JOURNAL OF CATALYSIS **118**, 255–265 (1989)

Oxidative Dehydrogenation of Ethane over a Lithium-Promoted Magnesium Oxide Catalyst

EDRICK MORALES AND JACK H. LUNSFORD[1]

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received December 20, 1988; revised March 10, 1989

Lithium-promoted magnesium oxide is an effective catalyst for the conversion of ethane to ethylene. A selectivity of 75% for ethylene was obtained at 40% ethane conversion over 6.5 g of 3 wt% Li^+/MgO catalyst at 600°C. These results were obtained with initial pressures of 95 Torr C_2H_6 and 47 Torr O_2 at a space velocity of 260 h^{-1}. An apparent activation energy of 37.3 kcal mol^{-1} was observed for this process. The carbon oxides are formed both by the direct oxidation of ethane and the secondary oxidation of ethylene. In the reactor employed in this study homogeneous reactions became dominant at temperatures greater than 675°C. The catalytic system is believed to involve the generation of $C_2H_5\cdot$ radicals on the surface, followed by the emanation of these radicals into the gas phase where they react with O_2 to form C_2H_4. The ability of this catalyst to generate alkyl radicals from CH_4 or C_2H_6 appears to be a general phenomenon [*J. Phys. Chem.* **89**, 4415 (1985)]. The subsequent reactions of these alkyl radicals (e.g., coupling or reaction with O_2) determines to a large extent the final product distribution. Ethylene also may be formed via surface ethoxide ions.

INTRODUCTION

A new class of catalysts composed of Group IA/Group IIA oxides has been developed to promote the oxidative dimerization of CH_4 (*1–7*). Lithium-promoted MgO is the most extensively studied example of this group. Among the common oxidation catalysts these oxides are unique in that the oxygen ions, rather than the metal ions, undergo a change in oxidation state during the catalytic cycle (*1*).

As a secondary reaction in the oxidation of methane, the conversion of ethane to ethylene has been investigated briefly over Li^+/MgO and Na^+/CaO catalysts (*1, 3*). Moreover, Kolts (*8*) observed the oxidative dehydrogenation (OXD) of ethane over 0.5 wt% Li^+/MgO and has reported a conversion and selectivity of 56% and 92%, respectively, after a period of 60 min at 700°C. After a period of 16 h, however, the conversion decreased to 33%, which reduced the ethylene yield from 51% to 30%. Typical yields for the OXD of ethane are 30–48%.

The results obtained in the present study provide the basis for a comparison between the oxidation of methane and ethane over a Li^+/MgO catalyst. One significant difference between the two hydrocarbons is the greater propensity of ethane to undergo homogeneous oxidation at the temperatures employed in the catalytic reactions. The factors which affect the homogeneous reaction are briefly discussed here and are reported in more detail elsewhere (*9*).

There is substantial evidence from the methane research that methyl radicals are formed on these surfaces, but the radicals emanate into the gas phase (*10–12*). There they may undergo coupling reactions or they may react with molecular oxygen, which ultimately results in the formation of CO_2:

$$2CH_3\cdot \rightarrow C_2H_6 \quad (1)$$

$$CH_3\cdot + O_2 \leftrightarrows CH_3O_2\cdot \rightarrow\rightarrow CO_2 \quad (2)$$

Similarly, ethane reacts with the surface to form ethyl radicals, but in this case the cou-

---

[1] To whom correspondence should be addressed.

0021-9517/89 $3.00

pling reaction competes with the unimolecular decomposition of $C_2H_5\cdot$ or the reaction with O_2 to form ethylene (*13, 14*):

$$2C_2H_5\cdot \rightarrow C_4H_{10} \quad (3)$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot \quad (4)$$

$$C_2H_5\cdot + O_2 \rightarrow C_2H_4 + O_2H\cdot \quad (5)$$

Considering the pathways that are available to the respective alkyl radicals it is not surprising that the yields of the desired hydrocarbon products are about 10% greater for the oxidation of ethane than for the oxidation of methane.

EXPERIMENTAL SECTION

The catalysts were prepared by adding MgO (Fisher, ACS Certified) to an aqueous solution of Li_2CO_3 (Fisher, ACS Certified) which was at 70°C. The water was evaporated until a thick paste remained, and the paste was dried overnight at 140°C. The resulting $Li_2CO_3/Mg(OH)_2$ solid was sieved to 20–45 mesh and then calcined in air at 600°C for 12 h. This procedure was used to prepare catalysts with lithium loadings ranging from 1 to 7 wt% Li. Typical surface areas after reaction were about 4 $m^2\ g^{-1}$. A pure MgO, prepared for blank reactions, was calcined at 1100°C for 48 h to reduce the surface area to 7 $m^2\ g^{-1}$.

The ethane (99.0%) was obtained from Linde. The remaining gases including ethylene (99.5%), oxygen (99.6%), helium (99.995%), and 2% nitrogen in helium (Certified Standard) were obtained from Matheson. All gases except helium were used as received; helium was passed through indicating Drierite and molecular sieve 5A.

Because of the positive effect that an unpacked volume has on the homogeneous reaction (see below) the reactor was designed, as shown in Fig. 1, to minimize any large voids. The main body of the fused-quartz reactor (2.5 cm i.d. × 4 cm long) was connected at both ends by capillary tubes (2 mm i.d.). A side tube was located at the top of the reactor to facilitate the loading of the catalyst. After loading the reactor, the side tube was sealed with Autostic, which is a ceramic with a high temperature limit of 1100°C. A thermocouple well extended to the top of the catalyst bed. The reactor temperature was controlled and measured with a thermocouple to ±1°C. To prevent hot spots the space between the heating units and the reactor was packed with molecular sieve 4A.

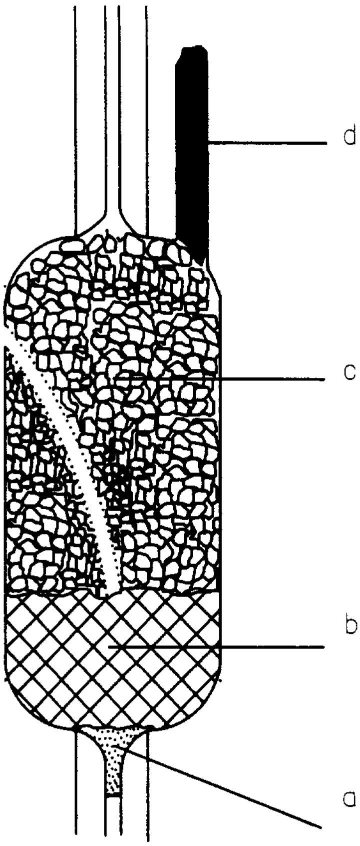


FIG. 1. Reactor loaded with a layer of 1.0 g of Li^+/MgO catalyst: (a) quartz wool; (b) Li/MgO catalyst; (c) quartz chips; (d) reactor sealed with Autostic.

Unless stated otherwise the catalyst was brought from 25 to 725°C in flowing helium. A reacting gas mixture (e.g., ethane, oxygen, and 2% N_2 in helium), prepared using mass flow controllers (Brooks Model 5850C) and a glass mixer, was allowed to flow over the catalyst for ca. 16 h at 725°C. The temperature of the catalyst was then adjusted to the desired level, and the gases exiting the reactor were analyzed using an on-line gas chromatograph (Varian Model 3700). Data reported are the average of three samplings, obtained after the reaction reached steady state (usually 2–4 h). Contact times (space times) are based on flow rates determined at 25°C and 760 Torr. Results from inductively coupled plasma (ICP) analysis indicated no significant loss ($<10\%$) in lithium content when the catalyst was exposed to temperatures $\leq 675°C$, whereas, the lithium content of the nominal 3 wt% Li^+/MgO catalyst was 2.8 wt% after the reaction had been carried out at 725°C.

The formation of surface-generated gas-phase ethyl radicals was detected by using the matrix-isolation electron spin resonance (MIESR) apparatus which has been described previously (*15*). Briefly, ca. 0.1 g of 3 wt% Li^+/MgO was used to produce the $C_2H_5\cdot$ radicals at temperatures between 525–620°C and at a pressure in the reactor of 1 Torr. Radicals exiting the catalyst bed enter a leak into a low-pressure zone (2×10^{-5} Torr) and are collected in a solid argon matrix on a sapphire rod. The sapphire rod is lowered into a TE_{102} microwave cavity for detection of the radicals by ESR spectroscopy.

RESULTS

Ethane Oxidation

The homogeneous and catalytic OXD of ethane are demonstrated by the data of Table 1 and the results of Fig. 2. The homogeneous OXD reaction, defined here as the reaction which occurs in the reactor packed with quartz chips, was limited to only 3.6% C_2H_6 conversion (5.7% O_2 conversion) at 625°C, but at a temperature of 674°C and a contact time of 11 s the reaction was almost complete with respect to oxygen consumption. It is important to note that the rate of the homogeneous oxidation reaction is greatly affected by the presence of solid material in the reactor and the partial pressure of water. For example, in an empty reactor of comparable dimensions, with a $C_2H_6 : O_2$ ratio of one and 155 Torr of H_2O, the C_2H_6 conversion was 64% at a residence time of 4.1 s and a temperature of 600°C. Under identical conditions including the same residence time, but with quartz rings in the reactor, the conversion was only 6%. Thus, "wall effects" greatly inhibit the extent of the homogeneous reaction (*9*).

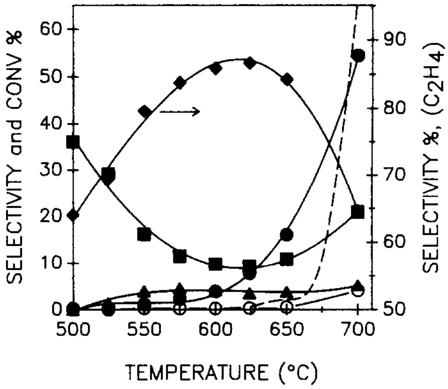


FIG. 2. The effect of temperature on selectivity and conversion in a reactor loaded with a 1 g layer of 3 wt% Li^+/MgO catalyst. Selectivities: ▲, to CO; ■, to CO_2; ○, to CH_4; ◆, to C_2H_4. ●, Conversion. (---) Ethane conversion under the same experimental conditions when the reactor was loaded with quartz chips.

The nonoxidative dehydrogenation of C_2H_6 was minimal in the reactor packed with quartz chips. Ethane conversions of 1.3 and 6.1% were observed at 624 and 775°C, respectively, and in both cases the C_2H_4 selectivity was $>99\%$.

With only MgO in a new reactor (i.e., a reactor which had not been exposed to lithium) the activity at 625°C increased by a factor of 2 relative to the homogeneous case, but the C_2H_4 selectivity decreased proportionally. Thus, the catalytic activity of MgO is modest and the C_2H_4 selectivity is poor.

By contrast, with 3 wt% Li^+/MgO in the reactor the conversion at 625°C was complete with respect to oxygen, and the C_2H_4 selectivity *also* increased. Moreover, small amounts of C_3 and C_4 hydrocarbons were detected. The C_2H_4 yield at 625°C was 34.3%, which is comparable to the C_2H_4

TABLE 1

Oxidative Dehydrogenation of Ethane over Quartz Chips, MgO and Li^+/MgO[a]

Catalyst	Temp. (°C)	C_2H_6 conv. (%)	O_2 conv. (%)	Selectivity (%)					
				CO	CO_2	CH_4	C_2H_4	C_3	C_4
Quartz[b] chips	600	1.5	1.9	5.2	20.8	0.7	73.4		
	625	3.6	5.7	3.2	14.6	0.9	81.3		
	674	70.3	97.1	35.9	3.9	10.6	49.8		
MgO[c]	600	4.9	17.4	22.7	36.9	1.6	38.9		
	625	7.6	23.1	15.8	35.7	1.9	46.6		
	650	13.0	35.7	10.9	32.1	2.2	54.8		
3 wt%[d] Li^+/MgO	600	39.3	68.4	6.1	17.7	0.5	74.8	0.5	0.4
	625	53.9	99.4	6.4	22.3	1.9	63.8	2.5	3.1
	650	56.6	99.8	5.2	21.3	3.8	59.8	5.2	4.7
7 wt%[d] Li^+/MgO	600	55.3	97.0	7.0	30.9	1.7	56.7	1.7	2.0

[a] $C_2H_6:O_2$ ratio was 2 : 1; initial pressure of C_2H_6 = 95 Torr; space velocity (SV) = 260 h^{-1} at NTP.

[b] Reactor was completely loaded with quartz chips; contact time = 11 s.

[c] Reactor was completely loaded with 10.3 g MgO; contact time = 12 s.

[d] Reactor was completely loaded with 6.5 g 3 wt% Li^+/MgO or 8.0 g 7 wt% Li^+/MgO; contact time = 12 s.

yield of 35.0% in the homogeneous case at 674°C. It is significant, however, that the C_2H_4 selectivity increased from 49.8% in the homogeneous reaction to 63.8% in the catalyzed reaction. When the initial Li^+ loading was increased to 7 wt%, the activity of the catalyst at 600°C increased but the C_2H_4 selectivity decreased. Significantly more C_3 and C_4 hydrocarbons were produced over the 7 wt% Li^+/MgO catalyst.

A series of reactions was carried out with 1 g of 3 wt% Li^+/MgO in the reactor and at a contact time of 1.9 s. The contact time is defined as the time that the reactants were in the region occupied by the Li^+/MgO catalyst; i.e., when 1 g of catalyst was used, the contact time with the quartz chips was not included. Under these conditions the reaction was not oxygen limited except at 700°C. The results of Fig. 2 are qualitatively similar to those obtained in the oxidative dimerization of CH_4 in that the selectivity of the intermediate oxidation product went through a maximum as the temperature was increased (*1*); albeit the maximum is shifted about 50°C to lower temperatures in the oxidation of C_2H_6. A maximum C_2H_4 selectivity of 87% was achieved. Below 650°C the reaction was largely promoted by the catalyst, but at 700°C the homogeneous reaction dominated in this reactor system. By reducing the heated volume above the catalyst bed it should be possible to limit further this homogeneous contribution, and perhaps maintain better C_2H_4 selectivities at greater conversions.

The conversions and selectivities for ethylene and C_1 compounds as functions of contact time are depicted in Fig. 3. For contact times ≥0.4 s the amount of catalyst was kept constant and the flow rate was varied. To obtain the data at the short contact time 0.0155 g of 3 wt% Li^+/MgO was loaded in a straight, fused-quartz reactor of 4 mm i.d. The space above and below the reactor was filled with quartz chips. At a contact time of 0.02 s the conversion and selectivity was 0.9% and 57%, respectively, at 652°C. It is apparent from the figure that the conversion of ethane does not follow a

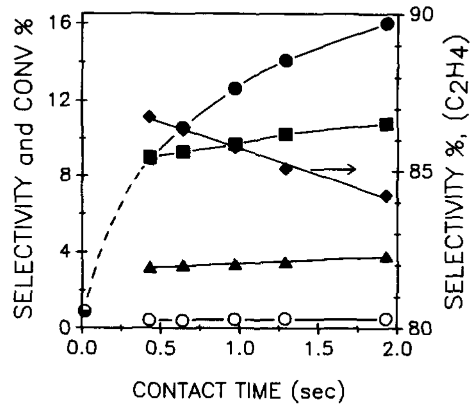


FIG. 3. Effect of contact time on selectivities and conversion over 1 g of 3 wt% Li/MgO catalyst at 650°C. Selectivities: ▲, to CO; ■, to CO_2; ◆, C_2H_4; ○, CH_4. ●, Ethane conversion. ◒, Microreactor was loaded with 0.0155 g of 3 wt% Li^+/MgO (temperature = 652°C, contact time = 0.02 s, conversion = 0.9%).

linear relationship with respect to contact time. Similar behavior has been observed previously for methane oxidation over Li^+/MgO and Na^+/CaO, and the phenomenon was attributed to the heterogeneous–homogeneous mechanism operating in this system (*1*, *3*). This phenomenon could also be attributed to the competition between ethane and ethylene or C_1 molecules for the active sites, i.e., a poisoning of the reaction by product formation. Korf *et al.* (*16*) reported a decrease in activity for CH_4 oxidation over Li^+/MgO when CO_2 was added to the feed. Except for the very small contact time the selectivity for CO and CH_4 remained essentially constant with respect to contact time, whereas, the selectivity for C_2H_4 exhibited a small decrease and the selectivity for CO_2 increased. The C_2H_4 selectivity in the microreactor was surprisingly small, considering the low conversion. This result suggests that at more extensive conversions the products which inhibit the conversion of ethane may even more efficiently inhibit secondary reactions of ethylene.

An Arrhenius plot was linear over the temperature range of 550–625°C, and from the slope an apparent activation energy of 37.3 ± 1.0 kcal mol^{-1} was determined. These data were obtained over 1.0 g of 3 wt% Li^+/MgO at a total flow rate of 0.8 ml s^{-1} and conversions which were <10% with respect to both ethane and oxygen.

The effect of ethane pressure on the amount of ethane reacted was studied between 35 and 210 Torr, while the initial oxygen pressure was held constant at 50 Torr. As shown in Fig. 4 the total amount of ethane converted increased in a linear manner over the entire pressure range, but the data do not extrapolate to zero conversion at zero partial pressure of ethane. The selectivity for C_2H_4 increased from 82.3 to 87.4% as the percentage of C_2H_6 converted decreased from 18.3 to 9.6% and the percentage of O_2 converted increased from 7.2 to 20.1%. At these low ethane conversions the selectivities for C_3 and C_4 products were very low.

The conversion of ethane with increasing partial pressures of oxygen is illustrated in Fig. 5. It is interesting to observe that the conversion of C_2H_6 depended very strongly upon the O_2 partial pressure up to ca. 40 Torr and then was almost independent of the O_2 partial pressure between 40 and 125 Torr. At greater pressures of O_2 the conver-

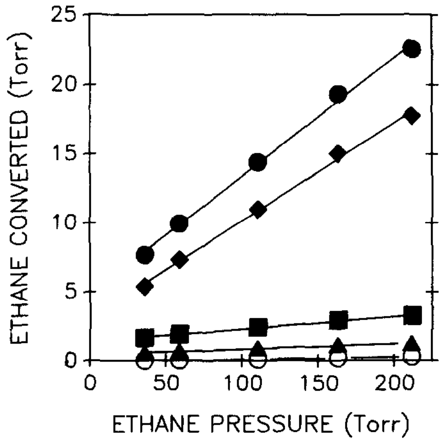


FIG. 4. The effect of ethane pressure on the amount of ethane converted over 1.0 g of 3 wt% Li^+/MgO and initial pressure of 50 Torr of oxygen at 650°C; contact time was 0.43 s. Pressures: ▲, to CO; ■, to CO_2; ○, to CH_4; ◆, to C_2H_4. ●, Total pressure of ethane converted.

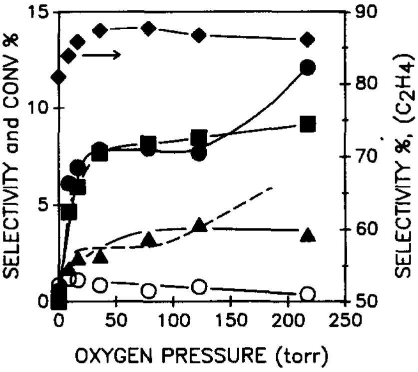


FIG. 5. The effect of O_2 pressure (initial partial pressure for C_2H_6 was 221 Torr; contact time was 0.43 s) on the conversion of C_2H_6 and selectivities for C_2H_4 and C_1 products over 1.0 g of 3 wt% Li^+/MgO at 650°C. Selectivities: ▲, to CO; ■, to CO_2; ○, to CH_4; ◆, to C_2H_4. ●, Ethane conversion. (---) Ethane conversion under the same experimental conditions when the reactor was loaded with quartz chips.

sion of C_2H_6 again increased. The dashed line represents the conversion of C_2H_6 in a blank experiment in which the catalyst was substituted by quartz chips of the same mesh size and under the same experimental conditions. (The entire reactor was at the same temperature; therefore the homogeneous reaction proceeded throughout the reactor.) Clearly, the response of the homogeneous reaction to O_2 is qualitatively similar to that of the heterogeneous reaction. It is significant to note that here the homogeneous conversion of C_2H_6 was greater at 650°C than that described in Fig. 2, even though the flow rate was greater. The higher pressure of C_2H_6 used to obtain the data for Fig. 5 may be responsible for the increased homogeneous component; i.e., the ethane pressure may have a more positive effect on the homogeneous component than on the heterogeneous component. Lane and Wolf (*17*) have reported that the rate for the homogeneous oxidation of CH_4 increases with increasing partial pressure of the reactants and with increasing oxygen partial pressure.

In the homogeneous system the conversion of ethane was found to depend on the partial pressure of water vapor in a linear manner (*9*); thus it was of interest to determine whether a similar effect was present in the heterogeneous system. Over 6.9 g of 3 wt% Li^+/MgO it was found that the presence of water vapor actually inhibited the catalytic conversion of C_2H_6. At 575°C the conversion decreased from 24.1% in the absence of H_2O to 19.5% in the presence of 132 Torr of added H_2O. As the conversion decreased the C_2H_4 selectivity increased from 68.4 to 73.4%.

Ethyl Radical Formation

As indicated in reactions (4) and (5) ethyl radicals are a primary intermediate in the OXD of ethane. The MIESR technique has previously been used to identify surface-generated $C_2H_5\cdot$ radicals formed at 475°C (*18*), and in Fig. 6 we show the spectra of $C_2H_5\cdot$ radicals formed over 3 wt% Li^+/MgO which had been used in a conventional catalytic reaction. The spectra obtained with the catalyst at two temperatures are com-

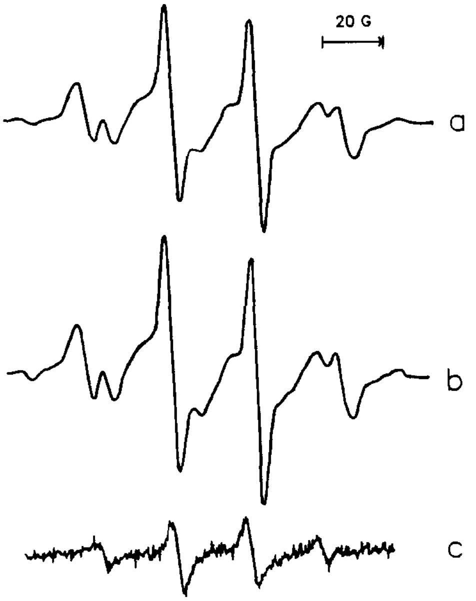


FIG. 6. Detection of surface-generated gas-phase $C_2H_5\cdot$ radicals over 0.1 g used sample of 3 wt% Li^+/MgO with the MIESR system: (a) T = 620°C, signal level (SL) = 32; (b) T = 525°C, SL = 200; (c) this is a blank reaction using 0.1 g of quartz chips, T = 525°C, SL = 1000.

pared with the background spectrum obtained over quartz chips. The results are not quantitative in the sense that the absolute rate of radical formation may not be compared with the rate of C_2H_4 formation; however, the role of the catalyst in generating ethyl radicals is clearly supported by these spectra.

Oxidation of Ethylene

The catalytic conversions of C_2H_4 and C_2H_6 were compared in order to determine the relative importance of ethylene oxidation in the formation of CO and CO_2. The results given in Table 2 indicate that for comparable partial pressures of C_2H_4 and C_2H_6, the alkane was about a factor of 3 more reactive than the alkene. The oxidation of C_2H_4 yielded mainly CO and CO_2. A second experiment was carried out in which the C_2H_4 pressure (36 Torr) was approximately equal to the sum of the pressures of carbon products (CO, CO_2, CH_4, and C_2H_4) obtained during the partial oxidation of 110 Torr C_2H_6 at 625°C. Here it was of interest to approximate the relative amounts of CO and CO_2 that might be derived from C_2H_6 and C_2H_4, respectively, during the partial oxidation of C_2H_6. At 625°C the total amount of carbon oxides produced from the 36 Torr of C_2H_4 was about 45% of the amount produced during the partial oxidation of C_2H_6. The value of 45% is probably an upper limit for the percentage of CO and CO_2 produced from C_2H_4 since in the normal OXD reaction C_2H_4 and C_2H_6 would compete for active sites on the catalyst, and the deep oxidation of C_2H_4 would be less than that observed when C_2H_4 was the only hydrocarbon reactant. Thus, during the OXD of C_2H_6 it appears that the carbon oxides are being formed by the direct oxidation of C_2H_6 and to a lesser extent by the secondary oxidation of C_2H_4. Of course, the latter reaction would become more significant as the partial pressure of C_2H_4 increased.

DISCUSSION

General Mechanism

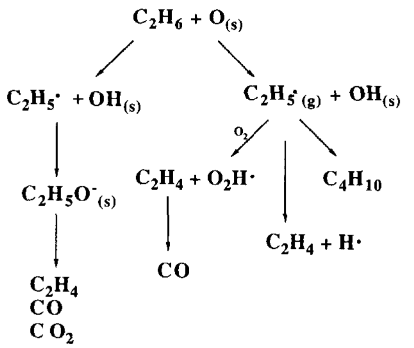
The proposed mechanism for the activation of ethane and methane over a Li$^+$/MgO catalyst are similar, but with some significant differences. Scheme 1 illustrates a simplified mechanism in the OXD of ethane. After an ethane molecule is activated over the surface, the resulting $C_2H_5\cdot$ radicals may either react further with surface oxygen ions to form a surface ethoxide ion

TABLE 2

Comparison of Ethane and Ethylene Reactivity over 3 wt% Li/MgO Catalyst[a]

T (°C)	C_2H_6 (Torr)	C_2H_4 (Torr)	C_2 conv. (%)	O_2 conv. (%)	Pressure (Torr)					
					CO	CO_2	CH_4	C_2H_4	C_3	C_4
551	110	—	2.6	2.0	1.1	1.3	—	1.6	—	—
575		—	5.5	10.6	1.7	2.5	—	4.0	—	—
625		—	21.8	31.4	3.5	8.0	0.2	17.5	0.1	0.1
551	—	96	0.7	5.8	0.9	0.5	—	—	—	—
575	—		1.4	8.7	1.8	1.0	—	—	0.1	—
625	—		8.8	27.5	11.0	5.6	0.4	—	0.5	0.1
551	—	36	0.8	—	0.4	0.2	—	—	—	—
575	—		1.8	0.4	0.9	0.5	—	—	—	—
624	—		6.8	6.8	3.0	2.2	—	—	0.1	—

[a] These data were collected when the reactor was loaded with 1.0 g of 3 wt% Li/MgO catalyst and total flow rate of 3.8 ml s^{-1}; contact time was 0.43 s. Initial pressure of O_2 = 52 Torr.



SCHEME 1

(i.e., $C_2H_5O^-$) or desorb into the gas phase. The ethoxide ion may either decompose to C_2H_4 or be further oxidized to CO and CO_2. Aika and Lunsford studied the reaction between small alkanes (*19*) and alkenes (*20*) with O^- ions on the surface of MgO. The electron spin resonance (ESR) signal for O^- ions on MgO disappeared when 1 Torr of ethane was introduced and the sample was warmed between −80 to −90°C. The conjugate olefin, C_2H_4, was observed in the gas phase even at 25°C, but most of the ethylene was formed at 300°C. Although no ethyl radicals were detected, it was proposed that the ethyl radicals were formed from the hydrogen abstraction by O^- ions and then reacted with surface O^{2-} ions to form ethoxide ions. The latter ions, produced either in this manner or by reacting MgO with ethanol, decomposed to ethylene at elevated temperatures.

Likewise, the ESR signal of O^- disappeared at −60°C when 1 Torr of ethylene was introduced to the sample. Vinyl radicals have never been detected on the surface nor in the gas phase, probably because of their short lifetime on the surface. For example, vinyl radicals have been proposed as intermediates species in the process (*21, 22*)

$$H_2C{=}CH_2 + (O^-)_s \rightarrow H_2C{=}CH\cdot + (OH^-)_s \quad (6)$$

$$H_2C{=}CH\cdot + (O^{2-})_s \rightarrow (H_2C{=}CH\cdot^- \text{---} OH^-)_s \quad (7)$$

The latter species, which may be an intermediate in the complete oxidation of ethylene, has been detected by ESR (*21*).

Another set of reaction channels becomes available when $C_2H_5\cdot$ radicals are desorbed into the gas phase. The formation of C_2H_4 or C_4 products is described by reactions (3)–(5). The C_4 hydrocarbons were observed with an appreciable selectivity only at high conversions and oxygen-limited conditions as shown in Table 1. The dimerization reaction is an undesirable termination step in the conversion of C_2H_6 to C_2H_4, but it is the most important reaction in the conversion of methane to C_2H_6 and C_2H_4. The activation energy for the unimolecular decomposition of $C_2H_5\cdot$ radicals to C_2H_4 is 30 kcal/mol (*13*) versus 5 kcal/mol (*14*) for the oxidation of $C_2H_5\cdot$ radicals; therefore, the reaction of $C_2H_5\cdot$ radicals with O_2 is the major pathway rather than the unimolecular decomposition to C_2H_4 under the conditions of these experiments.

It is evident from the spectra of Fig. 6 that C_2H_6 is activated on the surface of Li^+/MgO and part of the resulting $C_2H_5\cdot$ radicals are then desorbed into the gas phase. Although these spectra confirm the desorption of $C_2H_5\cdot$ radicals from the surface, it has not been demonstrated that the amount of $C_2H_5\cdot$ radicals desorbing from the catalyst surface is significant. Campbell *et al.* (*11*) demonstrated that the formation of C_2H_6 in the gas phase from surface-generated $CH_3\cdot$ radicals represents a major pathway in the catalytic oxidation of methane; however, the subsequent reactions that are available for $C_2H_5\cdot$ radicals preclude a quantitative evaluation of their importance using the MIESR system. Qualitatively it has been observed that over Li^+/MgO the amount of $C_2H_5\cdot$ radicals collected from C_2H_6 was less than the amount of $CH_3\cdot$ radicals collected from CH_4 (*18*). This observation at first was surprising because of the greater reactivity of C_2H_6, but the apparent decrease in the production of $C_2H_5\cdot$ radicals could be related to the formation of ethoxide ions or to the unimolecular decomposition of $C_2H_5\cdot$ radicals.

The role of the catalyst in generating ethyl radicals is further manifested by a decrease in the activation energy from 70 kcal mol^{-1} in the purely homogeneous system (*9*) to 37 kcal mol^{-1} over Li^+/MgO. The primary initiation step in the homogeneous reaction at elevated temperatures

$$C_2H_6 \rightarrow CH_3\cdot + CH_3\cdot \qquad (8)$$

has an activation energy of 87 kcal mol^{-1}. The activation energy of 37 kcal mol^{-1} is considerably less than the value of 55 kcal mol^{-1} for the oxidative dimerization of methane (*1*). In the latter case the activation energy for the overall reaction is essentially equal to the activation energy for the formation of $CH_3\cdot$ radicals (*12*), which confirms that the product C_2H_6 occurs via the formation of radicals, as the slow step in the sequence, followed by a simple coupling reaction. The much smaller activation energy for C_2H_6 oxidation may in part reflect the weaker C–H bond in C_2H_6 compared with CH_4, but, in addition, it probably is a result of the homogeneous chain-branching mechanism which occurs in the gas phase (see below).

The gas-phase mechanism operating in this catalytic system can be summarized by the abbreviated set of reactions

$$C_2H_5\cdot + O_2 \leftrightarrows C_2H_5OO\cdot \rightarrow C_2H_4 + O_2H\cdot \qquad (9)$$

$$C_2H_5\cdot + O_2 \rightarrow C_2H_4 + O_2H\cdot \qquad (5)$$

$$C_2H_6 + O_2H\cdot \rightarrow C_2H_5\cdot + H_2O_2 \qquad (10)$$

$$H_2O_2 + M \rightarrow OH\cdot + OH\cdot + M \qquad (11)$$

$$OH\cdot + C_2H_6 \rightarrow C_2H_5\cdot + H_2O \qquad (12)$$

Ethyl radicals can react with O_2 through two different channels as indicated by reactions (5) and (9). Reaction (5) becomes the dominant reacting channel as temperature increases (*23, 24*). The hydroperoxy radicals produced in reaction (5) can remove a hydrogen atom from C_2H_6 to form $C_2H_5\cdot$ radicals and hydrogen peroxide. At the temperatures used in this study ($T > 500°C$) hydrogen peroxide is the chain-branching agent that decomposes through reaction (11) to produce $OH\cdot$ radicals. For this reaction water is an effective third body (*9, 25*). Hydroxyl radicals are very reactive species that initiate a chain mechanism via reaction with C_2H_6 molecules (reaction (12)). Wall effects severely inhibit the chain-branching process by promoting the decomposition of H_2O_2 to H_2O and O_2. Thus, the catalyst is responsible both for generating radicals and for quenching chain reactions.

One would like to be able to separate the homogeneous and heterogeneous contributions of a combined heterogeneous–homogeneous reaction; however, this is difficult because of the dual role of the surface in generating and reacting with radical intermediates. The presence of gas-phase $C_2H_5\cdot$ radicals suggests that there is a homogeneous component, but the chain length in the gas phase may not be long since water vapor has a negative, rather than a positive, effect as would be expected from reaction (11). In principle it should be possible to model the gas-phase contribution since the rate constants are reasonably well known, but such a calculation is limited by the complete absence of data on the reaction rates of the radicals with the metal oxide surface.

In earlier studies on the oxidative dimerization of CH_4 over Li^+/MgO and Na^+/CaO it was shown that at 620°C and at low conversion levels (~6%) the dominant route to produce CO and CO_2 was via the oxidation of methane, rather than the further oxidation of the relatively small amount of ethane in that system (*1, 3*). The current results demonstrate that the Li^+/MgO catalyst also is effective in the formation of CO and CO_2 from both C_2H_6 and C_2H_4, but, of course, the partial pressures of the C_2 hydrocarbons were much greater in these experiments, and there was no methane to compete for the active centers on the catalyst. In absolute terms the $Li^+/$

MgO catalyst is about one order of magnitude more active for the conversion of C_2H_6 than for the conversion of CH_4 at 650°C. On a noncoordinating oxide such as Li^+/MgO it is not surprising that C_2H_6 reacts about 3 times more rapidly than C_2H_4 (Table 2) since the C–H bond strengths in C_2H_6 and C_2H_4 are 98 and 108 kcal mol^{-1}, respectively.

The Role of Lithium

By comparing the selectivities for C_2H_6 and C_2H_4, obtained from the oxidative dimerization of CH_4 over pure MgO and Li^+/MgO catalysts, Hutchings *et al.* (*26*) concluded that the addition of lithium suppressed the OXD of C_2H_6 to C_2H_4. Yet, it is clear from the data of Table 1 that the presence of lithium resulted in a marked increase in the conversion of C_2H_6 and selectivity for C_2H_4. The differences in the activity of the Li^+/MgO catalyst relative to the MgO catalysts may be related to the surface areas of the MgO employed in the two studies. In the present study the MgO was purposely sintered to provide a material of comparable surface area to the Li^+/MgO catalyst, whereas, Hutchings *et al.* apparently used a high-surface-area form of MgO.

It has been proposed that Li^+ activates CH_4 by forming $[Li^+O^-]$ centers in the MgO, and that the resulting O^- species is responsible for the formation of methyl radicals by the reaction (*1, 10, 27*)

$$CH_4 + O_s^- \rightarrow CH_3\cdot + OH_s^- \qquad (13)$$

As noted previously, surface O^- ions are very reactive species, and they are capable of abstracting hydrogen from alkanes at temperatures well below 25°C (*19*). One would not expect, therefore, that reaction (13), or the analogous reaction with C_2H_6, would be the slow step in a catalytic process at temperatures in excess of 600°C. Recently, however, Cant *et al.* (*28*) reported that the oxidative dimerization of methane exhibited a normal kinetic isotope effect over Li^+/MgO, and we have found that the formation of methyl radicals also exhibits a similar effect (*29*). Thus, it appears that hydrogen atom abstraction is indeed the slow step in the catalytic process.

In view of these results and previous work on this catalyst we suggest that specific sites involving the substitution of Li^+ for Mg^{2+} are involved, but that the active form of oxygen is not O_s^- in its highly ionic form (*30*). Two alternatives are immediately obvious. It is possible that at the high temperatures of these reactions the electron hole is not localized on a single oxygen atom, and therefore the resulting species has a greatly reduced ionicity; i.e., it should be described as $O_s^{\delta-}$. As an alternative, it is known that O^- reacts with O_2 to form O_3^-, and the ozonide ion in turn is transformed to O_2^- (*31*). Both species have been observed by ESR following the quenching of Li^+/MgO which was heated in O_2 (*27*). Ozonide ions also react with simple alkanes at lower temperatures, but O_2^- is much less reactive and requires temperatures in excess of 200°C (*32, 33*). One cannot rule out the involvement of a peroxide ion, but there is no spectroscopic evidence to confirm the presence of such a species on the Li^+/MgO catalyst.

CONCLUSIONS

Lithium-promoted MgO is an effective catalyst for ethane OXD, and ethylene yields of up to 34% have been observed. Ethyl radicals are formed on the surface and desorb into the gas phase where they react with O_2 to produce ethylene. At temperatures of 700°C the homogeneous oxidation of ethane is the predominant reaction. The carbon oxides are formed from the direct oxidation of C_2H_6 and to a lesser extent from the secondary oxidation of C_2H_4.

Although the oxidation of methane and ethane over Li^+/MgO have many similarities, there are some fundamental differences. Both methyl and ethyl radicals, the initial intermediates, react with surface oxygen ions to form alkoxides; however, only the ethoxide ion can decompose into the alkene. Similarly, in the reaction between the alkyl radical and oxygen, only the ethyl radical can yield the corresponding alkene. The coupling of methyl radicals to form ethane is the most important reaction in the selective oxidation of methane, whereas the coupling of ethyl radicals is only a minor channel in the OXD of ethane.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of Youdong Tong in obtaining the ESR spectra of ethyl radicals. This research was supported by the National Science Foundation under Grant CHE-8617436.

REFERENCES

1. Ito, T., and Lunsford, J. H., *Nature (London)* **314,** 721 (1985); Ito, T., Wang. J.-X., Lin, C.-H., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107,** 5062 (1985).
2. Lin, C.-H., Ito, T., Wang, J.-X., and Lunsford, J. H., *J. Amer. Chem. Soc.* **109,** 4808 (1987).
3. Lin, C.-H., Wang, J.-X., and Lunsford, J. H., *J. Catal.* **111,** 302 (1988).
4. Moriyama, T., Takasaki, N., Iwamatsu, E., and Aika, K., *Chem. Lett.*, 1165 (1986).
5. Roos, J. A., Bakker, A. G., Bosch, H., van Ommen, J. G., and Ross, J. R. H., *Catal. Today* **1,** 133 (1987).
6. Amorebieta, V. T., and Colussi, A. J., *J. Phys. Chem.* **92,** 4576 (1988).
7. Kimble, J. B., and Kolts, J. H., *Energy Prog.* **6,** 226 (1986).
8. Kolts, J. H., Eur. Pat. Appl. EP0205765 A2.
9. Morales, E., Ph.D. dissertation, Texas A&M University, 1988.
10. Driscoll, D. J., Martir, W., Wang, J.-X., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107,** 58 (1985).
11. Campbell, K. D., Morales, E., and Lunsford, J. H., *J. Amer. Chem. Soc.* **109,** 7900 (1987).
12. Campbell, K. D., and Lunsford, J. H., *J. Phys. Chem.* **92,** 5792 (1988).
13. Olson, D. B., Tanzawa, T., and Gardiner, W. C., *Int. J. Chem. Kinet.* **11,** 23 (1979).
14. Westbrook, C. K., Dryer, F. L., and Schug, K. P., "Proc. 19th Symp. (Int.) Combust.," p. 153, 1983.
15. Martir, W., and Lunsford, J. H., *J. Amer. Chem. Soc.* **103,** 3728 (1981).
16. Korf, S. J., Roos, J. A., de Bruijn, N. A., van Ommen, J. G., and Ross, J. R. H., *J. Chem. Soc. Chem. Commun.*, 1433 (1987).
17. Lane, G. S., and Wolf, E. E., *J. Catal.* **113,** 144 (1988).
18. Driscoll, D. J., and Lunsford, J. H., *J. Phys. Chem.* **89,** 4415 (1985).
19. Aika, K., and Lunsford, J. H., *J. Phys. Chem.* **81,** 1393 (1977).
20. Aika, K., and Lunsford, J. H., *J. Phys. Chem.* **82,** 1794 (1978).
21. Ben Taarit, Y., Symons, M. C. R., and Tench, A. J., *J. Chem. Soc. Faraday Trans. I* **73,** 1149 (1977).
22. Naccache, C., *Chem. Phys. Lett.* **11,** 323 (1977).
23. Benson, S. W., *J. Amer. Chem. Soc.* **87,** 972 (1965).
24. Knox, J. H., *Combust. Flame* **9,** 297 (1965).
25. Hoare, D. E., Protheroe, J. B., and Walsh, A. D., *Trans. Faraday Soc.* **55,** 548 (1959).
26. Hutchings, G. J., Scurrell, M. S., and Woodhouse, J. R., *J. Chem. Soc. Chem. Commun.*, 1862 (1987).
27. Wang, J.-X., and Lunsford, J. H., *J. Phys. Chem.* **90,** 5883 (1986).
28. Cant, N. W., Lukey, C. A., Nelson, P. F., and Tyler, R. J., *J. Chem. Soc. Chem. Commun.*, 766 (1988).
29. Tong, Y., and Lunsford, J. H., unpublished results.
30. Wong, N. B., and Lunsford, J. H., *J. Chem. Phys.* **55,** 3007 (1971).
31. Wong, N. B., and Lunsford, J. H., *J. Chem. Phys.* **56,** 2664 (1972).
32. Takita, Y., and Lunsford, J. H., *J. Phys. Chem.* **83,** 683 (1979).
33. Iwamoto, M., and Lunsford, J. H., *J. Phys. Chem.* **84,** 3079 (1980).