

Partial Oxidation of Ethane to Ethylene and Acetaldehyde over a Supported Molybdenum Catalyst

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The catalytic conversion of ethane to acetaldehyde has been achieved using nitrous oxide as the oxidant. Water vapor is essential for high selectivity to acetaldehyde. The product distribution is strongly dependent upon the mode of preparation of the Mo/SiO₂ catalysts, the type of silica support, and the molybdenum loading. Typical conversions of 7% with combined selectivities to CH₃CHO and C₂H₄ of 70% may be attained. At partial pressures between 30 and 280 Torr the rate of ethane conversion is first order with respect to nitrous oxide and ca. 0.4 order with respect to ethane. A mechanism is proposed in which O⁻ ions, derived from N₂O, react with C₂H₆ by hydrogen-atom abstraction. The resulting ethyl radical reacts with surface Mo=O to produce a surface ethoxide, which may either decompose to ethylene or react further with surface OH⁻ to form acetaldehyde or with water to form C₂H₅OH. The latter is rapidly converted to acetaldehyde under reaction conditions. © 1985 Academic Press, Inc.

INTRODUCTION

The selective oxidation of hydrocarbons in general and of alkanes in particular is one of the most important issues in heterogeneous catalysis. The activation of alkanes for oxidation reactions to selectively produce products such as alcohols and aldehydes is of considerable interest for the chemical industry and in fundamental catalysis. Previous results from this laboratory have shown that molybdenum supported on silica is an effective catalyst for the oxidative dehydrogenation of ethane to ethylene using nitrous oxide as the oxidant (1). More recently, using a similar catalyst the partial oxidation of methane to formaldehyde and methanol was achieved with N₂O in the presence of steam (2).

The oxidative dehydrogenation of ethane has been reported by Thorsteinson (3) on mixed oxides of molybdenum and vanadium using oxygen as the oxidant. Although the activity and selectivity for ethylene was relatively high no oxygenated compounds were obtained in this case. The selective dehydrogenation of ethane by ni-

trous oxide on a series of metal oxides, including supported Mo/SiO₂, has also been reported recently (4), but we have not been able to reproduce the relatively high activity under similar experimental conditions.

It has been demonstrated that N₂O decomposes at Mo^V centers on the surface of partially reduced MoO₃/SiO₂ to produce Mo^{VI}-O⁻ (5). The O⁻ ions react with alkanes by hydrogen-atom abstraction producing alkyl radicals (6). It is believed that ethyl radicals formed in this manner react with lattice oxygen of the molybdenum oxide to produce a surface ethoxide intermediate which by subsequent reactions will yield ethylene and acetaldehyde.

In this work the partial oxidation of ethane to acetaldehyde and ethylene is reported. Kinetic data along with an overall reaction mechanism are presented. Further support for the proposed mechanism is obtained from spectroscopic and thermal desorption studies.

EXPERIMENTAL

Materials. The gases used in this study were C₂H₆ (Linde, 99.0%), N₂O (Matheson,

99.0%), CO (Matheson, 99.8%), O₂ (Matheson, 99.6%), and He (Airco, 99.995%). He was passed through a gas purifier filled with indicating Drierite and Molecular Sieve 5A. The CO was purified from iron carbonyls using a copper tube filled with a mixture of Molecular Sieves 5A and 4A. The other gases were used as received. Ammonium paramolybdate was obtained from Climax Molybdenum and the silicas, used as the support, were obtained from Davison (grades 57 and SMR-7) and Cabot Corporation (Cab-O-Sil, M-5).

Catalyst preparation. The supported molybdenum catalysts were prepared by adding a solution of ammonium paramolybdate to the silica support. To obtain the desired molybdenum loading the concentration of the paramolybdate solution was varied accordingly. The pH of the solution was usually adjusted to 11 with NH₄OH, prior to addition to the silica. In some preparations the pH was adjusted to a different value by adding HNO₃ or NH₄OH. The slurry was usually mixed in a rotatory evaporator for 0.5 hr at 25°C. The liquid phase was completely evaporated over a period of 1 hr at 65°C (if not stated otherwise), and at a reduced pressure. Catalysts prepared by impregnation to incipient wetness were dried completely in air at 120°C after contacting the silica gel with an appropriate volume of the paramolybdate solution. Catalysts prepared by impregnation from excess of solution were obtained by mixing the silica with the paramolybdate solution in a beaker and slowly evaporating the liquid phase while stirring on a hot plate. All of these catalysts were dried in air at 120°C for 2 hr and calcined at 500°C for 17 hr. The results reported in this study were obtained using the catalysts prepared in a rotatory evaporator with Davison grade 57 silica, unless stated otherwise.

Flow reactor. The kinetic experiments were carried out in a fixed-bed flow reactor operated under differential conditions. The reactor consisted of a quartz tube (17-mm i.d. × 120 mm) which was connected to a

capillary quartz tube (2-mm i.d. × 60 mm) so that the products could be rapidly removed from the heated zone. The catalysts (1–3 g) in the form of chips, 20–42 mesh, were packed between two thin layers of quartz wool. A bed of quartz chips (50-mm depth) was placed above the upper layer of quartz wool to preheat the reactant mixture. The temperature was controlled and monitored by a thermocouple placed in a thermowell which was in contact with the catalyst bed. The temperature was controlled within ±1°C. In a typical experiment the reacting gas mixture which included C₂H₆ and N₂O, with He as a diluent, was introduced at flow rates between 40 and 60 cm³/min into a glass vaporizer-mixer at 120°C, into which water was admitted from a syringe pump. Precautions were taken to minimize pressure fluctuations in the system which may occur from the vaporization of water. The total pressure was 760 Torr. The stainless-steel inlet and outlet lines were maintained at ~150°C to prevent liquid condensation. Prior to reaction the catalysts were oxidized with O₂ for 1.5 hr and reduced with CO for 1 hr at 500°C under flow conditions. The system was flushed with He between these steps.

The reactants and products were analyzed with a Varian 3700 gas chromatograph with both TCD and FID connected in series and attached to a 4270 Varian dual channel integrator. Porapak Q (2 m, programmed 40–175°C) was used to analyze for N₂O, CO₂, CH₄, C₂H₄, C₂H₆, CH₃CHO, C₂H₅OH, and C₃ and C₄ hydrocarbons. Molecular sieve 13X (2 m, 45°C) was used to analyze for O₂, N₂, and CO. Both columns were connected in series through a bypass switching valve to isolate the MS-13X column while N₂O, CO₂, and the hydrocarbons eluted from the Porapak column. The carbon balance achieved usually was better than 5%, which is within the limits of the GC analysis.

Circulation reactor. The reactor for these experiments consisted of a U-shaped quartz tube (5-mm i.d.) which included a

section of quartz tubing (13-mm i.d. \times 50 mm). The catalyst was held in this section over a thin layer of quartz wool. The circulation system, including the glass-pump and the reactor, had a total volume of 140 cm³. The catalyst was activated by evacuation and oxidation (O₂, 100 Torr) at 500°C followed by evacuation and reduction (CO, 100 Torr) at 600°C for 1 hr each. This procedure was followed by evacuation at the same temperature for 0.5 hr. After activation the temperature was adjusted to the required value and the reaction mixture (200–300 Torr) was admitted to the circulation reactor. At preset intervals a sample was collected in a sampling valve and injected to the GC for analysis.

TPD experiments. The reactor and activation procedure was the same as for the experiments in the circulation reactor. After activation the catalyst was cooled under vacuum to 25°C. The adsorbate gas or vapor was admitted and circulated over the catalyst at 25°C for 1 hr. After evacuation for 15 min at the same temperature, the catalyst was heated for 0.5 hr at the following temperatures: 150, 300, 400, 500, and 600°C. The desorbed products were collected in a trap at –196°C. After isolating the reactor from the system, the trap was warmed and the desorbed gases were analyzed by GC. The same procedure was repeated at each temperature.

In the TPD experiments the amount of desorbed products is reported as a percentage of the total amount of adsorbate gas or vapor retained by the catalyst, multiplied by a suitable stoichiometric factor. The total amount retained (or adsorbed), was estimated from the amount of products recovered at the highest desorption temperature and the CO₂ produced following oxidation with O₂ at 500°C at the end of each experiment.

ESR experiments. Experiments designed to detect O⁻ and C₂H₅[·] by ESR spectroscopy were carried out in a reactor consisting of a large quartz tube (12-mm o.d.) connected along a common axis to a smaller

quartz tube (4-mm o.d.). A vacuum stopcock with a conical joint was attached to the center of the reactor so that the reactor could be rotated, while on the vacuum line, to transfer the sample from the large part of the container to the 4 mm ESR tube. N₂O and C₂H₆ used in these experiments were purified several times by a pump-and-freeze technique. The ESR spectra were recorded at 77 K with a Varian E6 spectrometer. A phosphorous-doped silicon standard was used to determine the *g* values and estimate the spin concentrations.

Experiments to obtain the concentration of Mo^V as a function of the partial pressure of C₂H₆ and N₂O were carried out in a U-shaped quartz reactor (10-mm o.d.) equipped with an EPR sidearm (4-mm o.d.). The catalyst, under flow conditions, was exposed to the reaction mixture in the large part of the reactor. After the system reached steady state the reactor was rapidly quenched from the reaction temperature to 0°C and flushed with He at 25°C for ~15 min. The catalyst was transferred to the sidearm for ESR analysis.

RESULTS

Effect of catalyst preparation. It was found that the product distribution was very sensitive to experimental parameters such as the method of preparation, the type of silica, and the Mo content. Table 1 shows the effect of the preparation method on the activity and selectivity of the catalysts. It is apparent from the results that the catalysts prepared in a rotatory evaporator at 65°C (and 90°C, not shown) generally gave better selectivity toward acetaldehyde, especially at higher temperatures. An exception to this is the catalyst prepared in the rotatory evaporator at 40°C, probably because the diffusion of the molybdenum solution into the silica pores is less efficient at this temperature. This may produce a catalyst with lower dispersion.

The catalyst prepared by impregnation from excess of solution gave better activity. At the higher conversions (14.5%), selectiv-

TABLE 1
 Effect of Preparation Method^a

Catalyst preparation	T (°C)	Conversion (%)	Rate (μmol/min g)	Selectivity ^b (%)			
				C ₂ H ₄	CH ₃ CHO	CO ₂	CO
Impregnation from excess of solution	553	5.4	11.8	49.0	21.0	19.1	8.1
	575	14.5	31.6	51.9	7.8	25.6	13.8
Impregnation by incipient wetness	552	3.3	7.2	42.3	26.3	21.4	8.6
	576	6.2	13.4	47.9	20.2	17.3	12.0
Impregnation in a rotatory evaporator, 40°C	551	3.6	7.8	37.4	26.5	23.3	11.4
	574	6.5	14.1	42.4	18.7	23.5	13.0
Impregnation in a rotatory evaporator, 65°C	552	3.7	8.1	35.6	36.4	18.3	8.0
	575	6.7	14.7	40.4	30.5	17.5	11.4

^a 1.65 g of 2 wt% Mo/SiO₂, $F_v = 45$ ml/min, $P_{C_2H_6} = 147$ Torr, $P_{N_2O} = 234$ Torr, $P_{H_2O} = 332$ Torr.

^b The formation of C₂H₅OH, CH₄, HCHO, and C₃ and C₄ hydrocarbons accounts for 2–4% in selectivity.

ity to acetaldehyde was lower, but the selectivity toward C₂H₄ remained high. The reason for this behavior is not fully understood; however, the catalysts prepared in the rotatory evaporator may produce a more uniform distribution of the molybdenum and a better dispersed catalyst. Further oxidation of CH₃CHO may be more rapid on larger molybdenum oxide particles.

Table 2 shows the effect of the type of silica used in the preparation. The selectivity to acetaldehyde was considerably better

on the high-surface-area materials, but the combined selectivity to ethylene and acetaldehyde was better on the low-porosity silica (SMR-7) and on the Cab-O-Sil. Although the rates based on the mass of catalyst were similar, the rates of conversion at constant space velocity were different for the three catalysts because their densities differ (Table 2). The relative activities at 550°C become 3.4, 2.3, and 1.0 for the catalysts prepared from Silica SMR-7, Silica 57, and Cab-O-Sil, respectively. In an attempt to maximize the selectivity toward

 TABLE 2
 Effect of the Silica Support^a

Type of silica support	T (°C)	Conversion (%)	Rate		Selectivity ^b (%)			
			(μmol/min g)	(μmol/min ml)	C ₂ H ₄	CH ₃ CHO	CO ₂	CO
Davison 57, Porous silica, 300 m ² /g	552	3.7	8.1	3.1	35.1	36.9	18.3	8.0
	574	6.8	14.7	5.9	40.4	30.5	17.5	11.4
Davison SMR-7, Low-porosity silica, 70 m ² /g	550	3.3	7.1	3.8	67.5	14.7	16.2	—
	575	7.5	16.1	8.7	74.3	12.6	6.6	3.9
Cab-O-Sil M-5 Fumed amorphous silica, 200 m ² /g	555	3.0	6.5	1.6	51.2	33.7	6.9	7.3
	578	5.0	10.8	2.6	55.5	25.9	6.1	11.1

^a 1.65 g of 2 wt% Mo/SiO₂, $F_v = 44.9$ ml/min, $P_{C_2H_6} = 146$ Torr, $P_{N_2O} = 229$ Torr, $P_{H_2O} = 229$ Torr.

^b The formation of C₂H₅OH, CH₄, HCHO, and C₃ and C₄ hydrocarbons accounts for 2–4% in selectivity.

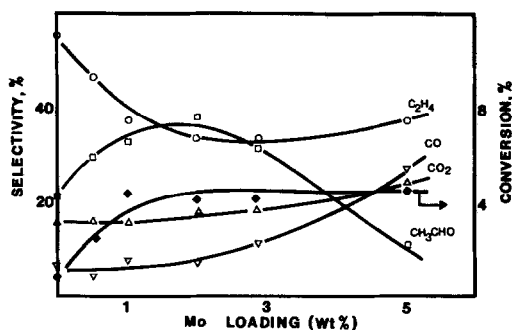


FIG. 1. Ethane conversion and product distribution as a function of molybdenum concentration: 1.65 g of 2 wt% Mo/SiO₂, $T = 551^{\circ}\text{C}$, $F_v = 44.9$ ml/min, $P_{\text{C}_2\text{H}_6} = 150$ Torr, $P_{\text{N}_2\text{O}} = 230$ Torr, $P_{\text{H}_2\text{O}} = 200$ Torr.

acetaldehyde, the rest of this work was performed using Silica 57. Blank experiments performed on each of the supports showed that ca. 1.0–1.5% of the conversion obtained in the catalytic runs was due to the support.

Another variable examined was the initial pH of the ammonium paramolybdate solution during preparation of the catalysts. Preparation at initial pH values of 2, 5, and 11 was tested. The effect of this parameter was found to be small; essentially the same activity and slightly higher selectivity for acetaldehyde at pH 11 were observed. The results reported here are for catalysts prepared at this pH.

From experiments in which the concentration of Mo was varied (Fig. 1), it is apparent that the product distribution was strongly dependent on the Mo loading; whereas, the activity increased at loadings of Mo up to about 2 wt%, and thereafter remained essentially constant. The latter phenomenon may result from a saturation of sites on the silica which are able to retain Mo in an active configuration. It is important to point out here that the possibility of diffusional limitations was considered according to the accepted criteria (7), and it was concluded that the reaction is not diffusion-limited under these experimental conditions.

Effect of steam. As reported previously

for the partial oxidation of methane (2), the presence of steam is essential to obtain high selectivities to oxygenated products. Figure 2 shows that the selectivity to acetaldehyde doubles as the water vapor pressure was increased from 0 to 180 Torr and then remained constant. The small decrease in conversion over this same range may be caused by competitive reactions between O⁻ ions and H₂O. The effect of steam on the selectivity toward acetaldehyde will be discussed later.

Catalyst activation and deactivation. As mentioned before under Experimental, the catalysts were activated prior to reaction by subsequent oxidation and reduction with oxygen and carbon monoxide at 500°C. This procedure was followed as a "standard" activation method so catalysts may be compared independently. Examination of different activation procedures, including variations in times and temperatures or heating the catalyst in a helium stream, showed that these parameters did not have a significant effect on the results obtained at *steady state*, though *initial* activities and selectivities were different following the various activation procedures. A completely oxidized catalyst had very little initial activity, but the activity reached the same steady-state activity after ~3 hr as was observed for the pre-reduced catalyst. These results show that regardless of the initial state of the catalyst the catalytic reaction eventually reaches a steady-state con-

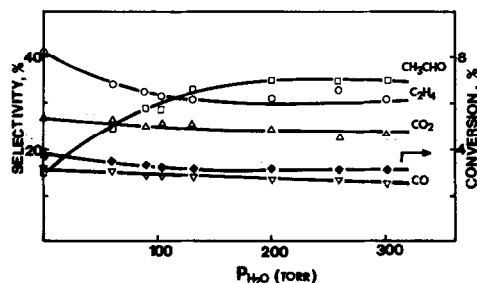


FIG. 2. Ethane conversion and product distribution as a function of H₂O partial pressure: 2.0 g of 2 wt% Mo/SiO₂, $T = 552^{\circ}\text{C}$, $F_v = 54.7$ ml/min, $P_{\text{C}_2\text{H}_6} = 131$ Torr, $P_{\text{N}_2\text{O}} = 222$ Torr.

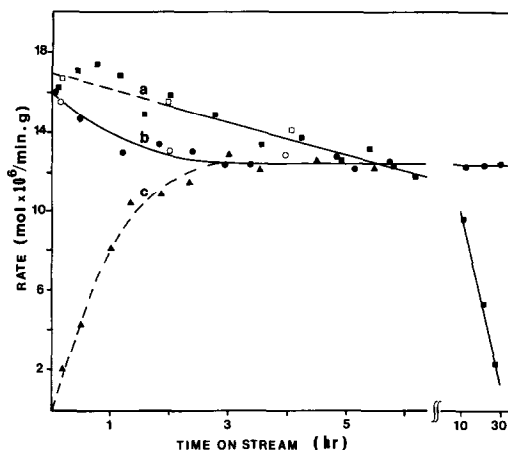


Fig. 3. Catalyst activity as a function of time on stream: 2.0 g of 2 wt% Mo/SiO₂, $T = 552^{\circ}\text{C}$, $F_v = 53.9$ ml/min. (a) $P_{\text{C}_2\text{H}_6} = 297$ Torr, $P_{\text{N}_2\text{O}} = 225$ Torr, $P_{\text{H}_2\text{O}} = 216$ Torr; (b) $P_{\text{C}_2\text{H}_6} = 166$ Torr, $P_{\text{N}_2\text{O}} = 219$ Torr, $P_{\text{H}_2\text{O}} = 218$ Torr; (c) same as (b), completely oxidized catalyst. Open symbols indicate points recorded after reactivation of the catalyst.

dition which depends only on the temperature and the reaction mixture used.

When the reaction was carried out over a period of 30 hr at partial pressures of ethane higher than ca. 200 Torr (at 225 Torr of N₂O and 200 Torr of H₂O), there was a continuous deactivation of the catalyst. Typical results are shown in Fig. 3a. At an ethane partial pressure of 297 Torr, steady-state conditions were not achieved. After 30 hr the rate decreased from 16.9 to 2.4 $\mu\text{mol}/\text{min g}$. In contrast, at 166 Torr of ethane (Fig. 3b), steady-state conditions are obtained after 2 hr, and after 27 hr of reaction the rate remained essentially the same (12.7 $\mu\text{mol}/\text{min g}$). Reactivation of the catalysts gave reproducible results in both cases for the initial activity and after 2 and 4 hr of reaction. The deactivation of the catalyst at high partial pressures of ethane (>200 Torr) is probably a result of poisoning by coke, which could be oxidized with oxygen at 500°C to give CO₂ and restore the activity. At lower partial pressures of ethane the nitrous oxide and steam, present in the reaction mixture, are probably capable of oxidizing the carbonaceous deposit to some

extent, preventing in this way the continuous deactivation of the catalyst. As shown by these results the poisoning is a reversible process and reproducible activities can be obtained after reactivation. At lower partial pressures of ethane, it is reasonable to assume that the initial decay in activity is mainly the result of the oxidation of the originally reduced catalyst by nitrous oxide until a steady state is obtained.

Kinetic parameters. The effect of contact time is shown in Fig. 4. In this series of experiments the contact time was varied both by changing the amount of catalyst while holding the volumetric flow rate constant, and vice versa. The results obtained in both cases gave the same conversion for the same space velocity, which indicates that the reaction is not limited by external mass transport under these conditions. From Fig. 4 it is apparent that in order to obtain high selectivities toward acetaldehyde and ethylene, the reactor should be operated at high space velocities and hence low conversions. At conversions of about 2% the combined selectivity for acetaldehyde and ethylene is over 90%. The drastic decrease in selectivity to acetaldehyde is probably a result of further oxidation of this product.

The conversion of ethane and the product distribution as a function of tempera-

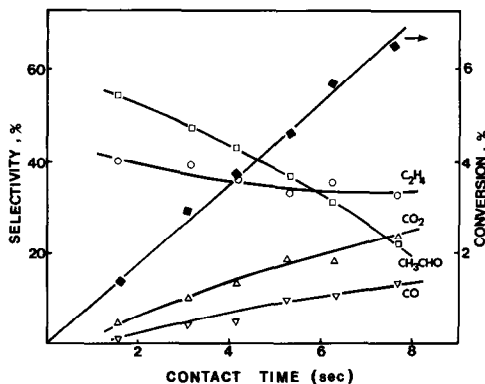


Fig. 4. Ethane conversion and product distribution as a function of contact time: 2.0 g of 2 wt% Mo/SiO₂, $T = 550^{\circ}\text{C}$, $P_{\text{C}_2\text{H}_6} = 149$ Torr, $P_{\text{N}_2\text{O}} = 228$ Torr, $P_{\text{H}_2\text{O}} = 218$ Torr.

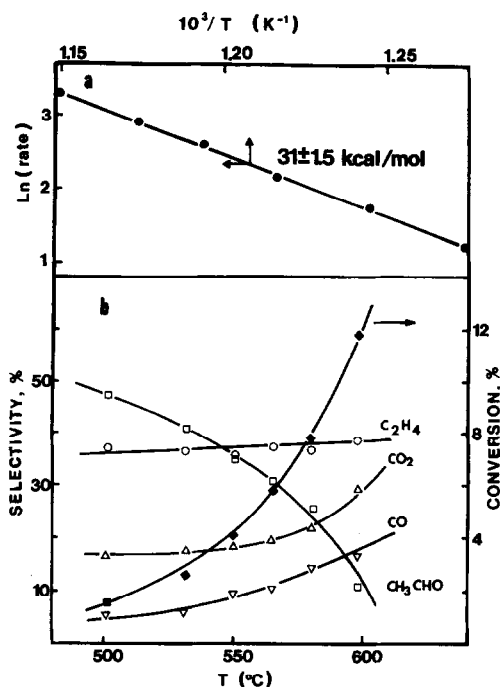


FIG. 5. Ethane conversion and product distribution as a function of temperature: 2.0 g of 2 wt% Mo/SiO₂, $F_v = 55.2$ ml/min, $P_{C_2H_6} = 150$ Torr, $P_{N_2O} = 231$ Torr, $P_{H_2O} = 209$ Torr.

ture are depicted in Fig. 5a. The selectivities for all the products except C₂H₄ are strongly dependent on the temperature. This behavior further suggests that acetaldehyde is readily oxidized at $T > 500^\circ\text{C}$. An Arrhenius plot of the rate of ethane conversion versus the reciprocal of the absolute temperature gave rise to an apparent activation energy of 31 ± 1.5 kcal/mol. The rate of C₂H₆ conversion, recorded for a random sequence of temperatures over a period of 18 hr (Fig. 5b), indicates that the catalyst was stable with respect to time over the temperature range 500–600°C.

The conversion and selectivity as a function of the partial pressures of C₂H₆ and N₂O are given in Fig. 6. These experiments were performed at constant temperature and space velocity. The partial pressure of C₂H₆ or N₂O was varied, while holding constant the partial pressures of the other reactants (H₂O and N₂O or C₂H₆). The flow rate

of He was adjusted to obtain the required space velocity. In order to understand better the mechanism and to establish the rate equation for the C₂H₆ conversion, the order of reaction was obtained from a plot of the logarithm of the rate of C₂H₆ conversion versus the logarithm of the partial pressures of C₂H₆ and N₂O. The overall rate of C₂H₆ conversion may be described by

$$-\frac{d[C_2H_6]}{dt} = k[C_2H_6]^{0.4}[N_2O] \quad (1)$$

over the range of partial pressures $P_{C_2H_6} = 30$ –300 Torr, and $P_{N_2O} = 30$ –280 Torr. At $P_{N_2O} > 280$ Torr the rate of C₂H₆ conversion remained constant, giving an apparent zero order with respect to N₂O. An accurate determination of the order with respect to eth-

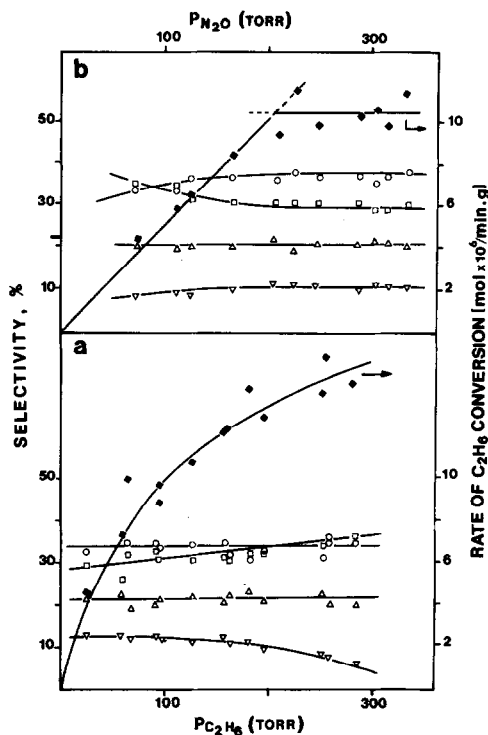


FIG. 6. Ethane conversion and product distribution as a function of (a) partial pressure of C₂H₆, $F_v = 58.3$ ml/min, $P_{N_2O} = 236$ Torr, $P_{H_2O} = 200$ Torr, and (b) partial pressure of N₂O, $F_v = 57.9$ ml/min, $P_{C_2H_6} = 124$ Torr, $P_{H_2O} = 199$ Torr: 2.0 g of 2 wt% Mo/SiO₂. (◆) Rate of C₂H₆ conversion, (○) C₂H₄, (□) CH₃CHO, (△) CO₂, (▽) CO.

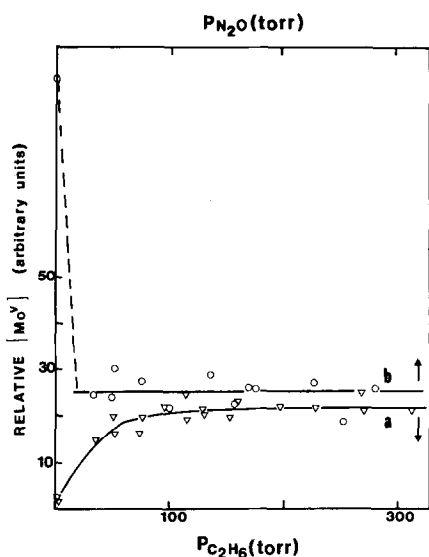


Fig. 7. Relative concentration of Mo^{V} at steady state as a function of (a) partial pressure of C_2H_6 , $P_{\text{N}_2\text{O}} = 251$ Torr; and (b) partial pressure of N_2O , $P_{\text{C}_2\text{H}_6} = 151$ Torr: 0.70 g of 2 wt% Mo/SiO_2 , $F_v = 30.0$ ml/min, $T = 550^\circ\text{C}$.

ane is difficult because the catalyst deactivated at relatively high partial pressures of C_2H_6 as reported above.

In the reaction mechanism discussed below, the steady-state concentration of Mo^{V} will play an important role. The relative concentration of Mo^{V} was determined by ESR as a function of the partial pressure of C_2H_6 and N_2O . The experiments were carried out as before in a mixture of C_2H_6 , N_2O , and He. After the system reached steady state, the reactor was rapidly quenched as described before (Experimental) and the EPR spectrum of Mo^{V} was recorded (Fig. 7). The results show that the steady-state concentration of Mo^{V} was essentially zero order with respect to N_2O , whereas with respect to C_2H_6 the order was ca. 0.45 up to 100 Torr and zero order at higher pressures. The concentration of Mo^{V} did not exceed 1% of the total molybdenum even at the highest concentration. Similar XPS experiments showed, however, that the concentration of Mo^{V} increased up to ca. 40% of the total molybdenum present at 250 Torr of C_2H_6 . Moreover a similar

amount of Mo^{IV} was also observed in those experiments. Based on the XPS results, the Mo^{V} concentration followed an order of ca. 0.36 with respect to ethane. It is worthwhile to note that the amount of Mo^{V} detected by ESR is much smaller than the amount observed by XPS. Similar observations were previously reported for molybdenum-alumina catalysts (8).

Reaction of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO with N_2O . In the reaction mechanism which follows, ethanol is believed to be an important intermediate in the production of acetaldehyde. In order to establish the stability of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO under reaction conditions, separate experiments in the flow reactor were carried out in which ethanol or acetaldehyde were reacted with nitrous oxide and water in the temperature range 400 – 550°C . At 400°C the ethanol was almost completely converted (94%) to acetaldehyde (92% selectivity). Contact times in the flow reactor are in the order of ~ 5 sec, which indicates that the conversion of $\text{C}_2\text{H}_5\text{OH}$ is a very effective reaction even at 400°C . Under the same conditions 7% of the acetaldehyde was converted to CO_2 , CO , and CH_4 , with selectivities of 51, 38, and 9%, respectively. Small amounts of C_2H_4 , C_3 , and C_4 were also observed. At 480°C the conversion reached 46%, whereas selectivities remained essentially the same. These results show that acetaldehyde, though more stable than ethanol, is also unstable under reaction conditions and will undergo subsequent reactions to produce mainly carbon oxides.

Experiments in the circulation reactor. In order to establish whether C_2H_4 , CH_3CHO , and CO_2 are primary or secondary products and to obtain an insight into the reaction pathway, experiments were carried out in a circulation reactor at a relatively low temperature (400°C). The results obtained (Fig. 8) show that after 5 min of reaction C_2H_4 , CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, and CO_2 were detected. As the reaction proceeds the CO_2 formation rate changed, the concentration of CH_3CHO reached a constant value, and

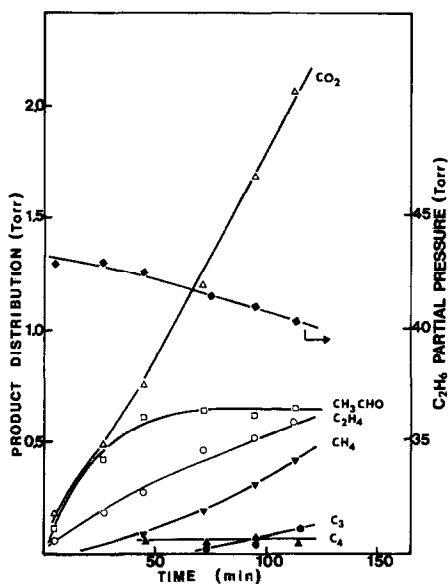


Fig. 8. Ethane conversion and product distribution as a function of time in a circulation reactor: 0.50 g of 2 wt% Mo/SiO₂, $T = 400^{\circ}\text{C}$.

C₂H₅OH was observed only in trace amounts. This behavior can be understood by realizing that at the beginning of the reaction CO₂ is mainly produced from further reduction of the catalyst, whereas at a latter stage CO₂ is produced by subsequent reaction of the other products, mainly acetaldehyde. The steady concentration of acetaldehyde suggests that the rate of formation equals the rate of reaction.

Spectroscopic experiments. ESR was used to identify the intermediates O⁻ and C₂H₅·. The O⁻ ion was generated on this catalyst by exposure of the reduced Mo/SiO₂ catalyst to N₂O. Upon addition of C₂H₆ at -196°C the intensity of the O⁻ signal did not change, even after 3 hr. It should be noted that the vapor pressure of ethane at this temperature is $<10^{-6}$ Torr. The O⁻ reacted slowly with C₂H₆ at temperatures as low as -119°C and rapidly at -107°C ; however, the ESR spectrum of the ethyl radical was not observed, presumably because at -119°C , the C₂H₅· was not stable enough to be detected. Attempts to trap the radical by rapid heating and cooling

failed. The stability of C₂H₅· produced on this surface was tested using a technique reported by Kazansky and co-workers (9) in which ethyl radicals were generated by irradiation of the Mo/SiO₂ catalysts in the presence of C₂H₆. The irradiation (254 nm) of the catalyst is believed to produce Mo^{VO}- centers which react at -196°C with C₂H₆ to produce C₂H₅· radicals and Mo^V-OH⁻. Using this method a clearly resolved ESR spectrum of C₂H₅· was observed. The radical was stable at -196°C ; however, the spectrum disappeared upon heating to -160°C for >5 min or after 30 sec at -131°C . Hence, the high reactivity of the ethyl radicals on the Mo/SiO₂ surface at relatively low temperatures is established.

The spectrum of C₂H₅· was detected using the matrix isolation method described by Martir and Lunsford (10). After activation as previously described, a mixture of C₂H₆ and N₂O in Ar was passed over the Mo/SiO₂ catalyst at 550°C for 3 hr, and a matrix was allowed to form over 20 min on a sapphire rod at 12 K. The ESR spectrum of Fig. 9 shows that ethyl radicals were formed on the catalyst, subsequently entered the gas phase and were trapped in the matrix. Over a period of 36 hr several matrices were formed, and the intensity of the C₂H₅· spectra remained unchanged. In a similar experiment in which N₂O was absent no radicals were detected, showing that the ethyl radicals are formed as a result of the reaction between N₂O (or O⁻) and C₂H₆ over this catalyst and not as a result of

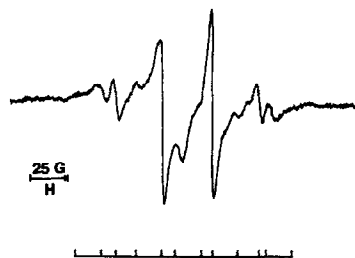


Fig. 9. ESR spectra of matrix-isolated C₂H₅· after reaction of C₂H₆ with N₂O over 2 wt% Mo/SiO₂ at 550°C .

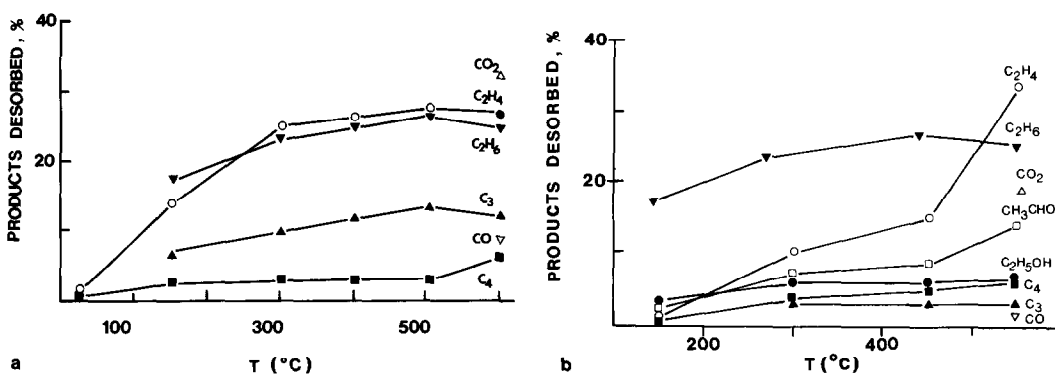


FIG. 10. Product distribution as a function of the thermal desorption program following (a) reaction of O^- with C_2H_6 and (b) reaction of O^- with C_2H_6 and subsequent adsorption of H_2O vapor, at $25^\circ C$ over 2 wt% Mo/SiO_2 .

the mere interaction of C_2H_6 with the catalyst.

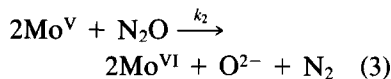
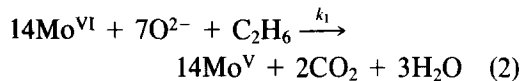
Thermal desorption experiments. In these experiments O^- was produced by treatment of the activated catalyst with 90 Torr of N_2O at $150^\circ C$ for 1 hr. The catalyst was cooled to $25^\circ C$ and 5 Torr of C_2H_6 were recirculated over the catalyst for 1 hr. The gas phase was evacuated, and the temperature program started. In another experiment the same procedure was followed except that after the evacuation of the C_2H_6 , the catalyst was exposed to 5 Torr of H_2O for 0.5 hr and then evacuated again before the temperature program was initiated. The amount of products desorbed as a function of temperature is depicted in Fig. 10. The major product was C_2H_4 , which was desorbed mainly at $300^\circ C$. Unreacted C_2H_6 was mainly desorbed at $150^\circ C$. A comparison of Fig. 10a with 10b illustrates again the importance of H_2O in the formation of the oxygenated products C_2H_5OH and CH_3CHO . When the catalyst was not exposed to water, a very small amount of CH_3CHO (not shown) and no C_2H_5OH were detected.

As a surface ethoxide is believed to be the most likely intermediate in the selective oxidation reaction, it was instructive to examine the thermal desorption pattern after adsorption of pure ethanol and acetaldehyde. The thermal desorption of ethanol (Fig. 11a) produced mainly C_2H_4 and

CH_3CHO , whereas the thermal desorption of acetaldehyde (Fig. 11b) gave rise to carbon oxides, C_2H_4 , and other hydrocarbons.

DISCUSSION

In many respects the mechanism for the partial oxidation of ethane parallels the previously proposed mechanism for the oxidative dehydrogenation of ethane in the absence of H_2O , and the mechanism for the partial oxidation of methane. Ethane oxidation over the Mo/SiO_2 catalyst may be described in terms of a selective cycle which produces C_2H_4 and CH_3CHO and a nonselective cycle which yields CO_2 . The other products are apparently produced by further oxidation of CH_3CHO and C_2H_4 . The nonselective cycle may be represented by the stoichiometric reactions



The selective cycle is based on the reaction of N_2O with Mo^V to form $Mo^{VI}-O^-$ which is the active oxygen species in the selective oxidation. The O^- reacts with C_2H_6 by hydrogen abstraction to produce $C_2H_5\cdot$ which may further react with lattice oxygen to form a surface ethoxide. The latter decomposes to either C_2H_4 or CH_3CHO .

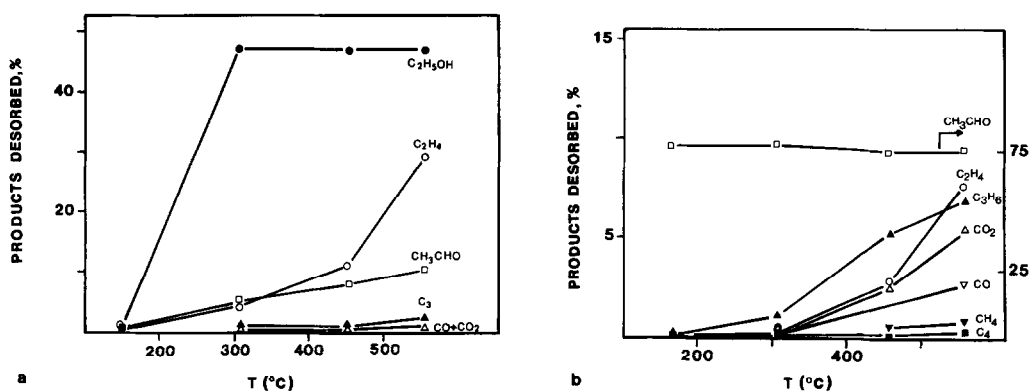
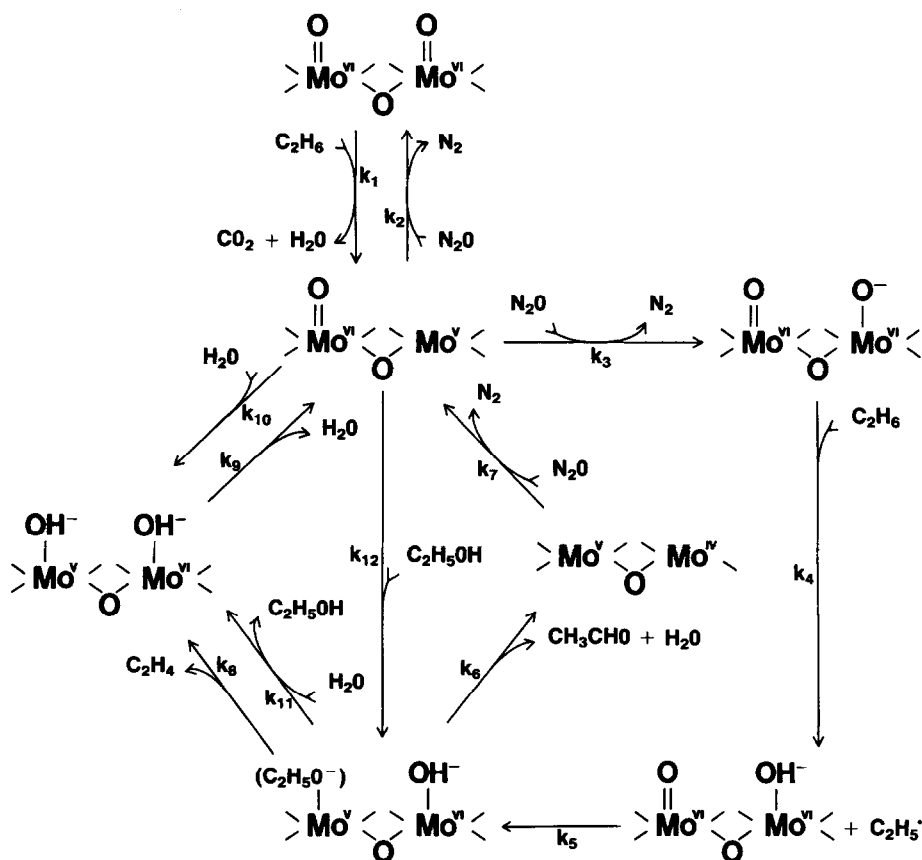


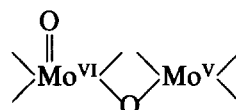
FIG. 11. Product distribution as a function of the thermal desorption program after adsorption of (a) C₂H₅OH and (b) CH₃CHO at 25°C over 2 wt% Mo/SiO₂.

The proposed mechanism is described:



An important feature of the mechanism is that the active Mo^V species, once formed by reaction (2), may be regenerated according to the selective cycle until it is removed by reaction (3). This active Mo^V species is believed to be an isolated Mo^V species rep-

resented in the scheme by the complex



The results in Fig. 1 show that catalytic activity no longer increased with increasing Mo loading after a saturation level of ~2 wt%. This behavior is further supported by the ESR results and previous conclusions from this laboratory (1) which showed that the active form of Mo is only a very small fraction of the total molybdenum present. Likewise, our ESR experiments showed that the intensity of the O^- signal did not increase beyond molybdenum loadings of ~2 wt% and actually decreased at higher loadings of 5 and 6.6%. This indicates that at the higher loadings the O^- is only formed on a small fraction of the total Mo, and presumably at the isolated Mo^V sites. If the active site is indeed an isolated Mo^V , then agglomeration at higher loadings would be detrimental to the catalytic activity. This view is further supported by comparing the XPS spectra of oxidized Mo/SiO_2 catalysts containing 2 and 6.6% Mo. On the high-Mo-content sample the $Mo\ 3d_{3/2}$ and $Mo\ 3d_{5/2}$ peaks were clearly resolved while on the low-loading sample the peaks were very broad and not resolved at all. This indicates that a well-defined homogeneous Mo phase was formed at the higher loading.

The selective cycle may be repeated many times providing that reaction (3) or a similar two-electron transfer does not occur. Apparently the life of one Mo^V site is strongly dependent on the conversion. At higher conversions the active Mo species may be further reduced by acetaldehyde, providing a suitable situation for a two-electron transfer to occur.

Based on the mechanistic scheme above, the overall rate equation for the oxidation of C_2H_6 can be derived. Using the steady-state approximation for $d[Mo^V]/dt$, $d[Mo^{IV}]/dt$, $d[O^-]/dt$, and $d[C_2H_5\cdot]/dt$ and assuming that the active form of Mo^V is only a small fraction of the Mo present ($[Mo^V]_{active} \ll [Mo]_{total}$), the rate equation for the C_2H_6 conversion is

$$-\frac{d[C_2H_6]}{dt} = k_1[C_2H_6]^n \left(1 + \frac{k_3}{k_2}[N_2O]^{1-m}\right)[Mo]_t \quad (4)$$

As in the mechanistic scheme, step 3 occurs at low temperatures while step 2 occurs only at high temperatures (5), thus, the rate expression is reduced to

$$-\frac{d[C_2H_6]}{dt} = \frac{k_1 k_3}{k_2} [C_2H_6]^n [N_2O]^{1-m} [Mo]_t \quad (5)$$

where n and m can be evaluated from the measurement of the relative concentration of Mo^V as a function of C_2H_6 and N_2O partial pressure (Fig. 7). At intermediate pressures of N_2O (30–280 Torr) and lower pressures of C_2H_6 (0–100 Torr), it was found that $m = 0$ and $n \approx 0.45$, which yields

$$-\frac{d[C_2H_6]}{dt} = \frac{k_1 k_3}{k_2} [C_2H_6]^{0.45} [N_2O] [Mo]_t \quad (6)$$

in good agreement with the experimental rate equation with respect to the gas-phase reactants. At higher partial pressures of C_2H_6 the order (n) becomes zero (Fig. 7). This behavior can be understood if one assumes that at the higher partial pressures of ethane, the concentration of Mo^V increases to a level such that magnetic coupling prevents the observation of additional Mo^V ions (8). The XPS results showed that the Mo^V concentration actually increased at the higher pressures, and the experimental order with respect to C_2H_6 was 0.36, which is in fair agreement with the results above. As the sites become less isolated, the selectivity to acetaldehyde decreases (Fig. 6).

Although, the O^- and $C_2H_5\cdot$ intermediates have been identified on the catalyst and in the gas phase, respectively, direct evidence for the formation of $C_2H_5O^-$ by IR was not obtained. The detection of ethoxide on the surface of this catalyst by IR is difficult because there is no transmission in the region $1050\text{--}1150\text{ cm}^{-1}$ in which the characteristic stretching frequency of the CO group is observed, and identification relies only on the CH stretching modes. Experiments designed to confirm the presence of the surface ethoxide on Mo/SiO_2 catalysts were not successful, probably because the concentration of the ethoxide, in sam-

ples which gave adequate transmission, was below the detection limit of the instrument. Samples prepared with Cab-O-Sil gave better transmission; however, background in the region 2800–3000 cm^{-1} makes the identification difficult. Indirect evidence for the presence of $\text{C}_2\text{H}_5\text{O}^-$ is provided by the TPD experiments. Ethanol is known to form $\text{C}_2\text{H}_5\text{O}^-$ upon adsorption on oxide surfaces, as confirmed by IR spectroscopy (6). Indeed, the $\text{C}_2\text{H}_5\text{O}^-$ ion was detected by IR when $\text{C}_2\text{H}_5\text{OH}$ was adsorbed on the $\text{MoO}_3/\text{Silica 57}$ catalyst of this study. The resemblance between the TPD patterns in Figs. 10b and 11a is an indication that the C_2H_4 and CH_3CHO products were produced from the same intermediate, i.e., the ethoxide.

The surface ethoxide may decompose to produce ethylene or it may react with water or OH^- to produce ethanol and acetaldehyde as depicted in the mechanistic scheme. If $\text{C}_2\text{H}_5\text{OH}$ is produced, it will further react to give mainly CH_3CHO , even at relatively low temperatures. These results suggest that the primary products in the reaction are C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ which is probably the precursor of acetaldehyde. Nevertheless, the reaction of the surface ethoxide with adjacent OH^- to produce acetaldehyde should also be considered as a possible pathway. The increase in selectivity toward acetaldehyde in the presence of water (Fig. 2), may be rationalized in this manner. The TPD patterns (Figs. 10a and b) in the absence and in the presence of H_2O provides further support for this point. In the absence of H_2O , no $\text{C}_2\text{H}_5\text{OH}$ and only traces of acetaldehyde were obtained on the catalyst activated at 600°C which was in a highly dehydroxylated state. The slight reduction in conversion caused by H_2O may be explained as a result of competition for the active site, between N_2O and H_2O (steps 3 and 10, respectively, in the mechanistic scheme).

In addition to being produced by reaction (2), CO_2 may also be produced from further oxidation of acetaldehyde and other products. Acetaldehyde is known to form ace-

tate-like intermediates when adsorbed on solid surfaces (11). The acetate intermediate decomposes to give CH_4 and a carbonate-type surface complex which ultimately produces CO and CO_2 . The TPD pattern of adsorbed acetaldehyde (Fig. 11b) shows that indeed relatively large amounts of CO_2 and CO are produced. The different amounts of CO_2 and CH_4 , observed in the circulation experiments (Fig. 8), suggest that CO_2 and CO are also formed from other sources. The fact that CO was detected only in trace amounts in the circulation experiments is probably a consequence of its oxidation to CO_2 , which has been demonstrated to occur over this catalyst even at low temperatures (12). The detection of C_3 and C_4 hydrocarbons is probably a result of dimerization or oligomerization reactions of either the acetaldehyde or the ethylene. Further oxidation and cracking of these hydrocarbons, or C_2H_6 , may account for the relatively large amounts of CO_2 and CO .

The formation of C_2H_4 by another mechanism cannot be excluded. Ethylene may also be produced by a mechanism in which the $\text{C}_2\text{H}_5\cdot$, formed as explained above, loses another H atom by its reaction with lattice oxygen or O^- . The TPD experiments show that at room temperature small amounts of C_2H_4 and $n\text{-C}_4\text{H}_{10}$ were observed. The latter product, although present in small amounts, indicates that in addition to reacting with the surface to form ethoxide ions, ethyl radicals may couple to form $n\text{-C}_4\text{H}_{10}$. It is unlikely, however, that ethyl radicals initiate a homogeneous chain mechanism which contributes significantly to the observed products. As noted previously the reaction of $\text{C}_2\text{H}_5\cdot$ with the surface is facile; whereas the reaction of $\text{C}_2\text{H}_5\cdot$ with N_2O is expected to have considerable energy of activation. For example, Dean *et al.* (13) have shown that the reaction $\text{H}\cdot + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH}\cdot$ has an activation energy of 22 kcal/mol. Since molecular oxygen, derived via the decomposition of N_2O , was not detected as a product, this species probably was not an important intermediate, either on the surface or in the gas phase.

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