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Partial Oxidation of Ethane over Silica-Supported Alkali Metal Molybdate Catalysts

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The partial oxidation of ethane has been investigated on silica-supported M_2MoO_4 catalysts (M = Li, Na, K, Rb, Cs) in a fixed-bed continuous-flow reactor at 770–823 K using N_2O as oxidant. Additional measurements included pulse experiments, temperature-programmed reduction of the catalysts, and a study of the catalytic decomposition of N_2O and C_2H_5OH. The numbers of acidic and basic sites have also been determined. Temperature-programmed reduction of the alkali metal molybdates showed that the onset temperature of the reduction decreased from Li to Cs, while the extent of the reduction increased in this sequence. The main products of the oxidation reaction were ethylene, acetaldehyde, CO, and CO_2. Small amounts of CH_4 and C_2H_5OH were also identified. The ethane conversion and the rate of the C_2H_4 and CH_3CHO formation all increased from Li to Cs. Detailed kinetic measurements were carried out on K_2MoO_4/SiO_2. The activation energy of the ethane consumption was 71 kJ/mol. A possible mechanism for the oxidation reaction is discussed. © 1992 Academic Press, Inc.

INTRODUCTION

The catalytic oxidations of alkanes into alkenes, alcohols, and aldehydes are among the most important reactions at the focus of interest in both industrial and fundamental catalysis. In spite of the great economic importance of these reactions, relatively little has been published. Thus only a few papers have dealt with the selective oxidation of ethane (*1–9*), which is the subject of the present paper. Iwamoto *et al.* (*2*) examined the effects of various oxides on the formation of ethylene and acetaldehyde and found that, among others, MoO_3 supported on silica exhibited a particularly high activity. Mendelovici and Lunsford (*3*) also showed that MoO_3/SiO_2 is an effective catalyst for the oxidation of ethane, but they were not able to reproduce the relatively high molybdenum activity observed by Iwamoto *et al.* (*2*). Recently, we performed detailed kinetic measurements on the oxidation of ethane on a V_2O_5/SiO_2 catalyst (*8*). Higher yields of partial oxidation products were achieved when N_2O was used instead of O_2. Moreover, the rate of acetaldehyde formation was enhanced by the addition of alkali metal salts (*5*). The effects of alkali metal additives depended sensitively on their state and on the mode of preparation of the promoted catalyst. As regards the activity and rate of acetaldehyde formation, the best performance was exhibited by KVO_3 (*5, 9*). The other alkali metal metavanadates were also found to be active in the partial oxidation of ethane: the selectivity of CH_3CHO formation increased in the vanadate sequence Li < Na < K < Rb = Cs (*9*). This investigation clearly showed that the formation of a compound between the alkali metal salts and the V_2O_5 catalyst produces a particularly effective catalyst for the mild oxidation of ethane. This finding is tested in the present work, which deals with the oxidation of ethane on alkali metal molybdate catalysts, M_2MoO_4.

Supported molybdates, particularly

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$CoMoO_4$ (*10–12*), $NiMoO_4$ (*12–14*), and different Bi molybdates (*15, 16*) have been widely used in selective oxidation reactions and characterized extensively by various physical methods (*10–16*). Less attention has been paid so far to alkali metal molybdates. Their catalytic behavior has been studied in only a few cases. The oxidation of CH_3OH (*16*) and maleic acid (*17*) was studied on Na_2MoO_4, but that of butene was almost nil on Na and K molybdates (*18*) even though the $Na_2Mo_2O_7$ and $K_2Mo_3O_{10}$ structures present analogies with those of bismuth molybdates (*18*). Another important observation is that the activity of MoO_3 is poisoned by alkali metal addition, due to the formation of molybdates (*19*). Apart from our brief preliminary report dealing with K_2MoO_4 (*20*), the partial oxidation of ethane on alkali metal molybdates has not been investigated. We chose N_2O as oxidant as higher yields of partial oxidation products were found in the ethane oxidation when N_2O was used instead of O_2 (*1–5, 8*).

EXPERIMENTAL

Materials. The catalysts were prepared by impregnating the SiO_2 support (Cab-O-Sil) with a basic solution of ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] or different alkali molybdates, M_2MoO_4 (M = Li, Na, K, Rb, Cs) to yield a nominal 2% loading of MoO_3. The suspension was dried at 373 K and calcined at 873 K for 5 h. The alkali molybdates were prepared from alkali metal carbonates and MoO_3 (*21*). The MoO_3 was stirred in hot alkali metal carbonate solution containing the calculated amount of carbonate until it dissolved. The solution was filtered, and the alkali metal molybdates were crystallized.

Before the catalytic measurements, each catalyst sample was oxidized in an O_2 stream at 773 K in the reactor; the catalyst was then flushed with He and 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 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 made of quartz (100 × 27 mm o.d.). Generally a 0.8-g sample was used as catalyst. The reacting gas mixture consisted of 20% C_2H_6/40% N_2O and He as diluent. When the effect of water vapor was studied, the gas mixture was saturated with water by bubbling the gas mixture through preheated water. The concentration of water was regulated by the temperature of a water bath. The flow rate of the reactants was usually 50 ml/min, and the space velocity was 6,000 h^{-1}.

Analysis of the reaction products was performed with a Hewlett–Packard 5750 gas chromatograph. Columns were packed with Porapak QS and 5A molecular sieve, which allowed complete separation of the products. Conversion is defined as the ratio (moles of ethane reacted per minute)/(moles of ethane fed per minute) and selectivity as the ratio (moles of product formed per minute)/(moles of ethane reacted per minute).

A pulse reactor was also employed (8-mm-o.d. quartz tube), which was incorporated between the sample inlet and the column of the gas chromatograph. A 0.3-g sample was used and the dead volume of the reactor was filled with quartz beads (*8, 9*).

The temperature-programmed reduction (TPR) experiments were carried out in the pulse reactor. The catalysts were flushed in these cases with N_2 containing 10% H_2, and the reactor was heated linearly at a rate of 40 K/min up to 1100 K, while the H_2 consumption was determined.

Decomposition of N_2O was studied at 620–720 K in a static reactor fitted with a gas recirculation system. The reaction was followed by the pressure change, and the gas phase was analyzed by a mass spectrometer.

Decomposition of C_2H_5OH was investigated in a the same fixed-bed reactor as the oxidation of ethane. He flowed through ab-

TABLE 1

Some Characteristic Data of Silica-Supported Alkali Molybdates

	Melting point[a] (K)	r_M[b] (Å)	BET surface area (m^2/g)	Acidic sites (μmol/g)	Basic sites (μmol/g)	O_2[c] Uptake (μmol/g)	D[d] (%)
MoO_3/SiO_2	1068	—	166	360	16.3	45.5	65.5
Li_2MoO_4/SiO_2	978	0.68	111	336	12.6	5.5	
Na_2MoO_4/SiO_2	960	0.97	69	276	31.0	6.7	
K_2MoO_4/SiO_2	1192	1.33	48	139	35.0	3.0	
Rb_2MoO_4/SiO_2		1.52	73	239	34.0	8.7	
Cs_2MoO_4/SiO_2		1.70	110	250	41.9	4.2	

[a] Melting point of the SiO_2-free molybdates.

[b] Ion radius of the alkali ion.

[c] The O_2 uptake was determined at 195 K after reduction of the sample at 773 K for 16 h.

[d] The amount of surface Mo atoms, determined by O_2 adsorption at 195 K, assuming $O_{ads}/Mo_{surf} = 1$ (*22*). As this method has been developed for MoO_3, it is not certain yet that it can be applied for alkali metal molybdates, too. Therefore values of D for these compounds are not given.

solute C_2H_5OH and then into the reactor. The saturator was kept in a water bath at a temperature that would give the desired partial pressure of alcohol.

The BET surface areas of the catalysts were measured by N_2 adsorption at 77 K in a conventional volumetric apparatus. Results are listed in Table 1.

The number of surface Mo atoms was calculated from O_2 adsorption isotherms at 195 K, after a reduction at 773 K for 16 h (*22*). The number of basic sites was determined by adsorption of CO_2 by dosing at 300 Torr (40 kPa) and room temperature (*23*), and the number of acidic sites was measured by *n*-butylamine titration (*24*). Data are collected in Table 1.

RESULTS

1. Temperature-Programmed Reduction

As the reduction and oxidation of catalysts may play an important role in the catalytic oxidation of hydrocarbons, we first examined the reducibility of alkali metal molybdates by means of TPR. Characteristic TPR spectra of alkali metal molybdates are shown in Fig. 1. For comparison, the TPR spectrum of MoO_3/SiO_2 is also displayed. The reduction of the latter compound starts above 773 K and occurs in a rather broad temperature range peaking at 946 K. The reduction of the alkali metal molybdates proceeds in practically the same temperature range. For the Li and Na salts, the reduction occurred in a narrow peak, while the TPR spectra of the other compounds were similar to that of MoO_3. It is an important feature that for the K, Rb, and Cs molybdates the main peaks are preceded by a small peak between 700 and 860 K. The onset of reduction of the alkali metal molybdates increases from Cs (614 K) to Li (760 K).

The H_2 consumptions calculated from the TPR peak areas (up to 1100 K) are shown in Table 2, which also contains some characteristic data on the reduction.

2. Oxidation of Ethane on MoO_3/SiO_2

In order to elucidate the catalytic performance of the alkali metal molybdates, some measurements were performed with supported molybdenum oxide. The catalysts were treated with the reacting gas mixture at the highest reaction temperature, usually 823 K, and the changes in the activity of the

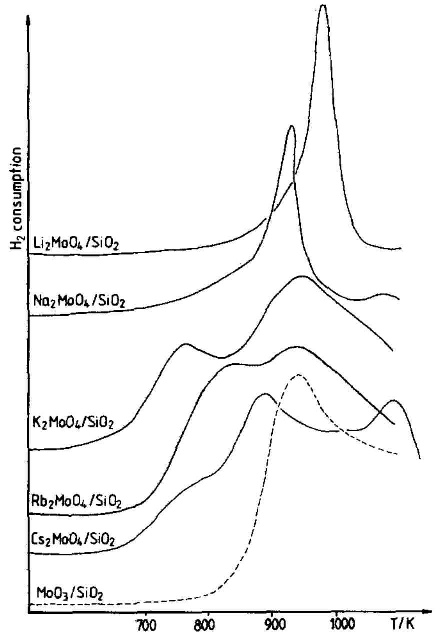

FIG. 1. Temperature-programmed reduction of alkali metal molybdates supported on SiO_2.

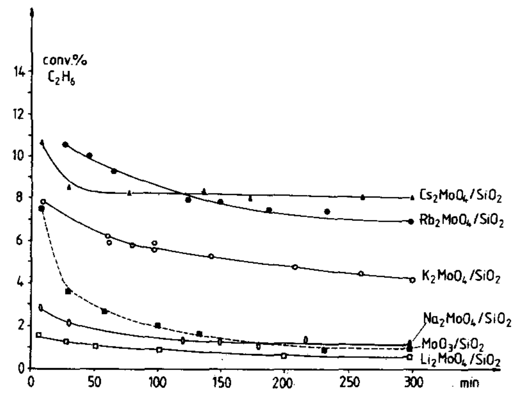

FIG. 2. Change in the C_2H_6 conversion on alkali metal molybdates supported on SiO_2 at 823 K. The concentrations of C_2H_6 and N_2O were 20 and 40%, respectively.

catalyst followed. Acetaldehyde, ethylene, CO, and CO_2 were the main oxidation products. Small amounts of CH_4, C_3, and C_4 compounds and traces of C_2H_5OH were also detected. O_2 formation was never observed. The conversion of ethane and the rate of product formation gradually decreased (Fig. 2), but the product distribution changed only slightly. The conversion was 4–5% at the beginning of the reaction; after 6 h it was only about 1%. A similar deactivation was observed in a previous study and was attributed to the deposition of carbon (*3*). The catalyst can be reactivated by N_2O or O_2 treatment at the reaction temperature. The selectivity of acetaldehyde production was about 21%, while that for ethylene formation was about 30% in the quasi-steady state.

TABLE 2

Temperature-Programmed Reduction of SiO_2-Supported Alkali Metal Molybdates

Catalyst	T_i (K)	T_p (K)	H_2 consumption (μmol/g)	$M_2O \cdot MoO_x$[a]
MoO_3	773	946	202.2	1.54
Li_2MoO_4	760	985	133.6	2.04
Na_2MoO_4	660	928	108.2	2.2
K_2MoO_4	615	768, 946	194	1.6
Rb_2MoO_4	630	833, 944	172.2	1.7
Cs_2MoO_4	614	772, 893, 1092	201.6	1.54

Note. T_i, Onset temperature of the reduction; T_p, temperatures of the TPR peak maxima.

[a] The composition of the alkali (*M*) molybdates after the TPR, as calculated from the H_2 consumption.

3. *Oxidation of Ethane on Alkali Metal Molybdates*

The reaction occurred in the same temperature range as that for MoO_3/SiO_2, but considerable differences were found in the rates and product distributions. High conversions were measured for Cs, Rb, and K molybdates, and much lower ones were measured for the Na and Li compounds (Fig. 2). The yields of acetaldehyde and ethylene were highest for Rb and Cs and lowest for Li and Na molybdates (Fig. 3). Interestingly, while the rates for acetaldehyde and CO_2 production changed in parallel with the conversion, i.e., they decayed in time, the rate of ethylene formation remained constant, or even increased (Rb molybdate) as a function of the reaction time (Fig. 3). The

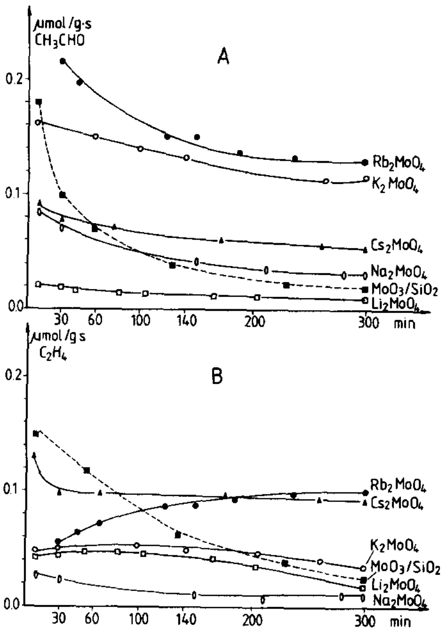

FIG. 3. Change in the formation rate of (A) CH_3CHO and (B) C_2H_4 on alkali metal molybdates supported on SiO_2 at 823 K. The concentrations of C_2H_6 and N_2O were 20 and 40%, respectively.

selectivities of ethylene and acetaldehyde formation were the highest for the less active catalysts, especially Li_2MoO_4 and Na_2MoO_4 (Table 3).

It is an interesting observation that, whereas the catalysts were white before the reaction, all were dark blue after the catalytic run. The intensity of the color increased with increasing duration of the reaction. The original white color could be reestablished by oxidation with O_2 and N_2O at 773 K, and this treatment also led to reactivation of the catalysts.

In the presence of H_2O (20%), the conversion of ethane was lower for all alkali metal molybdates, particularly for Li and Na compounds, than that measured under dry conditions. An important observation is the appreciable improvement in the selectivity of acetaldehyde formation for Rb molybdate, from 20 to 33%.

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 Mo-containing samples.

4. Catalytic Behavior and Kinetics for K_2MoO_4/SiO_2 Catalyst

The effects of the reactant concentration and the temperature on the product distribution were determined on a K_2MoO_4/SiO_2 sample pretreated with reacting gas mixture at 823 K until a steady-state activity was

TABLE 3

The Rate of C_2H_6 Consumption and the Selectivity of C_2H_4 and CH_3CHO Formation on Different Alkali-molybdate Catalysts at 823 K

Catalyst	Results at t = 30 min						Results at t = 300 min	
	C_2H_6 conv. (%)	$W_{C_2H_6}$[a] (μmol/g · s)	C_2H_4 select. (%)	CH_3CHO select. (%)	$Y_{C_2H_4}$ (%)	Y_{CH_3CHO} (%)	$Y_{C_2H_4}$ (%)	Y_{CH_3CHO} (%)
MoO_3/SiO_2	3.5	0.390	47	23	1.64	0.736	0.27	0.1
Li_2MoO_4/SiO_2	1.2	0.126	32	13	0.384	0.15	0.17	0.055
Na_2MoO_4/SiO_2	2.1	0.166	14	45	0.29	0.94	0.11	0.37
K_2MoO_4/SiO_2	7.3	0.587	7	27	0.51	1.97	0.32	1.12
Rb_2MoO_4/SiO_2	10.5	0.995	5	20	0.52	2.10	0.95	1.08
Cs_2MoO_4/SiO_2	8.5	0.815	12	7	0.984	0.59	0.96	0.48

Note. Y, Yield of product formation (selectivity × conversion).
[a] Rate of C_2H_6 consumption.

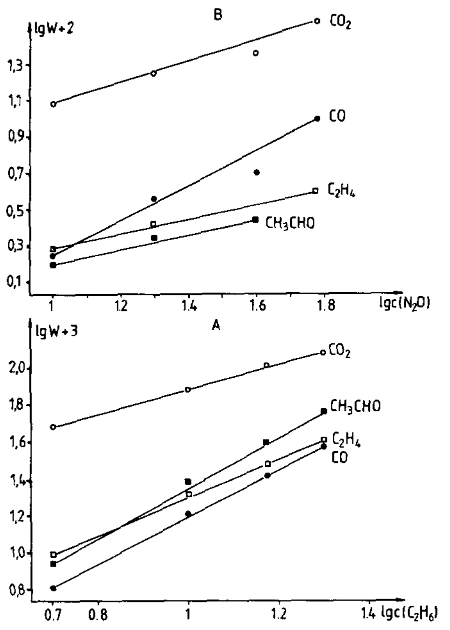

FIG. 4. Dependence of the initial rate (*w* [μmol/g · s]) of the product formation as a function of (A) C_2H_6 and (B) N_2O concentration at 823 K on K_2MoO_4/SiO_2. The N_2O concentration for (A) was 40% and the C_2H_6 concentration for (B) was 10%.

reached. We have found that the conversion of ethane and the amount of products linearly increased in the range of space velocity used. On increase of the N_2O concentration, the conversion of ethane and the rates of product formation increased, but the selectivities of acetaldehyde and ethylene formation slightly decreased. Regarding the effects of the concentration of ethane, it was found that an increase in its concentration enhanced the rates of product formation. The selectivities of acetaldehyde and CO formation also increased, whereas that of CO_2 decreased significantly. No change was observed in the selectivity of ethylene (Figs. 4 and 5). The overall rate of C_2H_6 consumption can be described by

$$d(C_2H_6)/dt = k(C_2H_6)^{0.85}(N_2O)^{0.54}$$

over the concentration range $5 < C_{C_2H_6} < 20\%$ and $10 < C_{N_2O} < 60\%$. The kinetic orders of the reaction products were determined from logarithmic plots of the various rates vs the volume percentage of the reactants (Fig. 4). The kinetic order with respect to N_2O was found to be nearly the same for C_2H_4 and CH_3CHO formation, viz. 0.43 and 0.36, respectively, but it was higher for CO (0.96) and CO_2 (1.7) formation. The order with respect to C_2H_6 was about 1 for C_2H_4 formation and slightly higher for CO (1.26) and CH_3CHO (1.33) formation. Data are listed in Table 4.

The temperature dependence of the reaction was studied in the range 765–823 K. The selectivity of acetaldehyde formation increased and that of ethylene formation decreased with the elevation of the temperature (Fig. 6). The temperature dependences of the initial rates of CH_3CHO, C_2H_4, CH_4, and CO_2 formation gave Arrhenius fits within the limits of experimental uncertainty (Fig. 6). The apparent activation energies for the formation of these compounds were

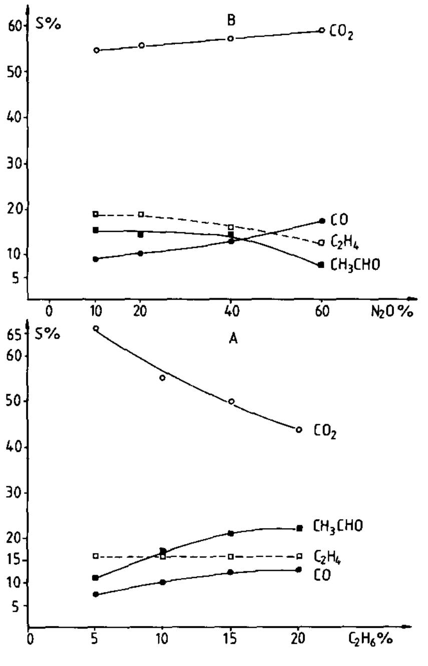

FIG. 5. Dependence of the selectivities (*S*) of various products as a function of (A) C_2H_6 and (B) N_2O concentration at 823 K on K_2MoO_4/SiO_2. The N_2O concentration for (A) was 40% and the C_2H_6 concentration for (B) was 10%.

TABLE 4

Kinetic Data for Ethane Oxidation on K_2MoO_4/SiO_2 Using N_2O as Oxidant

Product	Kinetic order		Activation energy (kJmol)
	C_2H_6	N_2O	
C_2H_4	0.97	0.43	125
CH_3CHO	1.33	0.36	50
CO	1.26	0.97	—
CH_4	—	—	63
CO_2	0.62	1.73	57
C_2H_6 (consumption)	—	—	71

50.0, 125.0, 63.0, and 57.0 kJ/mol, respectively. The activation energy of ethane consumption was found to be 71 kJ/mol. Kinetic results are listed in Table 4.

5. *Pulse Experiments*

In subsequent measurements, the interaction of K_2MoO_4 with C_2H_6 was investigated by the pulse technique. One pulse contained 20.5 μmol gas and the amount of the catalyst was 300 mg. The catalyst was treated as usual with O_2 at 773 K and washed with He before the admission of C_2H_6 pulses for 15 min. Only about 0.2% of the oxygen content of the K_2MoO_4 (0.57 μmol O_2/g) reacted with the first C_2H_6 pulse at 823 K, to yield C_2H_4, CH_4, CO, and CO_2. In the subsequent pulses the conversion of ethane decreased, but even in the fifth pulse traces of CO_2 and C_2H_4 were detected.

N_2O decomposition was investigated similarly. The gas underwent a slight decomposition (less than 1–2%) on the oxidized catalyst 823 K. When the catalyst was treated first with CO (80.8 μmol) at 773 K (which resulted in a reduction of 13–14% relative to K_2MoO_4), the extent of decomposition of the N_2O pulse was much higher, as indicated by the N_2 evolution. Most of the oxygen formed in the decomposition was used for the oxidation of the reduced sample. However, the next N_2O pulse produced N_2 and O_2 in same quantity as on the unreduced surface, suggesting that the first N_2O pulse fully oxidized the surface.

In the next series of experiments, C_2H_6 + N_2O gas mixture (16.3 μmol each) was injected onto K_2MoO_4/SiO_2 catalyst treated in different ways. Results are plotted in Fig. 7. The conversion of ethane in the first pulse increased when the catalyst was prereduced and the yields of acetaldehyde and ethylene

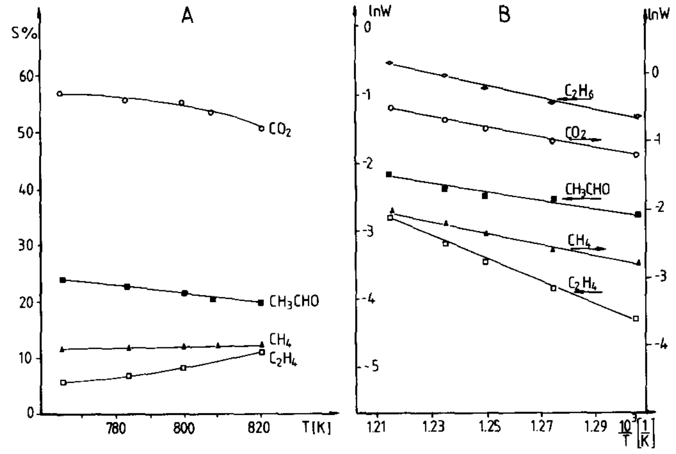

FIG. 6. (A) Temperature dependence of the selectivities for different products. (B) Arrhenius plots for C_2H_6 consumption and for the formation of products on K_2MoO_4/SiO_2 (*w* means initial rate μmol/g · s). The concentrations of N_2O and C_2H_6 were 40 and 20%, respectively.

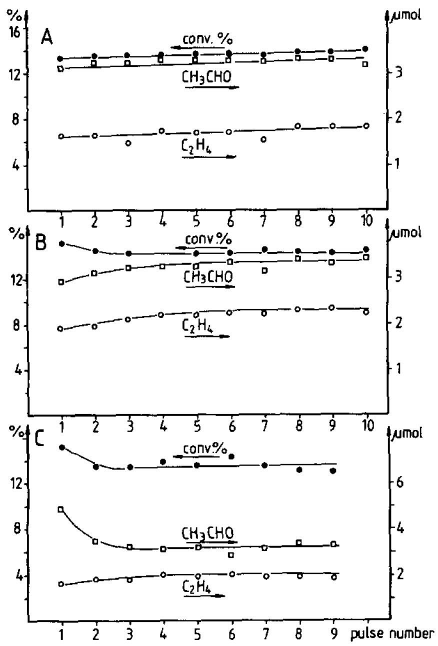

FIG. 7. The conversion of ethane (%), the amounts (μmol) of CH_3CHO and C_2H_4 formed as a function of the number of C_2H_6 + N_2O (1 : 1) pulses (32.6 μmol) on K_2MoO_4/SiO_2 at 823 K. Pretreatment of the catalyst: (A) with He for 10 min at 823 K; (B) with C_2H_6 pulses at 823 K, O_2 consumption is 14.8 μmol/g; (C) with CO pulses at 823 K, O_2 consumption is 26.0 μmol/g.

were also enhanced. In the subsequent pulses, however, the behavior of the catalyst differed only slightly from the unreduced sample and showed a constant activity.

6. *Decomposition of N_2O on Alkali Metal Molybdates*

As the decomposition of N_2O on alkali metal molybdates may also play an important role in the partial oxidation of ethane, extensive kinetic measurements were made on this reaction on all catalyst samples used in the present study. The experiments were performed in a closed circulation system. Detailed results will be published in a separate paper (*25*); here we summarize only the main features of the reaction. The decomposition of N_2O on alkali metal molybdates supported on silica and activated in vacuum at 700 K occurs above 600 K. A comparison of the catalytic activities of the alkali metal molybdates with that of MoO_3/SiO_2 under the same conditions led to the following activity sequence:

$$K_2MoO_4 > MoO_3 > Li_2MoO_4 > Na_2MoO_4$$
$$> Rb_2MoO_4 > Cs_2MoO_4.$$

As was observed for K molybdate in pulse experiments, the decomposition proceeded more rapidly when the alkali metal molybdates were prereduced with CO or H_2. The rate of the decomposition, however, soon dropped, and a steady-state activity, which corresponds to that measured for the oxidized surface, was reached.

7. *Decomposition of Ethanol on Alkali Metal Molybdates*

A previous study (*3*) demonstrated that one of the reaction intermediates in the oxidation of ethane is the ethoxy species, C_2H_5O. This is valid for the present case, too, as ethanol was detected in small quantities in the oxidation products. It is highly probable that the stability of ethoxy and the direction of its decomposition may vary with the alkali metal molybdates and hence influence the product distribution. This consideration made it essential to perform some exploratory measurements on this reaction on alkali metal molybdates. Experiments were carried out in the same flow system as used for the oxidation.

Ethanol decomposed on the alkali metal molybdates above 500 K. The main products of the decomposition were acetaldehyde and ethane. The rate of the decomposition and the product distribution showed a great variation with the alkali metal cation. This is illustrated by the results in Table 5.

The selectivity for CH_3CHO formation was 46% on MoO_3/SiO_2 and more than 75% on alkali metal molybdates. The selectivity of ethane production was highest on MoO_3/SiO_2. On all the alkali metal molybdates, with the exception of Cs_2MoO_4, ethylene was detected only in traces.

TABLE 5

CH_3CH_2OH Decomposition on Alkali Molybdates at 603 K

Catalyst	Conv.%	Selectivity %					
		CH_3CHO	C_2H_4	C_2H_6	CH_4	CO	CO_2
MoO_3/SiO_2	13.83	46.3	27.09	26.53	2.10	0.70	—
Li_2MoO_4/SiO_2	7.93	88.91	—	9.36	—	0.86	—
Na_2MoO_4/SiO_2	4.14	92.82	—	7.17	—	—	—
K_2MoO_4/SiO_4	2.93	90.78	—	9.21	—	1.62	—
Rb_2MoO_4/SiO_2	7.58	76.78	—	20.57	—	1.32	—
Cs_2MoO_4/SiO_2	8.66	75.72	3.11	17.86	—	1.64	—

Note. The amount of catalyst was 0.5 g except for MoO_3/SiO_2 when it was 0.125 g.

DISCUSSION

1. Some Properties of Alkali Metal Molybdates

Before discussing the catalytic results, we summarize some of the important properties of alkali metal molybdates.

Very few investigations have been reported on the structures of the alkali metal molybdates. According to Bragg (*26*), the alkali metal molybdates have a phenacite structure; the compounds contain MoO_4 tetrahedra (*27*). The structure of Li_2MoO_4 changes from phenacite to spinel as the temperature is increased. The Na and K molybdates are polymorphs. At low temperature K_2MoO_4 crystallizes in the monoclinic system, but it transforms into an orthorhombic form at 573 K and to a hexagonal arrangement above 723 K (*27*). Cs_2MoO_4 was found to be orthorhombic at lower temperatures, but is transformed into a hexagonal structure at 848 K (*28*). Six of the nearly regular MoO_4 tetrahedra form a pseudohexagonal ring. The apices of four tetrahedra point upwards, those of two tetrahedra downwards along the c axis. The Cs atoms have two independent positions, one with ninefold and the other with elevenfold coordination (*29*).

The melting points of the alkali metal molybdates are between 950 and 1200 K (*30*). This means that the catalyst samples did not melt during the relatively high-temperature reaction.

We found no information in the literature regarding the nature of the interaction of alkali metal molybdates and supports. The interaction of MoO_3 with silica supports is considered to be weaker than that with alumina, which may result in a greater ease of reduction (*31, 32*). Three different molybdenum species have been identified on silica supports: these are the MoO_3 phase, an isolated tetrahedral molybdenum species dispersed on silica surface, and a so-called surface paramolybdate phase containing octahedral Mo^{6+} (*31*). On the basis of infrared spectroscopic study, Seyedmonir and Howe (*33*) suggested that a M–O–Si species is also present on the surface. At higher temperature the occurrence of a solid-state reaction between SiO_2 and MoO_3 was also observed producing various oxometalate species, such as polymolybdates, paramolybdates, and molybdosilicic acid ($H_4SiMo_{12}O_{40}$) (*34, 35*). Moffat and co-workers (*34, 36*) suggested that the latter species is the active phase in the selective oxidation of methane.

A significant interaction between alkali molybdates and the silica support is indicated by the marked decrease in the BET area of silica after calcination of the alkali metal molybdate/silica system at 873 K

(Table 1); the area showed a minimum value for the potassium compound. We found that the addition of MoO_3 or potassium salts to silica reduced only to a smaller extent the BET area of silica (SiO_2, 200 m^2/g; MoO_3/SiO_2, 166 m^2/g; K_2CO_3/SiO_2, 160 m^2/g; KOH/SiO_2, 138 m^2/g).

Alkali metal molybdates exhibited a large variation as concerns the surface acidity and basicity (Table 1). We found that the number of acidic sites decreased from Li to K, then increased to Cs. In contrast, the amount of basic sites seems to increase from Li to Cs.

2. *Reduction of Molybdates*

Whereas the reduction of supported molybdena has been the subject of several studies, the reduction of supported alkali metal molybdates has not yet been reported. The reduction of MoO_3 on silica starts above 773 K with a maximum rate at 946 K in good agreement with the previous data (*33, 37*). Following the reduction of MoO_3/SiO_2 by infrared spectroscopy Seyedmonir and Howe (*33*) distinguished several steps of this process: the reduction at 673 K involves only the polymolybdate phase, producing octahedral Mo^{5+} by breaking bonds to the support, and at 773 K further reduction to Mo^{4+} occurs through removal of terminal oxide ligands as H_2O. Similar chemistry occurs at terminal oxide ligands of the MoO_3 phase at this temperature. There was no spectroscopic evidence indicative of the formation of tetrahedral Mo^{5+} through thermal reduction of isolated tetrahedral Mo^{6+}. The addition of KOH or KNO_3 to MoO_3 lowered the onset temperature of the reduction and increased its extent (*20*).

The TPR spectra presented in Fig. 1 indicate that the reduction of the silica-supported Li and Na compounds proceeded in one stage, similarly to MoO_3/SiO_2, but in a much narrower temperature range. For the other three molybdates, the main reduction step was preceded by a low-temperature state, where the hydrogen consumption was about 20% of the total consumption in the reduction. The average valency of the molybdenum was calculated from the H_2 consumption after completion of reduction up to 1100 K. It was around 3 for K, Rb, and Cs and 4 for Li and Na molybdates (Table 2).

3. *Oxidation of Ethane on MoO_3/SiO_2*

In the oxidation of C_2H_6, we identified the following major products: CO, CO_2, C_2H_4, and CH_3CHO. Minor products were C_2H_5OH, CH_4, and other higher hydrocarbons. In the case of MoO_3/SiO_2, the C_2H_6 conversion was similar to that obtained by Mendelovici and Lunsford (*3*). We found lower selectivity for CH_3CHO formation and higher selectivity for C_2H_4, but the combined selectivity was almost the same. If the oxidation of C_2H_6 on MoO_3/SiO_2 is compared with that on V_2O_5/SiO_2 (*8*), we may state that the C_2H_6 consumption is lower but the CH_3CHO formation rate is higher on MoO_3/SiO_2.

4. *Oxidation of Ethane on Alkali Metal Molybdates*

Qualitatively the same oxidation products were found on alkali metal molybdate catalysts as on MoO_3. The reaction occurred in the same temperature range, but the activity decay of the catalysts was much less than for MoO_3/SiO_2. At the steady state, some of the alkali metal molybdates (K, Rb, and Cs) exhibited a considerably higher activity than that of MoO_3. The rates of acetaldehyde and ethylene formation were sometimes 5 or 10 times higher than those measured for MoO_3/SiO_2 (Fig. 3). Moreover, the selectivity of acetaldehyde formation was also improved (Na and K). However, the combined selectivity for acataldehyde and ethylene formation was always lower than that determined for silica-supported MoO_3 (Table 3). When the areas of the catalysts are also taken into account, the difference between the catalytic performance of MoO_3

and alkali metal molybdates (Cs, Rb, K) is more striking (see data in Tables 1 and 3).

5. *Mechanism of Ethane Oxidation*

Previous studies on supported MoO_3 catalyst strongly suggested that O^- ion is the oxidizing agent in the partial oxidation of ethane (*3*). There is convincing evidence for the formation of O^- species in the surface decomposition of N_2O on oxide surfaces, including MoO_3 (*4*). We believe that O^- plays an important role in the partial oxidation of ethane on alkali metal molybdate catalysts, too.

We found that the decomposition of N_2O is fast on all alkali metal molybdates (activated in vacuum at 773 K) in the temperature range of ethane oxidation. We may count on the occurrence of the following reactions:

$$Mo^{5+} + N_2O = Mo^{6+}\text{–}O^- + N_2 \quad (1)$$

$$2Mo^{6+}\text{–}O^- = 2Mo^{5+} + O_2. \quad (2)$$

We observed that a mild reduction of the molybdate catalysts led to an enhancement of the rate of the N_2O decomposition, possibly through an increase in the concentration of Mo^{5+} centers. Accordingly, Mo^{5+}, and hence the $Mo^{6+}\text{–}O^-$ surface species are considered to be active centers in the partial oxidation of ethane on alkali metal molybdate catalysts. This surface species can be produced by the dissociation of molybdates at the high reaction temperature and by the reduction of Mo^{6+} ions by ethane, very probably in a nonselective step.

In the subsequent steps, the activation of the ethane molecule that involves the removal of a hydrogen atom by O^- proceeds to give the ethyl radical

$$C_2H_6 + O^- = C_2H_5 \cdot + OH^-. \quad (3)$$

It seems very likely that this reaction is the most important step in the selective oxidation of ethane. As the reduction of Mo^{6+} is facilitated in alkali metal molybdates, the increase in the conversion of ethane oxidation on these catalysts can be attributed to the ease of the reduction of Mo^{6+} ion and hence to the enhanced production of $Mo^{6+}\text{–}O^-$ centers important in the ethane activation. (Note that the addition of KNO_2 and KOH to MoO_3 catalyst exerted a similar influence on the reduction of MoO_3 and on the conversion of ethane oxidation (*20*).)

The C_2H_5 surface species may combine with O^- to form ethoxide

$$C_2H_5 + O^- = C_2H_5\text{–}O^-, \quad (4)$$

which may react with H_2O to produce ethanol

$$C_2H_5\text{–}O^- + H_2O = C_2H_5\text{–}OH + OH^-. \quad (5)$$

Ethoxide and ethanol can react further to give acetaldehyde

$$2Mo^{6+} + C_2H_5\text{–}O^- + OH^- = CH_3CHO + H_2O + 2Mo^{5+} \quad (6)$$

or decompose to ethylene

$$C_2H_5\text{–}O^- = C_2H_4 + OH^-. \quad (7)$$

Attempts to identify $C_2H_5\text{–}O$ species during the oxidation by means of infrared spectroscopy were hampered by the low transmission of our silica-supported catalyst in the region 1000–1200 cm^{-1}. However, traces of ethanol were found among the reaction products in some cases, so we can reckon with its transitory existence on the surface of alkali metal molybdate catalysts.

As was demonstrated by the data in Table 5, in this temperature range the decomposition of ethanol is very fast and cannot be the rate-determining step. Another important observation is that although the rate of the decomposition of ethanol on alkali metal molybdates is less by a factor of 3–5 than that measured on silica-supported MoO_3, the acetaldehyde is formed with a much higher selectivity on molybdates than on MoO_3 catalysts (Table 5). (Interestingly, most of the ethylene reacted with hydrogen formed in the alcohol decomposition, to give ethane. The same observation was made for the decomposition of ethanol on alkali metal vanadate catalysts (*9*).)

Because the dehydration of ethanol and ethoxide requires acidic sites of the catalysts, and these are many fewer on alkali metal molybdates than on MoO_3 (Table 1), the change in product distribution of the alcohol decomposition may be associated with this property of alkali metal molybdates.

We may assume that the other products of the oxidation, CO_2 and CO, are probably produced in the secondary reaction, the decomposition and/or oxidation of acetaldehyde.

6. *Comparison of the Catalytic Behavior of Alkali Metal Molybdates*

From the comparison of the catalytic performances of alkali metal molybdates, we can state that the conversion of ethane at the steady state is increased with the size of the cations, i.e., in the sequence of Li, Na, K, Rb, Cs. The acetaldehyde and ethylene yields roughly also follow this pattern (Figs. 2, 3 and Table 3). This order corresponds well with the ease of the reduction of alkali metal molybdates (Table 2), which supports the role of reduced sites in the formation of Mo^{6+}–O^- centers important in the activation of ethane.

This correlation will be different when the surface areas of the supported catalysts are also taken into account. However, we are not sure that the values so obtained would be more reliable for the comparison, as some of the alkali metal molybdates strongly reduce the surface area of SiO_2, while others exert only a slight influence. If we assume that the method developed for the determination of the number of surface Mo atoms in the case of MoO_3/SiO_2 (*22*) can be applied for alkali metal molybdates, then K_2MoO_4 would exhibit the highest activity for acetaldehyde formation.

As regards the selectivity of the ethane oxidation, we found a large variation for different alkali metal molybdates, which showed no direct correlation with either acidity or basicity of the catalysts.

Recently, we investigated the partial oxidation of ethane with N_2O on silica-supported alkali metal vanadates (*9*). The extent of ethane oxidation and the selectivity of ethylene formation (in the absence of water) were somewhat higher, while the selectivity of acetaldehyde formation was lower than with the molybdates. In the vanadate case we found that the selectivity of CH_3CHO production is connected with the basic properties, while the selectivity of ethylene formation is associated with the acidic properties of the vanadate catalysts. In contrast to molybdates, the addition of water to the reacting gas mixture greatly enhanced the selectivity of acetaldehyde production. All these features suggest that the surface properties of the two systems are different and further measurements are required for their characterization.

The following conclusions were drawn from the present study:

(i) The oxidation of ethane on silica-supported alkali metal molybdates occurred in the same temperature range as on MoO_3/SiO_2, but the activity decay was considerably less.

(ii) At the steady state, some of the alkali metal molybdates (K, Rb, Cs) exhibited a much higher activity than that of MoO_3.

(iii) The selective oxidation products were ethylene and acetaldehyde.

(iv) The conversion of ethane increased in the sequence $Li < Na < K < Rb < Cs$. The yields for acetaldehyde and ethylene formation roughly followed this pattern.

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