25$.

TABLE 2

Product Distributions at Selected Temperatures[a]

Temperature (°C)	Products (mol%)		
	CH_4	CO_2	C_2H_4
280	4	16	80
300	4	18	78
350	6	21	73

[a] Recirculating system; 30-min reaction; pretreatment: $\chi = 0.25$.

determined that CO had no effect on the activity at 280°C.

The effects of reaction temperature and evacuation on the catalytic conversion were investigated. In the experiment, one catalyst was evacuated for 15 min at reaction temperature after each 30-min run, and a fresh batch of N_2O–C_2H_6 was introduced. Alternately, the reaction was allowed to proceed for the same total time without intermittent evacuation. The results for three temperatures are shown in Table 1. It is evident that the effect of evacuation at 350°C was to restore significant activity, since the C_2H_4 produced during five 30-min runs (five runs, 150-min total) was much greater than during one 150-min run (one run, 150-min total). By way of contrast, one should note that at 280°C there was very little difference in the total amount of C_2H_4 produced between five 30-min runs and one 150-min run. In addition, it was rather surprising to find that the percentage of CO_2 increased only from 16 to 21% of the products upon increasing the temperature from 280 to 350°C. Table 2 illustrates the change in the product distribution as a function of the temperature for 30 min of reaction.

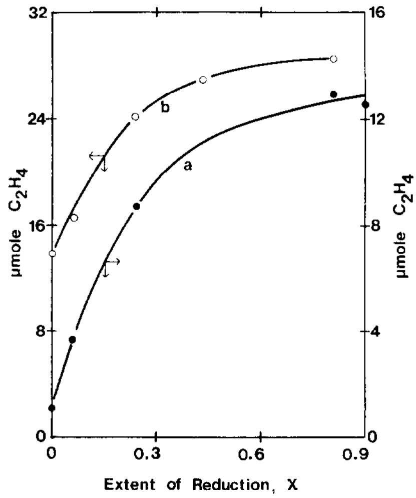

FIG. 2. Amount of C_2H_4 formed versus extent of reduction for 3-min (a) and 100-min (b) reactions. P_{N_2O} = 51.0 Torr, $P_{C_2H_6}$ = 47.0 Torr; T = 280°C.

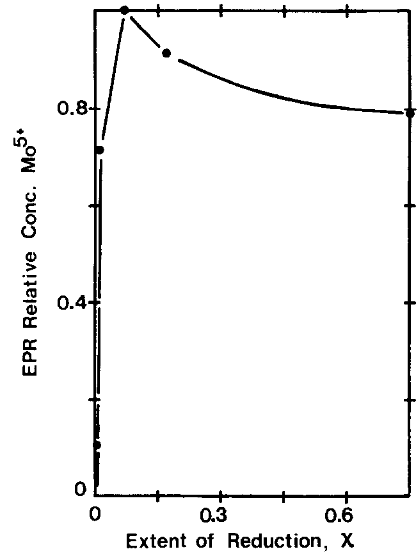

FIG. 3. The relative concentration of Mo^{5+} obtained by EPR as a function of the extent of reduction.

The effect of reduction on the conversion was studied in order to determine whether there was any strong dependence of the conversion on the oxidation state of the molybdenum. From Curve a of Fig. 2 it is evident that the conversion for 3 min of reaction at 280°C was dependent on the extent of reduction and approached zero for no reduction. For small amounts of reduction, the conversion increased significantly, but the increase in conversion became less for more extensive reductions. Curve b of Fig. 2 illustrates the change in conversion for 100-min reactions. The conversion in the absence of reduction by CO suggests that C_2H_6 was also capable of reducing the catalyst.

Effect of Reduction on the Oxidation States of Molybdenum

When C_2H_6 was heated with the oxidized catalyst at 300°C for 2 hr, the catalyst turned light blue, which was suggestive of oxides of molybdenum with oxidation states of +5 and +6 (*21*). An EPR spectrum later confirmed that Mo^{5+} was

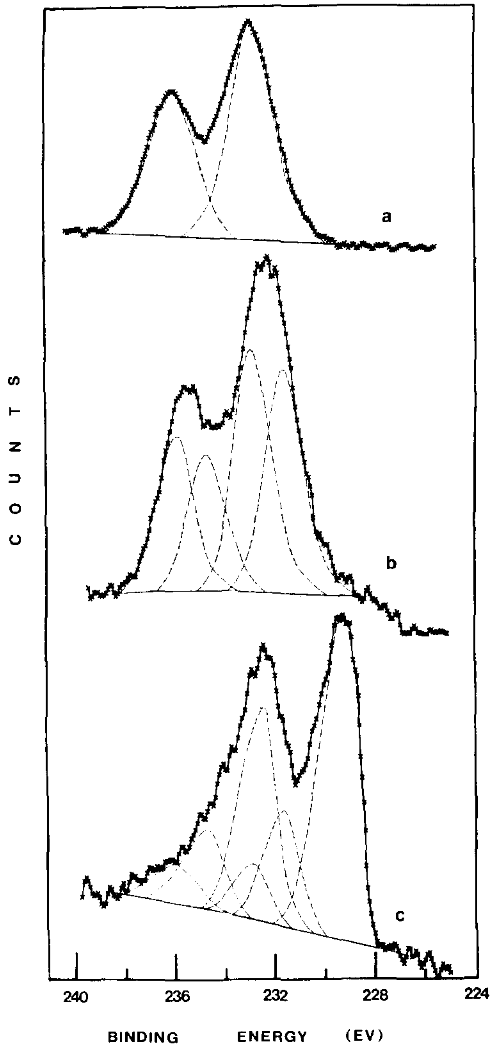

FIG. 4. ESCA spectra of Mo^{6+}, Mo^{5+}, and Mo^{4+} ions: (a), Oxidized sample; (b), after reduction in 150 Torr of CO for 5 min at 480°C; (c), after reduction in 150 Torr of CO for 4 hr at 480°C.

present at concentrations of about 180 nmol/g of catalyst. No Mo^{5+} was detected on the oxidized sample prior to C_2H_6 reduction. Therefore, the activity exhibited by the catalyst for "zero" reduction, apparently, was due to small amounts of reduction by C_2H_6. Since the amount of reduction by C_2H_6 was quite small, one may conclude that only a very small fraction of the total molybdenum was involved in the catalytic reaction. Based on the concentrations of Mo^{5+} and O^- as determined by EPR, this active form of molybdenum is probably less than 0.3% of the total.

From an EPR study, it was determined that the Mo^{5+} concentrations increased significantly for small amounts of reduction and later decreased slightly for increasing values of X as shown in Fig. 3. Other investigators have reported similar results (*22*, *23*). It is apparent that the conversion to C_2H_4 did not precisely follow the Mo^{5+} concentration as detected by EPR, although both the conversion and the Mo^{5+} concentration increased markedly for a small extent of reduction.

In ESCA experiments designed to determine the relative concentrations of Mo^{6+}, Mo^{5+}, and Mo^{4+} for various times of reduction, a $3d_{5/2}$ to $3d_{3/2}$ peak intensity ratio of 3:2 was used in the deconvolution of the spectra, and the separation of the doublets was assumed to be the same for the three oxidation states. The calculated $3d_{5/2}$ and $3d_{3/2}$ binding energies were 233.0 and 236.1 eV for Mo^{6+}, 231.8 and 234.9 eV for Mo^{5+}, and 229.8 and 232.9 eV for Mo^{4+}. The deconvoluted ESCA spectra for various times of reduction are depicted in Fig. 4. An analysis of the concentrations of the molybdenum ions at specific times of reduction is given in Fig. 5. The results revealed that the Mo^{6+} concentration (Curve c)

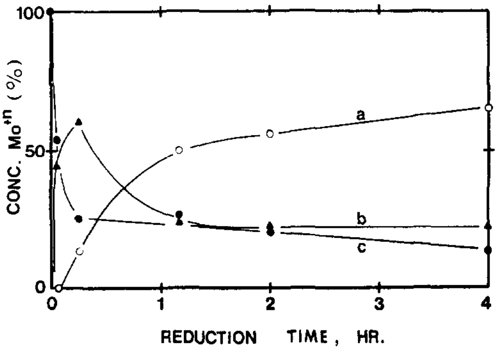

FIG. 5. The variation of the Mo^{4+} (a), Mo^{5+} (b), and Mo^{6+} (c) concentrations as determined by ESCA versus the time of reduction.

decreased, while the Mo^{5+} concentration (Curve b) increased significantly for small times of reduction, then decreased, and later reached a constant value. (It was not possible to detect the CO_2 produced during reduction in the ESCA experiment; thus the values of x could not be calculated.) The Mo^{4+} ion (Curve a) was absent after the initial period of reduction, but the concentration of the ion increased upon further reduction. All of these results are consistent with previous ESCA data obtained for molybdena on alumina (*24*). Again, there was no exact correlation between Mo^{5+} concentration and catalytic conversion, but there was a reasonable similarity for small amounts of reduction.

Reactions of O_2 with C_2H_6

When a comparable amount of O_2 was substituted for N_2O, it was found that extremely small amounts of C_2H_4 were produced at 280°C for 100 min of reaction. In fact, the amounts formed were similar to those obtained for reaction of pure C_2H_6 with the reduced catalyst (ca. 50 nmol/min/g of Mo). Interestingly, at 350°C the reaction of C_2H_6 with O_2 showed much the same behavior; however, after 100 min at this temperature, the catalyst was visibly oxidized to a large extent. Therefore, O_2 had reacted with the molybdenum, but in a strikingly different manner than N_2O.

Stability and Reactivity of the O^- Ion

In view of the reported stability (*13*) and reactivity (*25*) of the O^- ion on molybdena supported on silica, the ion was considered to be the active form of oxygen in the dehydrogenation reaction. Moreover, O^- can be generated by the decomposition of N_2O over molybdena, as mentioned earlier. The EPR spectrum of O^- is characterized by $g_\perp = 2.019$ and $g_\parallel = 2.002$.

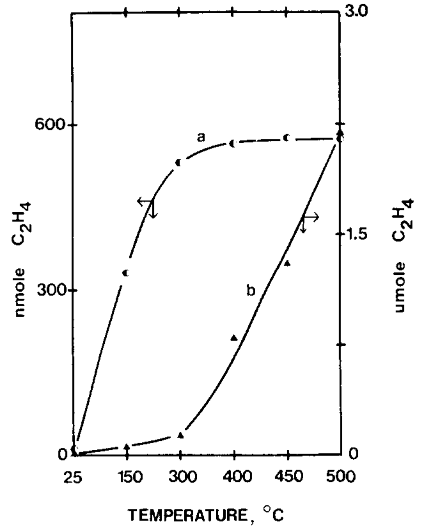

FIG. 6. Ethylene desorbed following (a) the C_2H_6–O^- reaction and (b) the C_2H_5OH decomposition as a function of the temperature program: 0.5 hr at 25, 150, 300, 400, and 450°C and 1 hr at 500°C.

The stability of O^- over molybdena was found to be directly related to the presence of N_2O. When N_2O was partially removed by evacuation for several minutes at 25°C, the concentration of O^- was reduced by 50%. Upon further removal of the N_2O by heating at 150°C or higher *in vacuo*, the O^- intensity decreased still more. Yet, the O^- was found to be stable at 200°C for several hours in the presence of a small excess of N_2O.

The reactivity of O^- with ethane at 25°C was investigated in an effort to determine the products of the reaction. After attempting to remove most of the N_2O, without destroying the O^- concentration completely, the spin concentration of O^- was obtained by EPR. A small amount of ethane was allowed to react with the O^-. Immediately, the O^- signal decreased by 95%, but no new signals were observed. The products formed were desorbed by heating at 350°C for 1 hr, collected, and analyzed. It was found that C_2H_4 was the predominant product, but the C_2H_4 to O^- stoichiometric ratio was greater than unity, although the ratio never exceeded 2.7. The unexpectedly large ratio may have been due to excess N_2O, which in many of these experiments was still present after the thermal desorption step. It is conceivable that the excess N_2O generated more C_2H_4 by the reaction with C_2H_6 in a manner analogous to the N_2O–C_2H_6 mixtures described previously.

Since the C_2H_4 to O^- ratios were not unity as expected, it was necessary to explore the possibility that other reactive forms of oxygen were present that were not observable by EPR. For example, if O^- were present as Mo^{5+}–O^-, the EPR spectrum would not have been observable because of large magnetic dipole interactions. Similarly, any other O^- that was generated in close proximity to another paramagnetic species would not have been detected. Indeed, it was determined from mass spectrometry–EPR experiments that the amounts of N_2 obtained from the decomposition of N_2O were 20 to 30 times as great as the O^- observed by EPR. This result indicates that a substantial amount of some form of oxygen was produced from the N_2O reaction with the surface, but considering the observed C_2H_4 to O^- ratios of ca. 2, it is evident that a large fraction of this oxygen was unreactive or, at least, did not give observable products. It seems likely that the reaction of N_2O with a Mo^{4+} ion or a pair of Mo^{5+} ions results in a two-electron transfer, with the formation of an oxide ion rather than an O^- ion. Since Mo^{5+} to O^- ratios of approximately 10 were observed by EPR after the formation of O^-, this ion is apparently formed only on a fraction of the isolated Mo^{5+} ions.

Thermal Desorption Experiments

In order that the structure of the adsorbed intermediate might be examined, a series of experiments was performed in which the products of C_2H_5OH decomposition and the desorption of C_2H_4 were compared with the products of the C_2H_6–O^- reaction. Of particular interest were the temperatures at which the majority of the ethylene was desorbed in each case. Ethanol has been shown to form an alkoxide intermediate on Al_2O_3 (*26*) and is dehydrated by chromium oxide to produce ethylene (*27*). The results for C_2H_5OH are depicted in Curve b of Fig. 6, and, as expected, the predominant product was ethylene. Lesser amounts ($<5\%$) of CH_4, CO_2, C_2H_6, and C_3H_6 were produced. It is evident that the ethylene produced from C_2H_5OH did not desorb at the same temperature as the ethylene produced from the reaction of C_2H_6 with O^- (Curve a). The ethylene formed from the C_2H_6–O^- experiment was desorbed at temperatures less than 300°C, whereas the ethylene from C_2H_5OH desorbed mainly at temperatures in excess of 400°C. It was found that pure C_2H_4 was very weakly complexed, and all of it desorbed at a temperature lower than 150°C. Since most of the ethylene from the C_2H_6–O^- experiment desorbed at 150°C, the intermediate of this surface reaction must resemble chemisorbed C_2H_4 more closely than the alkoxide ion, which presumably is formed from ethanol adsorption.

DISCUSSION

Catalytic Activity

The initial reaction rate for the formation of C_2H_4 was relatively large, presumably because the surface sites were uncontaminated by the products. In later stages the reaction rate became constant and was essentially zero order with respect to gas-phase concentrations of C_2H_6 and N_2O. In view of results which will subsequently be discussed, it appears likely that the steady-state rate must ultimately depend on the desorption of gases such as CO_2 or H_2O. The decline in the activity is probably due to the formation of coke and hydroxide ions, with the OH^- being at least partially removed as H_2O by evacuation at 350°C. Poisoning of molybdena–alumina catalysts by coking has been alluded to in previous research (*28*).

Although the amount of C_2H_4 produced never exceeded the total amount of molybdenum in the system, the remarkable ability of the surface to exhibit some activity for long periods of time at minimum levels of reduction is suggestive of catalytic activity. Definite proof of catalytic activity requires that the number of active sites be known, and in the present case it has been demonstrated that the amount of ethylene produced exceeded the number of reduced molybdenum ions. Furthermore, the evidence is convincing that a reduced form of molybdenum is involved as the active site.

The conversion to C_2H_4 was dependent on the extent of reduction but did not precisely follow the Mo^{6+}, Mo^{5+}, or Mo^{4+} concentrations. Nevertheless, the Mo^{5+} concentrations obtained by EPR and ESCA could qualitatively explain the initial and final portions of the curve described in Fig. 2. The existence of Mo^{5+} in more than one symmetry, viz., tetrahedral, square pyramidal, and octahedral, has been discussed at length in several publications (*29–31*). It is proposed here that the active site is a coordinatively unsaturated form of Mo^{5+} which is present as a small fraction of the total Mo^{5+}. Therefore, it is reasonable to expect that the activity for the formation of C_2H_4 is due to one form of Mo^{5+} while not following, in general, the Mo^{5+} concentrations obtained by EPR and ESCA. The active Mo^{5+} can be generated by ethane reduction of the surface and also, quite possibly, by the N_2O oxidation of Mo^{4+} on samples which were sufficiently reduced. The absence of Mo^{4+} at small levels of reduction and the decrease of Mo^{6+} with increasing values of x, however, do not support the direct involvement of these species as active sites.

Evidence for O^- as the Active Form of Oxygen

The O^- ion is known to be stabilized at Mo^{6+} sites on MoO_3/SiO_2 catalysts (*13*) and is quite stable in the presence of excess N_2O at 200°C. Since the Mo^{5+} to O^- ratios as determined by EPR were consistently large (ca. 10), it is reasonable to expect that the O^- ions are only produced on "active" Mo^{5+} ions. The O^- ion was also shown to react rapidly with ethane at 25°C to form an intermediate which desorbed completely by 300°C to give ethylene. This is consistent with the relative ease at which the dehydrogenation occurs at 280°C for reactions of N_2O–C_2H_6 mixtures. Although the C_2H_4 to O^- ratios were not unity, a stoichiometry of one ethylene molecule per one O^- ion seems probable based on the results obtained on MgO (*20*). Evidence for O^- as an active intermediate is also provided by the rate data. The amount of C_2H_4 formed initially (ca. 6 μmol) was consistently the same order of magnitude as the maximum O^- concentrations obtained by EPR (ca. 3 μmol) in the presence of N_2O at 90°C. Vorotyntsev *et al.* (*29*) have shown that the O^- ion could not be formed on samples previously exposed to H_2O. This fact is in agreement with the observed poisoning effect of adsorbed water and lends support to the hypothesis that a coordinatively unsaturated form of Mo^{5+} is the active site. Therefore, the initial reaction involving N_2O and C_2H_6 at 280°C can be visualized as a rapid surface reaction occurring between C_2H_6 and adsorbed O^-.

Since the EPR signal from hydroxyl radicals was not detected after the reaction of ethane with O^-, it is proposed that O^- reacts with ethane on MoO_3/SiO_2 catalysts by hydrogen atom abstraction. The role of O^- in hydrogen atom abstraction reactions agrees with gas-phase (*32*) and solution (*33*) studies, as well as the reactions between O^- and H_2 or various alcohols on MgO (*19*). Moreover, on MgO there was evidence that the C_2H_6–O^- reaction proceeded via hydrogen atom abstraction (*20*). If a C_2H_6 to O^- stoichiometry of 1:1 is assumed, as was the case on MgO, the initial step in the reaction of O^- with ethane can be written as follows:

$$C_2H_6 + Mo^{6+}\text{–}O^- \rightarrow \cdot C_2H_5\text{–}Mo^{6+}\text{–}OH^-. \quad (2)$$

Since very small amounts of C_4 products were obtained, the dimerization reaction is unlikely as a primary second step in the mechanism. Also, no paramagnetic ethyl radicals were observed which indicates that the radicals must be rapidly transformed into diamagnetic species.

Two possible pathways are available for the rapid reaction of the ethyl radical and subsequent formation of a diamagnetic intermediate:

$$\cdot C_2H_5\text{–}Mo^{6+}\text{–}OH^- + O^{2-}(s) \rightarrow Mo^{5+}\text{–}OH^- + C_2H_5O^-(s) \quad (3)$$

or

$$\cdot C_2H_5\text{–}Mo^{6+}\text{–}OH^- \rightarrow C_2H_5^+\text{–}Mo^{5+}\text{–}OH^-. \quad (4)$$

Similar reactions have been proposed for the O^- reaction with ethane on MgO. A step similar to reaction (3) has also been proposed for the reaction of H_2 with O^- on MgO (*19*), whereas reaction (4) warrants consideration on the basis of work by Kochi (*34*) where there is evidence that ethyl radicals are oxidized to alkenes by Cu(II) in solution. The desorption experiments clearly revealed that the intermediate more closely resembled chemisorbed C_2H_4 than the more stable ethoxide ion. Therefore, the most probable reaction is the rapid oxidation of the radical by the d^0 Mo^{6+} ion to form the ethyl cation. A proton from $C_2H_5^+$ may be lost to OH^- on the same site, forming H_2O directly, or to an oxide ion, as was proposed on MgO. In view of the basicity of oxide ions relative to OH^-, the proton is probably lost to an oxide ion to form another OH^-:

$$C_2H_5^+\text{–}Mo^{5+}\text{–}OH^- + O^{2-}(s) \rightarrow C_2H_4\text{–}Mo^{5+}\text{–}OH^- + (OH^-)s. \quad (5)$$

The final step of the mechanism involves the desorption of the products. The reaction of O^- with ethane was shown to be quite rapid at 25°C, as was the oxidation of the ethyl radical, since no paramagnetic species were detected. Also, the ethyl cation probably is stabilized rapidly by the reaction with a surface oxide ion. Therefore, it is proposed that the slow step for the initial reaction between O^- and C_2H_6 is the desorption of the ethylene:

$$C_2H_4\text{–}Mo^{5+}\text{–}OH^- \rightarrow C_2H_4(g) + Mo^{5+}\text{–}OH^-. \quad (6)$$

In order for the catalytic process to continue, however, the active site must be regenerated by the removal of OH^- ions. This can be accomplished through the formation and subsequent desorption of H_2O as follows:

$$Mo^{5+}\text{–}OH^- + OH^-(s) \rightarrow Mo^{5+} + H_2O(g) + O^{2-}(s). \quad (7)$$

The catalytic reaction rate can also be affected by the presence of coke on the active surface sites. The coke can be removed slowly by reaction with N_2O to form CO_2.

A mechanism for the formation of C_2H_4 via the reactive O^- intermediate enables one to understand the observed difference between N_2O and O_2 as oxidants. Previous work has shown that O_2 forms O_2^-, rather than O^-, over partially reduced MoO_3/SiO_2. Although Shvets and Kazansky (*12*) have suggested that O^- may be formed from O_2 on V_2O_5/SiO_2, there is no evidence which indicates that such a reaction occurs on MoO_3/SiO_2. We suggest, however, that the O^- ion may be thermally generated by the equilibrium reaction

$$Mo^{6+}O^{2-} \rightleftharpoons Mo^{5+}O^{-}, \qquad (8)$$

which would explain the limited activity of the catalyst in the absence of N_2O. Molecular oxygen may function to replace the oxide ions which are removed by the reaction of alkanes with the O^- ions of Eq. (8). At sufficiently high temperatures reaction (8) may be the major source of O^- ions even in the presence of N_2O, thus the difference in the OXD reactivity between N_2O and O_2 would be expected to diminish with increasing temperature.

CONCLUSIONS

The markedly different reactivities of N_2O and O_2 for the OXD of ethane in this research indicate that the particular catalyst and oxidant chosen for the dehydrogenation may significantly affect the selectivities and conversions in the reaction. The results support the conclusion that each oxidant generates different forms of oxygen species when reacted over MoO_3/SiO_2 catalysts; nitrous oxide has the distinct advantage of generating O^- ions directly, whereas O_2 apparently does not. The results of this research strongly indicate that the O^- ion may be involved in catalytic OXD reactions where N_2O is employed as the oxidant and that the ion may be continuously regenerated over MoO_3/SiO_2 catalysts at 280°C in the presence of ethane. Probably, more than one form of Mo^{5+} exists on the catalysts used in this research, and both Mo^{4+} and Mo^{6+} may be indirectly involved in the catalytic reaction by generating an active form of Mo^{5+}, which is present as only a small fraction of the total Mo^{5+}.

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