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Partial Oxidation of Ethane over Supported Vanadium Pentoxide Catalysts

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The partial oxidation of ethane has been studied on silica-supported V_2O_5 catalyst in a fix-bed continuous-flow reactor at 775–823 K. The temperature-programmed reduction of V_2O_5 was also investigated. Using N_2O as oxidant, the main oxidation products were ethylene, acetaldehyde, CO, and CO_2. Small amounts of CH_4, and C_3- and C_4-hydrocarbons were also identified. The selectivities for ethylene and acetaldehyde at 823 K were 57.5 and 5.1%, respectively. The introduction of water increased the rate of acetaldehyde and CO formation, but decreased that of ethylene. Kinetic orders were determined for all products. The activation energies for the formation of C_2H_4, CH_3CHO, CO, and CO_2 were 47.7, 33.3, 27.9, and 21.5 kcal/mol, respectively. Using O_2 as oxidant, the same products were observed, but the conversion was higher and selectivities were lower. The addition of water to the reacting mixture enhanced the selectivity toward ethylene and acetaldehyde formation. A possible mechanism for the oxidation reaction is proposed.

INTRODUCTION

Many recent studies have shown that supported V_2O_5 is an excellent catalyst for the selective oxidation of hydrocarbons. Relatively little attention has been paid so far to the selective transformation of ethane into more valuable compounds.

The oxidative dehydrogenation of ethane on V–Mo–Nb oxides was reported by Thorsteinson *et al.* (*1*). Although they obtained a high activity and selectivity for ethylene formation, no oxygenated compounds were detected. Iwamoto and co-workers (*2*) studied ethylene and acetaldehyde formation in the catalytic oxidation of ethane on various metal oxides, using N_2O as oxidant. They found that some oxides exhibited high activity, among them V_2O_5 and MoO_3 supported on silica.

Mendelovici and Lunsford (*3*) recently showed that molybdenum oxide supported on silica is an effective catalyst for the oxidation of ethane to ethylene and acetaldehyde by nitrous oxide, but they were not able to reproduce the relatively high activity of the molybdenum catalyst found by Iwamoto *et al.* (*2*).

Iwamatsu *et al.* (*4*) studied the properties and reactivities of surface oxygen species, including O^-, on V_2O_5/SiO_2 in connection with the oxidative dehydrogenation of C_2H_6 by N_2O. It has been demonstrated by ESR spectroscopy that ethane reacts with the O^- centers of vanadium or molybdenum catalysts and produces ethyl radicals even at low temperature (*4*). These centers can also be generated by N_2O decomposition (*4*).

We have shown earlier in a brief report that the efficiency of silica-supported V_2O_5 catalysts increases in the presence of potassium (*5*). The activity of the catalyst was more stable when it was prepared from KVO_3 than when V_2O_5 was promoted with K-salts.

The present report gives an account of the selective oxidation of ethane on vanadium pentoxide supported on Cab–O–Sil–SiO_2 using nitrous oxide and oxygen as oxidant.

EXPERIMENTAL

Materials. The catalysts were prepared by impregnation of the support from a basic solution of ammonium metavanadate at pH 10.5 to yield a nominal 2% loading of V_2O_5. The suspension was dried at 373 K and heated at 823 K for 5 h. The following oxides were used as supports: SiO_2 (Cab–O–Sil), Al_2O_3 (Degussa), and TiO_2 (Degussa P25). For the studies, fragments of slightly compressed pellets (at 3–5 bar) were used. The size of the fragments was ~ 1 × 1 × 0.5 mm.

Before the catalytic measurements, the sample was oxidized in an O_2 flow for 1 h at 773 K in the reactor. After the oxidation, the catalyst was heated to the reaction temperature in flowing He.

The reactant gases, C_2H_6 (99.9%), N_2O (99.7%), and O_2 (99.9%), were used as received. He (99.9%) was purified with an Oxy-trap. The other impurities were adsorbed on a 5A molecular sieve at the temperature of liquid air.

Methods. The reactions were carried out in a fixed-bed continuous-flow reactor. Generally, 0.7–0.8 g of sample was used as catalyst. The reacting gas mixture, which consisted of 20% ethane, 40% oxidant, and He as diluent, was saturated with water by bubbling the gas mixture through preheated water. The concentration of water vapor was regulated via the temperature of the water bath. The residence time of the gases was 1.4–1.6 × 10^{-2} g min/ml.

The products were analyzed with a Hewlett–Packard 5750 gas chromatograph. An effluent splitter in the gas chromatograph permitted simultaneous detection by thermal conductivity and flame ionization detectors. Porapak QS (2 m, programmed 313–433 K) was used to analyze for N_2O, CO_2, CH_4, C_2H_4, C_2H_6, CH_3CHO, C_2H_5OH, and C_3- and C_4-hydrocarbons. Separation of O_2, N_2, and CO was accomplished with a 5A molecular sieve column.

Conversion is defined as moles of ethane reacted per minute/moles of ethane fed per minute, and selectivity as moles of product formed per minute/moles of ethane reacted per minute.

The pulse reactor was incorporated between the sample inlet and the analytical column of the gas chromatograph (*6*).

Temperature-programmed reduction (TPR) experiments were carried out in the pulse reactor. The dead volume was filled with quartz beads. The reactor was heated by an external oven at a linear rate of 40° min^{-1} to a final temperature of 1100 K. The catalysts were flushed with nitrogen containing 10% H_2, and the hydrogen consumption was measured. Details of the TPR have been described elsewhere (*6*).

The number of surface V ions was determined by oxygen uptake at 641 K, assuming $O_{ads.}/V_{surf.} = 1$ (*7*). In this experiment the sample was reduced at 641 K. We found that 83.7% of vanadium ions are available for oxygen adsorption. This value was 92.8% on TiO_2 and 66.0% on Al_2O_3. The surface area of 2% V_2O_5/SiO_2 (BET) was 112 m^2/g, which decreased only slightly (<10%) after the catalytic reaction.

RESULTS

Temperature-Programmed Reduction of V_2O_5 Samples

First we investigated the reduction of unsupported vanadium pentoxide, which started at about 830 K and peaked at 955 K. These values for V_2O_5/SiO_2 were lower, 690 and 940, respectively. The TPR spectra are displayed in Fig. 1, where the results obtained for V_2O_5/TiO_2 and V_2O_5/Al_2O_3 are also shown for comparison.

From the hydrogen consumption during TPR, we calculated the O/V ratio for different catalysts (Table 1). The extent of reduction of the V_2O_5 was the highest on TiO_2 (O/V = 1.5). In this case one oxygen atom

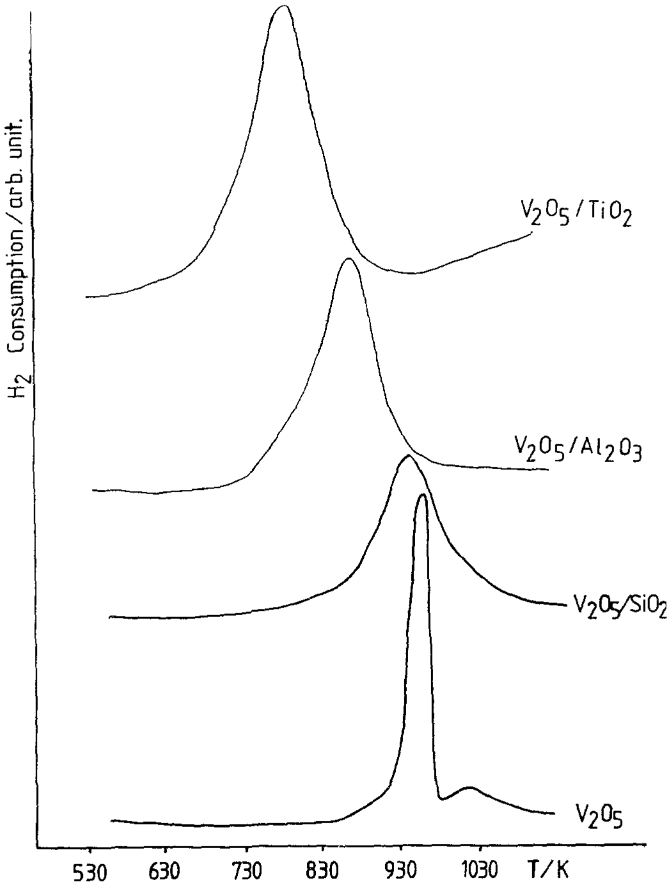

FIG. 1. The temperature-programmed reduction curves of V_2O_5 and supported V_2O_5. The amount of V_2O_5 on carrier oxides and that of clean V_2O_5 were the same.

reacted with hydrogen per V atom; i.e., the V^{5+} was reduced to V^{3+}. On silica and alumina surfaces, the V^{5+} was reduced only to V^{4+}. The extent of the reduction was the lowest for unsupported V_2O_5.

Oxidation of Ethane by N_2O on V_2O_5/SiO_2

Before the kinetic measurements, the catalysts were treated with the reacting gas mixture at the highest reaction temperature, usually 823 K, until a steady-state activity was obtained. During this period, in the case of vanadium pentoxide/silica catalyst the conversion of ethane and the rate of product formation decreased, but after 2 h the activity of the catalyst remained almost the same. In the reaction products, CO, CO_2, C_2H_4, and CH_3CHO, small amounts of CH_4 and C_3- and C_4-hydrocarbons and traces of C_2H_5OH were detected. The conversion of C_2H_6 at 823 K was about 8%. In the reaction, 42% CO, 25% CO_2, 30% C_2H_4, and about 2% CH_3CHO were formed.

With decreasing flow rate of the reactant under the given experimental conditions, the amount of product linearly increased (Fig. 2).

The introduction of water vapor into the reacting gas mixture changed the product distribution of the reaction. Figure 3 shows the effect of the water content, which was

TABLE 1

Some Characteristic Data of Temperature-Programmed Reduction of Different Supported V_2O_5 Catalysts

	T^a (K)	T max (K)	O (μmol)	O/V
V_2O_5	830	955	8.62	2.19
V_2O_5/Al_2O_3	680	870	35.0	1.95
V_2O_5/SiO_2	690	940	40.7	1.9
V_2O_5/TiO_2	565	785	61.5	1.57[a]

Note. T^a, the onset temperature of reduction; T_{max}, the temperature of the TPR peak maxima; *O*, the amount of the reacted oxygen; O/V, the ratio of the oxygen/vanadium after the TPR.

[a] Value corrected by the H_2 consumption in the case of the V_2O_5 free support.

varied between 0 and 32%. The rate of C_2H_4 formation decreased with an increase in the water concentration, but the amount of CO and CH_3CHO produced increased. The water had no influence on CO_2 formation.

In order to determine the rate law for the reaction, the rates of product formation were determined in terms of the partial pressure of the reactant.

With an increase in the C_2H_6 concentration (5–40%), CH_3CHO production increased, but no change occurred in the CO_2 formation. The production rates of C_2H_4 and CO were also enhanced with the C_2H_6 concentration up to 20%, but a further increase in the C_2H_6 concentration had no ef-

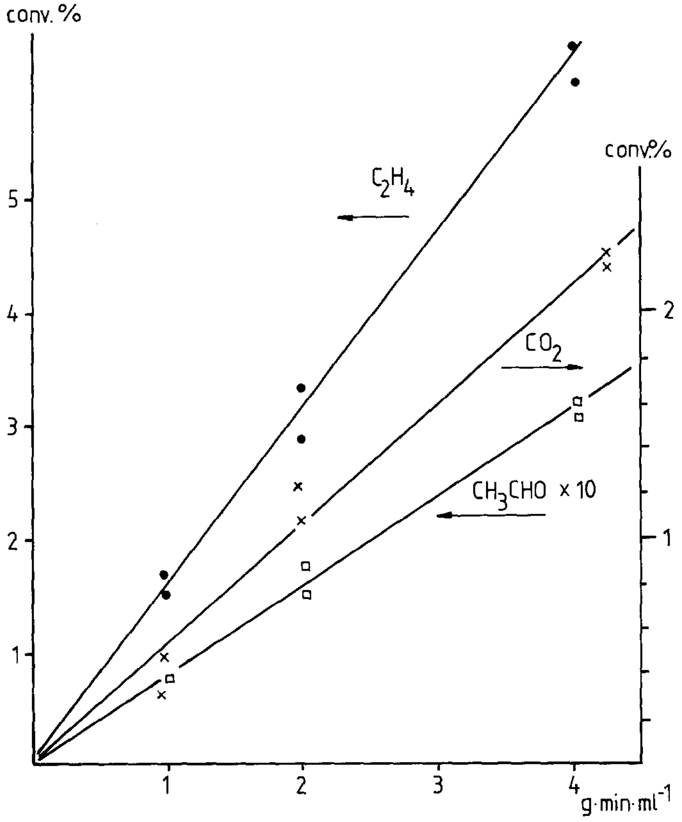

FIG. 2. The specific conversion of the products (μmol of product per μmol of reactant per g of catalyst) as a function of the residence time at 820 K. The concentrations of C_2H_6, N_2O, and H_2O were 20, 40, and 20%, respectively.

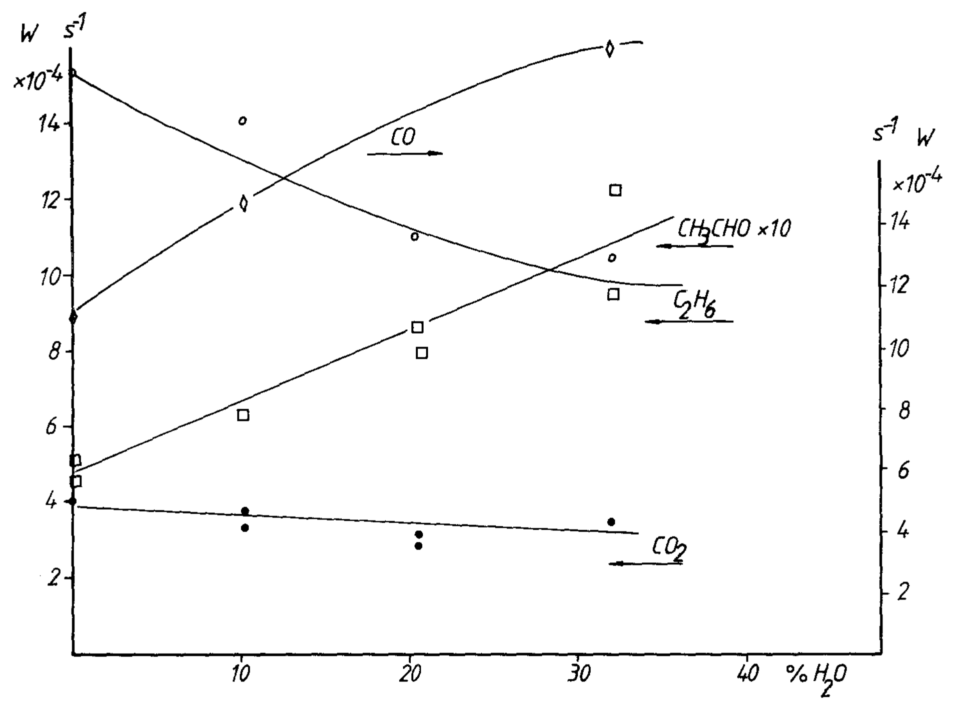

FIG. 3. The rate of the product formation as a function of the water concentration at 820 K. The concentrations of ethane and N_2O were 20 and 40%, respectively.

fect. The conversion of C_2H_6 decreased, while the selectivities of C_2H_4 and CH_3CHO formation increased with an increase in the C_2H_6 concentration (Fig. 4).

The conversion of C_2H_6 and the formation rates for all products increased with an increase in the N_2O content.

Logarithmic plots of the various rates vs the volume percentage of the reactants of interest are shown in Figs. 5 and 6. We observed that the kinetic order with respect to N_2O is 0.6 for the formation of all products (Fig. 5). The order with respect to C_2H_6 is zero for CO_2 formation in the entire concentration range (Fig. 6), but it is zero for CO and C_2H_4 production only above 20% C_2H_6 content. In the lower concentration range, the orders of reaction for C_2H_6 with regard to CH_3CHO and C_2H_4 formation were almost the same (0.82 and 1) (Table 2).

The temperature dependences of the reaction was studied in the range 775–823 K. The conversion of C_2H_6 changed between 1.0 and 5.2%. The selectivity of C_2H_4 formation was nearly constant (43–45%) in this temperature range, but the selectivity of acetaldehyde formation increased with decreasing temperature (at 775 K it was 7.2%).

As shown in Fig. 7, the temperature dependences of the rates of C_2H_4, CO, CO_2, and CH_3CHO formation give Arrhenius fits within the limits of experimental uncertainty. The activation energies for the formation of C_2H_4, CO, CO_2, and CH_3CHO were 47.7, 27.9, 21.5, and 33.3 kcal/mol, respectively. The results are listed in Table 2.

Pulse Experiments

In subsequent measurements, the reaction was investigated by means of a pulse technique. One pulse contained 0.5 ml gases, i.e., 20.8 μmol.

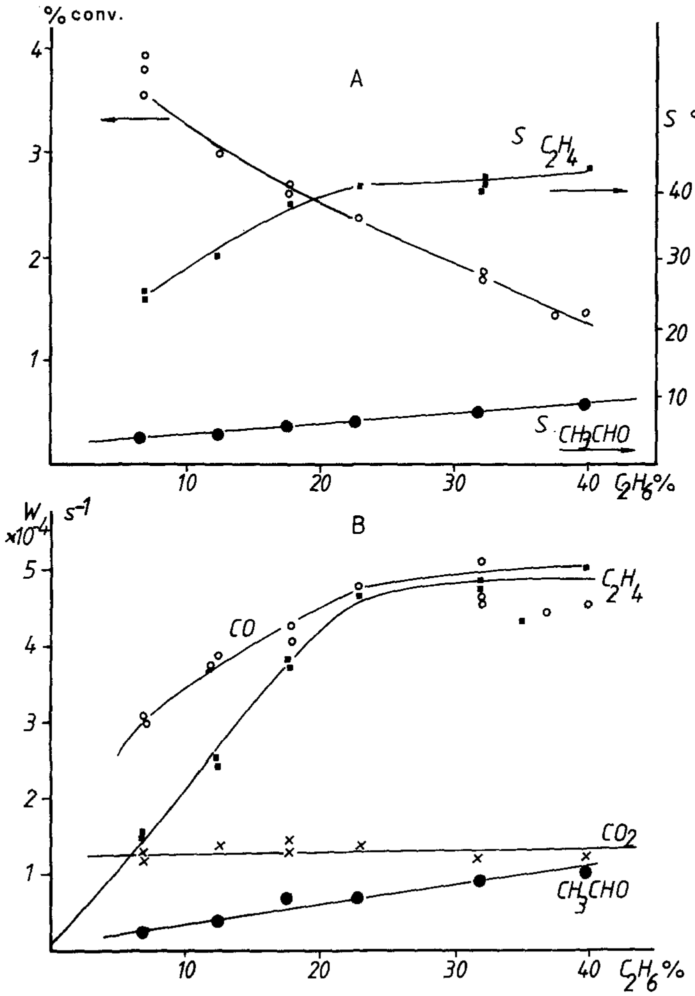

FIG. 4. (A) Ethane conversion and the selectivity of ethylene and acetaldehyde (B) and the rate of the product formation as a function of ethane concentration at 803 K. The N_2O and water contents of inlet gas were 40 and 20%, respectively.

When the V_2O_5/SiO_2 catalyst was treated at 823 K with pure ethane, CO, CO_2, C_2H_4, and acetaldehyde formation was observed. The C_2H_6 conversion was about 3–3.5%, which decreased only slightly in the subsequent pulses. The selectivity of C_2H_4 formation in the first pulse was about 40%, which increased as a function of pulse number (Fig. 8). After the C_2H_6 pulses, the catalyst was treated with O_2: oxygen consumption was detected, and only trace CO_2 formation was observed. The amount of oxygen sorbed by the catalyst and that calculated from the products agreed well with each other.

On injection of a C_2H_6–N_2O gas mixture onto the V_2O_5/SiO_2 catalyst, the conversion of ethane was about 30%. The selectivities of C_2H_4 and CH_3CHO formation were about 40 and 5%, respectively. These values changed only slightly as a function of pulse number. On treatment of the catalyst with O_2 after the C_2H_6 + N_2O pulses, a small amount of oxygen was adsorbed on the surface and trace CO_2 formation was observed.

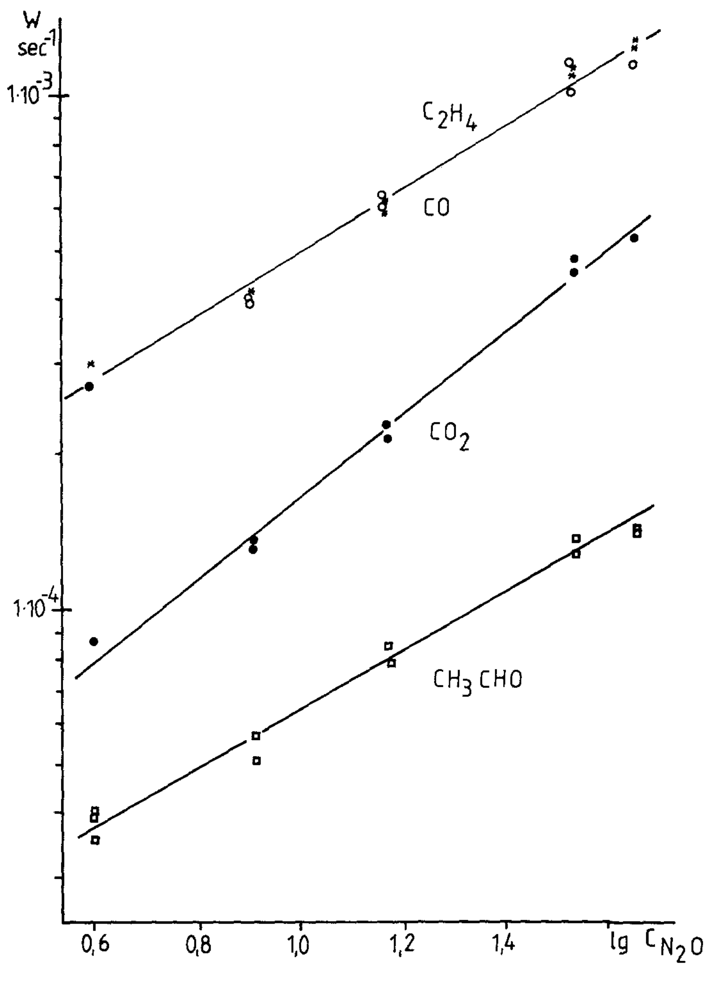

FIG. 5. N_2O pressure dependence of the rates at 803 K. Composition (mol%): N_2O, 5 to 50; C_2H_6, 20; H_2O, 20; and balance He.

Oxidation of Ethane with O_2 over V_2O_5/SiO_2

In the absence of H_2O, the rate of product formation continuously decreased with time and it was difficult to obtain a steady state. The main products of the reaction were the same as those described previously, but the conversion of C_2H_6 was higher: at 811 K it was about 30%. The selectivity of C_2H_4 formation was 22%, and that of CH_3CHO was 3%.

In the presence of water vapor (20%), a nearly steady state was achieved much faster. At 803 K, 17% of C_2H_6 was oxidized in the presence of water vapor. The selectivities of C_2H_4 and CH_3CHO formation were higher, 36–40 and 3–4%, respectively, than those in the absence of H_2O.

An increase in the O_2 concentration significantly enhanced the conversion of C_2H_6. It decreased the selectivity of C_2H_4 formation, but did not affect the selectivity of CH_3CHO formation in the range 5–40% O_2. In the presence of 10% O_2 at 803 K, the C_2H_4 selectivity was greater than 50% (the conversion of C_2H_6 was about 10%). The kinetic orders with respect to O_2 for the consumption of C_2H_6 and for the formation of CH_3CHO were nearly the same (0.53 and

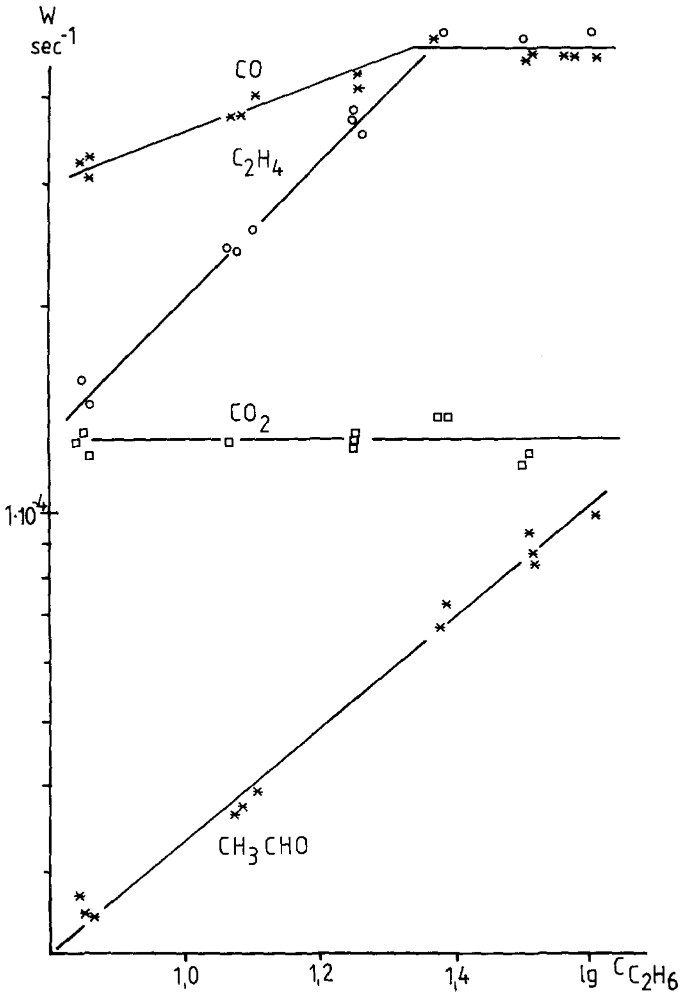

FIG. 6. C_2H_6 pressure dependence of the rates at 803 K. Composition (mol%): C_2H_6, 5 to 40; N_2O, 40; H_2O, 20; and balance He.

0.63), while those for C_2H_4 and CO_2 formation were 0.34 and 0.96, respectively.

The effect of the pure support was also studied under the same condition as those previously described. It was found that the activity of SiO_2 is more than one order of magnitude less than that of V_2O_5/SiO_2.

DISCUSSION

Before a discussion of the kinetic results, some characteristic features of V_2O_5 catalysts are summarized. Oxygen adsorption studies showed that the supported V_2O_5 catalysts are highly dispersed; the fraction of surface V ions for V_2O_5/SiO_2 is 83.7%. The reduction of supported V_2O_5 started at temperatures lower than those of unsupported V_2O_5 and depended on the nature of the support. The observations that the TPR peak maximum of supported V_2O_5 increases in the sequence TiO_2–Al_2O_3–SiO_2 is in accord with previous results (*8–11*). While the H_2 consumption corresponds well to the reduction of V^{5+} to V^{4+} in the case of unsupported and SiO_2- as well as Al_2O_3-supported V_2O_5, the extent of the re-

TABLE 2

Kinetic Data for the Ethane Oxidation on V_2O_5/SiO_2 Using N_2O as Oxidant in the Presence of 20% Water Vapor

Product[a] (%)	Kinetic order			Activation energy (kcal/mol)
	C_2H_6		N_2O	
	a	b	c	
C_2H_4 (57.6)	1	0	0.6	47.7
CH_3CHO (5.1)	0.8	0.8	0.57	33.3
CO (28.8)	0.37	0	0.6	27.9
CO_2 (8.4)	0	0	0.79	21.5

Note. (a) The order up to 20% C_2H_6 content at 803 K. (b) The order above 20% C_2H_6 content at 803 K. The N_2O concentration was 40%. (c) The C_2H_6 concentration was 20%.

[a] Product distribution at 823 K and 4.5% conversion.

duction was much higher for the V_2O_5/TiO_2 sample (Table 1).

The results of pulse experiments showed that the ethane can reduce the catalyst at high temperature, producing ethylene, acetaldehyde, CO, and CO_2 (Fig. 8). However, only a very limited reduction of the catalyst (1%) occurred in the presence of the $C_2H_6 + N_2O$ reaction mixture.

Although the vanadium-catalyzed oxidation of hydrocarbons has been the subject of several investigations, the selective transformation of ethane over supported V_2O_5 has been studied only by a few groups (*1*, *2*, *4*).

In the oxidation of C_2H_6 we have observed among the products carbon oxides, C_2H_4, CH_3CHO, C_2H_5OH, and traces of higher hydrocarbons. Iwamoto *et al.* (*2*) obtained almost the same results with regard to the product distribution on V_2O_5/SiO_2, but they found a higher conversion, although the V_2O_5 content was higher in their case. Iwamatsu *et al.* (*4*) reported on this reaction, but did not detect acetaldehyde or ethanol.

If the oxidation of ethane on V_2O_5/SiO_2 is compared with that on MoO_3/SiO_2 (*3*), we may state that under very similar conditions the ethane consumption and the ethylene formation are higher, but the selectivity is lower on V_2O_5/SiO_2. The rate of acetaldehyde formation is higher on MoO_3/SiO_2 and therefore there is a great difference in the acetaldehyde formation selectivity on two catalysts.

Taking into account the number of V ions (determined by oxygen titration) located on the surface, we obtain a turnover frequency of 2.8×10^{-3} s^{-1} for ethane oxidation on V_2O_5/SiO_2 at 823 K using N_2O as oxidant. Higher values (7.59×10^{-3} and 8.15×10^{-3} s^{-1}) were calculated for V_2O_5/TiO_2 and V_2O_5/Al_2O_3, respectively (*12*). However, in these cases no acetaldehyde production was observed.

The oxidation of ethane over supported vanadium catalysts may be described in terms of selective cycles which produce ethylene and acetaldehyde and nonselective cycles which yield carbon dioxide. The kinetic data on the reaction on V_2O_5/SiO_2 support these ideas.

We have found that CO_2 formation is in-

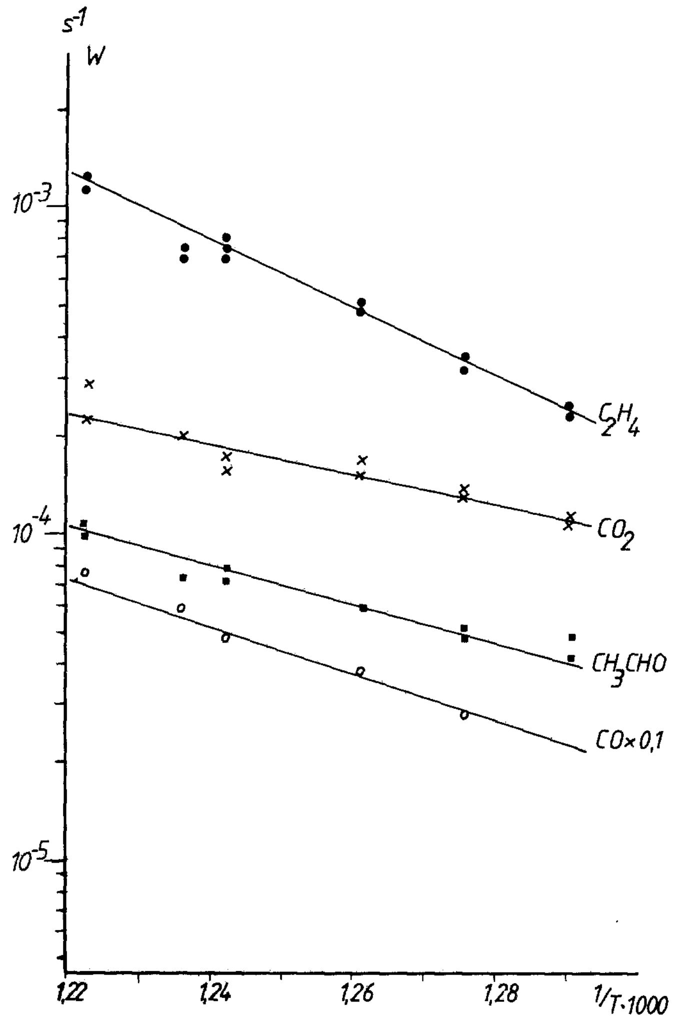

FIG. 7. Arrhenius plots for product formation. The concentrations of ethane, N_2O, and water were 20, 40, 20%, respectively.

dependent of the ethane and H_2O concentrations, but the partial order with respect to N_2O is ~1. This suggests that the rate-determining step of the total oxidation is either the surface decomposition of N_2O or the formation of the surface center generated by this process. We assume that the reaction mechanism is basically the same with oxygen as the oxidizing agent. The possible reason that the activity is lower with N_2O is that its decomposition is slow on an oxidized surface.

The first step of the selective cycle is very likely the formation of the surface ethoxide group from an ethyl radical. The possible mode of the radical formation is the removal of a hydrogen atom from the ethane by the oxide, most probably by the O^- centers (*3*), leaving an ethyl radical and a surface hydroxyl group, which may react further with lattice oxygen to give a surface ethoxide. It has been reported (*13*) that the partially reduced V_2O_5/SiO_2 upon exposure to N_2O and O_2 gives O^- and O_2 gives O^- and O_2^- ions, respectively. This observation may provide an explanation for our results that when O_2 was used as oxidant the combined selectivity of C_2H_4 and

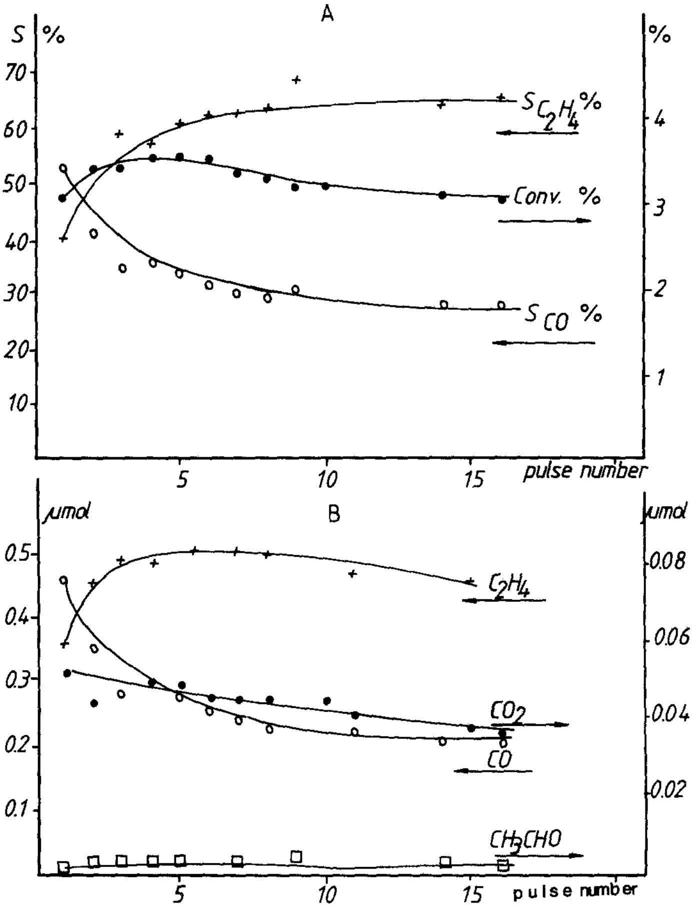

FIG. 8. Conversion of ethane, selectivity of ethylene, and acetaldehyde formation (A) and the amount of product formed in ethane pulse (20.8 μmol) on V_2O_5/SiO_2 at 823 K(B).

CH_3CHO formation was greatly decreased. The ethoxide species formed can decompose to give C_2H_4 or react with H_2O or OH groups to produce ethanol and acetaldehyde. This idea is supported by the fact that the amount of ethylene formed in the reaction decreased with an increase in the water concentration in the reacting gas mixture (Fig. 3):

$$2V^{5+} + (C_2H_5O)^- + OH^- \rightarrow CH_3-CHO + H_2O + 2V^{4+}$$

$$(C_2H_5O)^- + H_2O \rightarrow C_2H_5\text{-}OH + OH^-$$

$$(C_2H_5O)^- \rightarrow C_2H_4 + OH^-$$

If ethanol is formed, it will react further to give acetaldehyde even at a lower temperature (*7*). In this temperature range the decomposition of ethanol to acetaldehyde is favored (*14*). These results suggest that ethylene and acetaldehyde are formed in competitive reactions from the surface ethoxide.

In our opinion, CO may be produced in a secondary reaction, in the decomposition of CH_3CHO on the surface. Although the reactor was connected to a capillary quartz tube, so that the products could be rapidly removed from the heated zone, we cannot completely rule out the possibility that acetaldehyde decomposed in the gas phase, because methane was also detected. It is well known (*15*) that the homogeneous decomposition of CH_3CHO produces CH_4 and CO.

The formation of C_3 and C_4 hydrocarbons is probably a result of the recombination of methyl and ethyl radicals

$$CH_{3(a)} + C_2H_{5(a)} \rightarrow C_3H_{8(a)}$$

$$2C_2H_{5(a)} \rightarrow C_4H_{10(a)}$$

It cannot be excluded that a fraction of these recombination reactions occurs in the gas phase.

REFERENCES

1. Thorsteinson, E. M., Wilson, T. P., Young, F. G., and Kasai, P. H., *J. Catal.* **52,** 116 (1978).
2. Iwamoto, M., Taga, T., and Kagawa, S., *Chem. Lett.,* 1469 (1982).
3. Mendelovici, L., and Lunsford, J. H., *J. Catal.* **94,** 37 (1985).
4. Iwamatsu, E., Aika, K., and Onishi, T., *Bull. Chem. Soc. Japan* **59,** 1665 (1986).
5. Erdöhelyi, A., and Solymosi, F., *Appl. Catal.* **39,** L11 (1988).
6. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Catal.* **68,** 371 (1981); Erdöhelyi, A., and Solymosi, F., *J. Catal.* **84,** 446 (1983).
7. Oyama, T. S., Lewis, K. B., Carr, A. M., and Somorjai, G. A., "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 1489. Chem. Institute of Canada, Ottawa, 1988.
8. Kijenski, J., Baiker, A., Glinski, M., Dollenmeier, P., and Wokaun, A., *J. Catal.* **101,** 1 (1986).
9. van Hengstum, A. J., van Ommen, J. G., Bosch, H., and Gellings, P. J., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," p. 297. Dechema, Frankfurt-am-Main, 1984.
10. Roozeboom, F., Mittelmeijer-Hazeleger, M. C., Moulijn, J. A., Madema, J., de Beer, V. H. J., and Gellings, P. J., *J. Phys. Chem.* **84,** 2783 (1980).
11. Vogt, E., van Dilen, J., Gens, J., Biermann, J., and Janssen, F., "Proceedings, 9th International Congress on Catalysis, Calgary, 1988," p. 1976. Chem. Institute of Canada, 1988.
12. Erdöhelyi, A., and Solymosi, F., unpublished results.
13. Iwamoto, M., Hirata, J., Matsukami, K., and Kagawa, S., *J. Phys. Chem.* **87,** 903 (1983).
14. McMonagle, J. B., and Moffat, J. B., *J. Catal.* **91,** 132 (1985).
15. Rice, F. O., and Herzfeld, K. F., *J. Amer. Chem. Soc.* **56,** 284 (1934).