

Activation and Oxidative Dimerization of Methane over Lithium-Promoted Zinc Oxide

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Received September 15, 1987; revised February 22, 1988

Lithium-doped ZnO has been found to be a relatively good catalyst for the oxidative dimerization of methane to ethane and ethylene. Maximum C₂ yields of approximately 15% have been attained and are comparable with those previously observed over Li-doped MgO catalysts. Initial methane activation is believed to be via hydrogen atom abstraction by [Li⁺O⁻] centers on the catalyst surface, and this results in the formation of surface-generated gas-phase methyl radicals. Gas-phase radical reactions provide the primary pathway for the formation of selective C₂ products. Nonselective C₁ product formation is most likely promoted on the pure ZnO surface. Zinc oxide is a nonbasic semiconductor, whereas MgO is a basic insulator. However, these differences in electronic and basic properties tend to disappear when the oxides are doped with lithium, and the similarities are reflected in the catalytic properties. © 1988 Academic Press, Inc.

INTRODUCTION

The heterogeneously catalyzed partial oxidation of methane has received considerable attention in recent years. Early work focused primarily on the partial oxidation of methane to methanol and formaldehyde (1, 2); however, in more recent studies the oxidative dimerization of methane to ethane and ethylene (C₂'s) has been examined. A number of materials have now been examined for their ability to promote the latter reaction, and these include the rare-earth oxides (3, 4) as well as a variety of pure and doped transition and main group metal oxides (5-8).

Recent research in this laboratory has concentrated on the oxidative dimerization of methane over La₂O₃ (4) and several of the alkali-doped main group metal oxides (9), including Li-doped MgO (10, 11). On this material it is proposed that methane is activated via hydrogen atom abstraction by [Li⁺O⁻] centers which are present, under reaction conditions, on the surface of the catalyst (12, 13). Subsequent steps in the mechanism involve the release of these rad-

icals into the gas phase where they then undergo coupling reactions to produce the selective C₂ products.

The formation of [Li⁺O⁻] centers has also been reported on Li-doped ZnO (14, 15). Zinc oxide is considered to be a nonbasic *n*-type semiconductor, whereas magnesium oxide is considered to be a basic insulator. Upon doping with lithium the properties of the two oxides tend to become more similar in that the *n*-type conductivity of ZnO decreases remarkably, approaching intrinsic semiconductivity (16), and MgO becomes a reasonably good *p*-type semiconductor (17). Moreover, as discussed below, lithium-promoted ZnO becomes a much more basic oxide. A recent study by Matsuura *et al.* (18) has shown that Li-doped ZnO is indeed active for the oxidative dimerization of methane. In the present study, this catalyst has been examined in further detail to identify the active site on the catalyst surface and to determine the overall mechanism for product formation.

EXPERIMENTAL

Catalytic experiments. The Li-doped ZnO catalysts (Li/ZnO) used in most of the studies were prepared by adding appropri-

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ate amounts of ZnO (Fisher, Certified ACS) and Li_2CO_3 (Fisher, Certified ACS, 99.6%) to deionized water, and the resulting slurry was stirred and heated until only a thick paste remained. To ensure that a completely homogeneous catalyst was obtained, a fresh portion of deionized water was added to the paste and the procedure was repeated two more times. The resulting paste was air-dried in an oven at 120°C overnight, ground to a powder, and then calcined for 4 h in air at 650°C . This material was then pressed and broken into small chips (20–40 mesh) before being loaded into the reactor. By this method six catalysts promoted with 0.45, 0.9, 1.8, 2.7, 3.6, and 7.2 wt% Li were prepared (wt% is defined as the ratio of Li to the sum of Li plus ZnO). A pure ZnO sample was prepared in the same manner, but without added Li_2CO_3 . High-purity samples were prepared by the same method but employing Aldrich Gold Label ZnO (99.999%). A third sample was prepared by this procedure using Super Purity ZnO obtained from The New Jersey Zinc Co. A sample derived from acetates was prepared by dissolving the proper amounts of zinc acetate ($\text{Zn}(\text{O}_2\text{C}_2\text{H}_3)_2 \cdot 2\text{H}_2\text{O}$, Fisher Certified) and lithium acetate ($\text{LiO}_2\text{C}_2\text{H}_3 \cdot x\text{H}_2\text{O}$, Johnson Matthey Puratronic, 99.998%) in deionized water and then slowly evaporating the water, with stirring, until a thick paste was obtained. The methane (99.97%), oxygen (99.6%), helium (99.995%), and argon (99.995%) were obtained from Matheson Gas and were not purified further.

The catalytic experiments were carried out in a fixed-bed, fused-quartz reactor (130 mm length; 19 mm o.d.), fitted with a capillary exit tube (30 mm length; 2 mm i.d.), operated at atmospheric pressure. In order to minimize gas-phase ethane and ethylene oxidation, the catalyst bed was located directly above the capillary exit tube. The volume above the bed was filled with quartz chips which served to reduce the free volume and to preheat the methane. Unless otherwise specified in the text, the samples

were preconditioned in the reactor for 4 h at 750°C under a flow of molecular oxygen (50 ml min^{-1}). A 50 ml min^{-1} flow of $\text{He}:\text{CH}_4:\text{O}_2$ (85:10:5) was then passed over the sample at 720°C overnight before any results were obtained. Generally, this same gas mixture was employed during the reaction. Operating temperatures ranged from 620 to 770°C .

All of the products were analyzed by conventional GC techniques, and these have been previously described in detail elsewhere (2). Hydrogen (H_2) was detected by GC using argon as the carrier gas in both the reactor and the chromatograph. Surface areas were obtained by a volumetric BET technique using krypton gas as the absorbate at -196°C . X-ray data were obtained on a computer-controlled Siefert-Scintag Pad II automated powder diffractometer. Lithium concentrations were determined by atomic absorption on a Varian Model-30 AA spectrometer. Particle desorption mass spectrometry (PDMS) data were obtained employing a ^{252}Cf source and a compact time-of-flight (TOF) mass spectrometer (19).

EPR measurements. Detection of the $[\text{Li}^+\text{O}^-]$ centers was accomplished by EPR spectroscopy. Spectra were recorded using a Varian E-6S EPR spectrometer with the sample at -196°C . Briefly, the samples were heated in O_2 at the desired temperature, rapidly quenched into liquid oxygen, evacuated, and then quickly transferred into a quartz EPR tube for analysis (13). The g values were determined relative to a phosphorus-doped silicon standard with $g = 1.9987$.

Gas-phase methyl radicals were detected employing the MIESR technique which has been described in detail elsewhere (12). In summary, the reactant gases ($\text{Ar} = 3.8 \text{ ml min}^{-1}$, $\text{CH}_4 = 1.09 \text{ ml min}^{-1}$, and $\text{O}_2 = 0.024 \text{ ml min}^{-1}$) are passed over the catalyst in a low-pressure (1 Torr) fused-quartz flow reactor. The effluent is carried downstream, through a leak, into a lower pressure (approximately 10^{-5} Torr) collection

region and trapped on a sapphire rod maintained at a temperature of 16 K. The rod is then lowered into an EPR cavity and the spectrum recorded on a Varian V4500 spectrometer.

All of the EPR results are presented in terms of relative concentration. These were obtained by simply measuring and comparing peak heights of the various signals. This type of a comparison was possible because the shape of each spectrum (i.e., methyl or $[\text{Li}^+\text{O}^-]$) was independent of the amplitude.

RESULTS

Lithium concentration. Analysis of all of the Li-doped samples which had been heated to temperatures $\geq 650^\circ\text{C}$ showed a significant loss of lithium. Samples initially prepared at doping levels of 0.45, 0.9, 1.8, 2.7, 3.6, and 7.2 wt% were found to contain only 0.11, 0.18, 0.49, 0.72, 1.7, and 2.7 wt%, respectively, after reaction. A similar loss of lithium was reported by Kimble and Kolts (20) when Li-doped MgO and CaO were calcined at high temperatures ($\geq 750^\circ\text{C}$). In this paper, all of the doping levels presented are those of the catalysts after reaction.

Pretreatment. The pretreatment method was found to have a strong influence on the stability of the catalysts. Samples preconditioned for 3 h at 650°C in static air rapidly deactivated, regardless of the reaction temperature, CH_4/O_2 ratio, or sample purity. For example, over a high-purity 0.49 wt% Li/ZnO catalyst ($T = 720^\circ\text{C}$, $\text{CH}_4/\text{O}_2 = 2$), pretreated using the above conditions, methane conversion decreased from 30 to 10% and C_2 selectivity fell from 42 to 8% after only 18 h. However, by increasing the pretreatment temperature to 750°C and employing a 50 ml min^{-1} oxygen flow, one achieves a steady-state activity after only 2.5 h of reaction and maintains it even after 130 h on stream. This behavior is illustrated in Fig. 1 for a low-purity 0.18 wt% Li/ZnO catalyst. Therefore, to ensure that results were obtained after steady state had been reached, all samples, unless otherwise

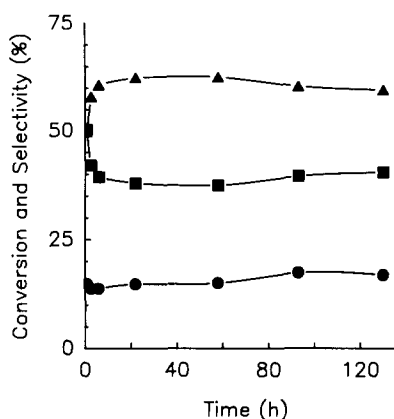


FIG. 1. Conversion and selectivity as a function of time on stream. A gas mixture containing 38 Torr O_2 , 76 Torr CH_4 , and 646 Torr He was reacted over 4 g 0.18 wt% Li/ZnO at 720°C : ●, CH_4 conversion; ■, C_1 selectivity; ▲, C_2 selectivity.

specified, were pretreated at 750°C for 4 h under an O_2 flow and measurements were not begun until after 12 h on stream. With only quartz chips in the reactor, there was no reaction below 725°C .

Catalytic studies. The effect of lithium doping on reactivity is considered first, and a plot of CH_4 conversion, C_2 selectivity, and C_1 selectivity versus lithium doping into ZnO is presented in Fig. 2. Methane

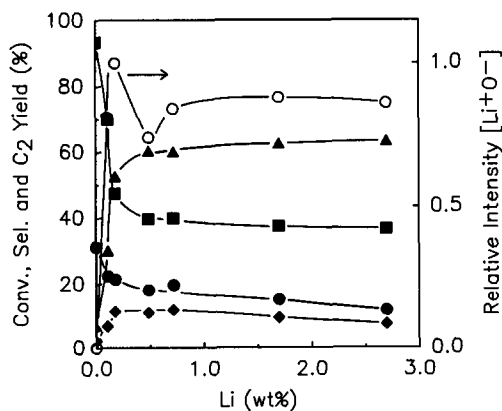


FIG. 2. Effect of Li^+ on conversion, selectivity and $[\text{Li}^+\text{O}^-]$ concentration. A gas mixture containing 38 Torr O_2 , 76 Torr CH_4 , and 646 Torr He was reacted over 4 g of catalyst at 720°C : ●, CH_4 conversion; ■, C_1 selectivity; ▲, C_2 selectivity; ◆, C_2 yield; ○, $[\text{Li}^+\text{O}^-]$ relative concentration.

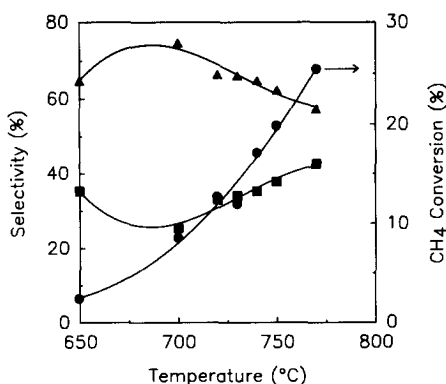


FIG. 3. Effect of temperature on conversion and selectivity for 0.18 wt% Li/ZnO catalyst. A gas mixture containing 38 Torr O₂ and 76 Torr CH₄ was reacted over 4 g of catalyst: ●, CH₄ conversion; ■, C₁ selectivity; ▲, C₂ selectivity.

conversion reached a maximum over the pure oxide; however, selectivity to C₂ products was extremely low. Addition of lithium resulted in a decrease in methane conversion, but the C₂ selectivity increased markedly and eventually leveled off at a doping level of approximately 0.2 wt% Li. A corresponding decrease in the C₁ selectivity was also observed. The major component in the C₁ fraction was CO₂ (>90%) while the C₂ fraction consisted of a mixture of ethane and ethylene at a constant ratio of C₂H₄/C₂H₆ ≈ 0.85. Molecular hydrogen also was detected as a reaction product. Over the 0.18 wt% Li/ZnO catalyst the partial pressure of H₂ was 2.7 Torr which may be compared with C₂H₄ and C₂H₆ partial pressures of 2.0 and 2.3 Torr, respectively. Surface area measurements of these used materials showed that the exposed surface decreased from 0.5 m² g⁻¹ over the pure oxide to a constant value of ≈0.1 m² g⁻¹ over all of the lithium-doped samples.

The effect of reaction temperature on CH₄ conversion and the selectivities has also been examined, and a typical plot is depicted in Fig. 3. These results were obtained over a 0.18 wt% Li/ZnO catalyst, but identical trends were observed over all of the doped materials. Methane conversion continually increased with increasing

temperature over the entire range examined. The C₂ selectivity reached a maximum at a temperature of approximately 700°C, while a reverse temperature dependence was observed for the C₁ selectivity. The increase in C₂ selectivity with increasing activity is contrary to expected behavior; however, a similar trend was previously observed during the oxidative dimerization of methane over Li-doped MgO catalysts (11).

The composition of the C₁ fraction remained essentially invariant over the entire temperature range, with CO₂ predominating at >90% selectivity. The C₂ portion showed considerable variation with respect to reaction temperature. The C₂H₄/C₂H₆ ratio was found to be 0.3 and 1.2 at 650 and 750°C, respectively, which obviously indicates that ethylene is the favored product at elevated temperatures. The activation energy for methane conversion, determined over the temperature range of 550 to 700°C, was found to be 51 ± 2 kcal mol⁻¹. It is important to note that at all temperatures ≥770°C the catalyst appeared to enter a molten phase; thus, 770°C was chosen to be the maximum reaction temperature in these studies.

The variation of reactivity with respect to O₂ partial pressure is presented in Fig. 4. These data were obtained over a 0.18 wt% Li/ZnO catalyst at 720°C; however, similar behavior was also observed at a temperature of 660°C. As the O₂ partial pressure was increased, methane conversion continued to increase. At low O₂ partial pressures the formation of the selective C₂ products was favored, whereas, as expected, high O₂ partial pressures tended to promote the production of the nonselective products, CO and CO₂. In addition, at low O₂ partial pressures and limited CH₄ conversion, CO₂ (100%) and C₂H₆ (75%) were the major products in the C₁ and C₂ fractions, respectively. By contrast, as high O₂ partial pressures and extensive CH₄ conversion, CO (62%) and C₂H₄ (67%) became the predominant products in each respective fraction.

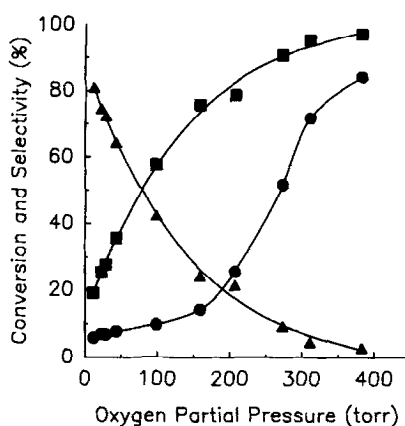


FIG. 4. Effect of oxygen partial pressure on conversion and selectivity. A gas mixture containing 76 Torr CH₄ and the indicated amount of O₂ was reacted over 1 g of 0.18 wt% Li/ZnO at 720°C: ●, CH₄ conversion; ■, C₁ selectivity; ▲, C₂ selectivity.

Several experiments were carried out to examine the effects of sample purity and preparation on the reactivity. The results given in Table 1 show that conversion, selectivity, and C₂ yield remained nearly constant for samples of different purity under identical reaction conditions and doping levels. In addition, relatively little change in these values was observed, even when a sample prepared from the acetates was employed.

In one experiment a catalyst after pretreatment in flowing O₂ at 750°C was thoroughly washed to remove any residual Li₂CO₃ from the surface. This material then exhibited an activity (or yield) for C₂ formation which was comparable to that of the unwashed catalyst; however, the rate of C₁ product formation increased considerably. These results are summarized in Table 2. The *surface* Li concentration of these samples was determined by particle desorption mass spectrometry (PDMS) (19), which is a surface-sensitive technique capable of analyzing only the top one to three monolayers of the sample. The analysis showed that the surface Li concentration fell from 10 wt% on the unwashed sample to 3 wt% on the washed material, which confirms that ex-

TABLE 1
Effect of Purity and Preparation on Activity^a

	Sample:	A	B	C
Selectivity (%)	CO ₂	41.7	46.3	39.5
	CO	5.6	4.5	2.7
	C ₂ H ₄	24.5	22.9	26.7
	C ₂ H ₆	28.1	26.2	31.2
	Total C ₂	52.6	49.1	57.8
Conversion (%)	CH ₄	21.4	19.1	15.5
	O ₂	32.4	40.3	29.5
C ₂ yield (%)		11.3	9.4	9.0

^a All samples at 0.18 wt% Li; (A) Fisher, (B) New Jersey Zinc, (C) via acetates. Over 4 g of catalyst at 720°C and flow rates of 42.5 ml min⁻¹ He, 5.0 ml min⁻¹ CH₄, and 2.5 ml min⁻¹ O₂.

cess Li₂CO₃ was being removed during the washing procedure.

A kinetic analysis was carried out to determine the reaction order. Data were obtained over a 0.18 wt% Li/ZnO catalyst at a temperature of 660°C, which limited conversions to a maximum of 6%. Reaction orders for methane and oxygen were found to be 0.5 and 1.3, respectively.

Maximum C₂ yields. In order to obtain the maximum C₂ yields, catalytic runs were carried out over 4.0 g of a 0.18 wt% Li/ZnO catalyst at several different reaction tem-

TABLE 2
Effect of Washing on Activity^a

	Sample:	A	B
Pretreatment Selectivity (%)	Original		
	CO ₂	41.7	57.4
	CO	5.6	3.0
	C ₂ H ₄	24.5	20.5
	C ₂ H ₆	28.1	19.0
Total C ₂		52.6	39.6
	Conversion (%)		
CH ₄	21.4	28.0	
O ₂	32.4	70.3	
C ₂ yield (%)		11.3	11.1

^a (A) Original catalyst, 0.18 wt% Li/ZnO; (B) A washed six times with 50 ml cold H₂O. Over 4 g of catalyst at 720°C and flow rates of 42.5 ml min⁻¹ He, 5.0 ml min⁻¹ CH₄, 2.5 ml min⁻¹ O₂.

TABLE 3
Maximum C₂ Yield^a

Temperature (°C):		650	700	720	750
Selectivity (%)	CO ₂	44.0	39.6	41.7	43.7
	CO	4.9	1.4	5.6	3.0
	C ₂ H ₄	10.4	22.2	24.5	28.7
	C ₂ H ₆	40.7	36.8	28.1	24.6
	Total C ₂	51.1	59.0	52.6	53.3
Conversion (%)	CH ₄	5.1	13.9	21.4	28.2
	O ₂	11.7	25.3	32.4	55.5
C ₂ yield (%)		2.6	8.2	11.3	15.0

^a Catalyst: 4 g 0.18 wt% Li/ZnO; flow rates: He = 42.5 ml min⁻¹, CH₄ = 5.0 ml min⁻¹, O₂ = 2.5 ml min⁻¹.

peratures. These results, along with some typical conversion and selectivity data, are presented in Table 3. A maximum C₂ yield of 15% was obtained at a temperature of 750°C. Higher yields apparently could be obtained at higher temperatures; however, as previously mentioned, the catalyst appeared to enter a molten phase under these conditions. Matsuura *et al.* (18) reported a maximum C₂ yield of 25% at 740°C over a Li/ZnO catalyst. It is of value to compare these yields with the C₂ yields previously observed over the Li-doped MgO catalysts for which a maximum C₂ yield of 18% was observed at 720°C (10).

EPR quenching studies. The EPR signal depicted in Fig. 5 was detected in all of the Li-doped ZnO samples which were

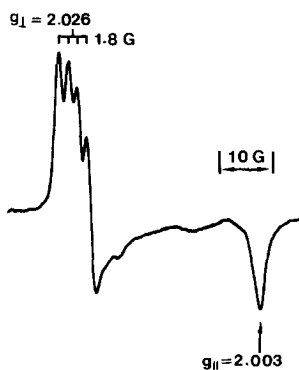


FIG. 5. EPR spectrum of the [Li⁺O⁻] center in ZnO.

quenched from 730°C, under 180 Torr of molecular oxygen, into liquid oxygen at 77 K. This signal is believed to result from the presence of thermally generated [Li⁺O⁻] centers within the ZnO lattice. The values of $g_{||} = 2.003$ and $g_{\perp} = 2.026$ are in excellent agreement with those previously reported for the [Li⁺O⁻] center produced in this material via irradiation techniques (14, 15). The four-line hyperfine structure results from the interaction of the ⁷Li⁺ nucleus ($I = \frac{3}{2}$, natural abundance = 92.6%) with the O⁻ ion. A more detailed discussion of these centers will be presented in a subsequent paper.

The variation of [Li⁺O⁻] concentration with respect to Li-doping levels is presented in Fig. 2. It is important to note that no [Li⁺O⁻] centers were observed in the pure ZnO sample, but instead the spectrum of O₂⁻ ions ($g_{||} = 2.048$, $g_{\perp} = 2.002$) was observed with the pure oxide. This species, however, was not detected on the Li-doped ZnO.

X-ray powder diffraction of these samples, even at the highest doping levels, showed only the presence of a ZnO phase. No Li₂CO₃ phase could be detected. This further supports the contention that [Li⁺O⁻] centers are actually being formed at substitutional sites in the ZnO lattice, rather than on ions located within a residual Li₂CO₃ phase. Furthermore, earlier studies had demonstrated that [Li⁺O⁻] centers were not produced on pure Li₂CO₃ during high-temperature quenching experiments.

EPR matrix isolation studies. The detection of surface-generated gas-phase methyl radicals during this reaction was carried out using the MIESR technique, and the results are presented in Fig. 6. Gas-phase methyl radicals were detected over all of the Li-doped samples in concentrations at least ten times greater than the background amount. By contrast, the amount of radicals detected over the pure ZnO sample was less than the background amount by a factor of approximately 1.5. This result obviously suggests that the pure material is

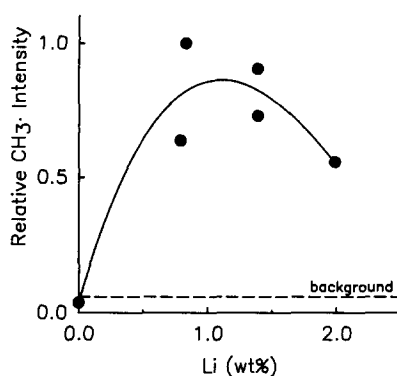


FIG. 6. Relative concentration of surface-generated gas-phase methyl radicals formed over pure ZnO and Li-doped ZnO at 700°C.

acting as a "sink" for the methyl radicals. Surface reactions of methyl radicals with ZnO were further demonstrated by placing a sample of the pure oxide immediately down stream from the Li-doped ZnO which served as a radical source. With the ZnO in place the radical concentration decreased by 37%. Had fused-quartz powder been present instead of ZnO, the decrease in radical concentration would have been negligible.

Basicity. A cursory determination of the basicity was made by placing 0.2 g of used catalyst which had recently been removed from the reactor into 40 ml of deionized water and measuring the pH of the aqueous phase. As expected, the liquid over the pure ZnO exhibited a pH = 7.5; however, the liquid over the 0.9 wt% Li/ZnO had a pH = 10.1, which reflects a dramatic increase in basicity. By comparison the pH of solutions over pure MgO and 7 wt% Li/MgO were 10.4 and 11.3, respectively.

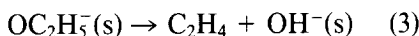
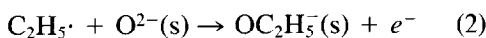
DISCUSSION

Methane activation. The presence of $[\text{Li}^+\text{O}^-]$ centers in the Li-doped materials during the quenching studies once again suggests that these sites are responsible for the initial methane activation during the oxidative dimerization reaction (10, 12). Even those $[\text{Li}^+\text{O}^-]$ centers in the bulk may participate in the activation process via an

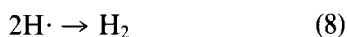
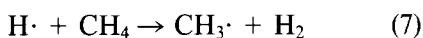
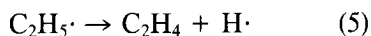
equilibrium with surface O^{2-} , which results in $\text{O}^-(\text{s})$ ions. Such an equilibrium simply involves hole transfer among the oxide ions. The $[\text{Li}^+\text{O}^-]$ concentration does not correlate well with CH_4 conversion (Fig. 2); however, relatively good agreement is observed with the C_2 yield, and there is even better agreement with the C_2 selectivity. In addition, as the C_2 selectivity increased, the surface area of the catalysts fell by a factor of approximately 5, which further suggests that the catalyst surface is not uniformly responsible for promoting C_2 product formation. Furthermore, over the pure oxide no $[\text{Li}^+\text{O}^-]$ centers could be detected, and this material was found to be relatively ineffective for the oxidative dimerization of methane. There is also qualitative agreement between C_2 yield (Fig. 2) and gas-phase methyl radical production (Fig. 6). This agreement indicates that surface-generated gas-phase methyl radicals are the primary species produced during the interaction of $[\text{Li}^+\text{O}^-]$ centers with methane. Therefore, it is likely that the initial activation of methane involves hydrogen atom abstraction by $[\text{Li}^+\text{O}^-]$ centers which results in the formation of free methyl radicals. Volodin and Cherkashin (21) have shown that photoinduced O^- centers on ZnO react with CH_4 to form $\text{CH}_3\cdot$ radicals at temperatures as low as -183°C . Further support for this type of an activation step is provided in a recent theoretical study by Mehandru *et al.* (22) which shows that the O^- ion on MoO_3 is highly active for the abstraction of a hydrogen atom from methane.

Stable product formation. All of the catalysts which were selective for C_2 (C_2H_6 and C_2H_4) product formation were also capable of generating relatively large amounts of gas-phase methyl radicals. This immediately suggests that these products are being produced by a mechanism involving coupling of surface-generated gas-phase methyl radicals, most likely to produce ethane initially. Moreover, no gas-phase methyl radicals could be detected during

the MIESR experiments over the pure zinc oxide, and this material was a poor catalyst for the oxidative dimerization of methane. Previous work by Ito *et al.* (10), over Li-doped MgO, suggested that ethylene is produced by subsequent dehydrogenation of ethane, primarily on the surface, via the reactions



However, recent mechanistic studies by Kimble and Kolts (20) and Labinger and Ott (23) have indicated that the formation of ethylene, from ethane, also appears to occur in the gas phase. The following mechanism has been proposed:

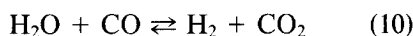


One must also consider the reaction



which is a major source of ethylene when oxygen is present in the gas phase.

Although the hydrogen produced in reactions (6), (7), and (8) may contribute to that detected as a final product, the amounts of H_2 , CO , and CO_2 which were observed, along with the estimated H_2O concentration as determined by mass balance, are consistent with those expected from the water-gas shift (WGS) reaction



at equilibrium. There was considerable error, however, in determining the small amounts of CO which were produced. Zinc oxide is known to be a good catalyst for this reaction at temperatures as low as 230°C (24); therefore it is not surprising that equilibrium would be achieved at temperatures

in excess of 700°C . Obviously the WGS reaction must be significantly more rapid than the oxidation of H_2 to H_2O .

The results also provide some insight into the mechanism of nonselective product formation. The presence of O_2^- on the ZnO surface suggests that this species may be important in the formation of C_1 compounds from CH_4 . In addition, washing of the sample to remove residual Li_2CO_3 resulted in increased CO_2 formation (Table 1). Analysis of this material by PDMS showed that the surface Li concentration decreased by approximately 70% which also implies that the percentage of exposed ZnO must increase accordingly. Therefore, it appears that the surface Li_2CO_3 moderates the nonselective activity by prohibiting access of the methyl radicals (or methane) to the pure ZnO surface. The surface carbonate does not appear to have any effect on the selective oxidative dimerization reaction; its removal only affected the nonselective reactions.

At higher temperatures a secondary route to CO and CO_2 appears to be in effect. The data presented in Fig. 3 suggest that at temperatures greater than approximately 700°C , C_2 's are being converted into nonselective CO and CO_2 , most likely in the gas phase. Furthermore, at these temperatures the predominant product in the C_2 fraction is ethylene, which further indicates that most of the nonselective oxides produced from this route are formed from secondary reactions of ethane rather than ethylene.

An increased oxygen partial pressure also appears to increase production of CO and CO_2 (Fig. 4); however, from these data it is not possible to determine whether this is being promoted on the surface or in the gas phase. The increase in the CO/CO_2 ratio tends to suggest that this is resulting from additional gas-phase reactions.

The differences in electronic and basic properties of Li-doped ZnO relative to Li-doped MgO are considerably less than those in the pure oxides, and nearly identical reactivity was observed over both mate-

rials. The electrical and catalytic properties are related through the $[\text{Li}^+\text{O}^-]$ centers, which serve as hole donors and active sites. Basicity probably is not a major factor in the catalytic oxidative dimerization of CH_4 except for the role of specific ions such as O^- which themselves are highly basic. Even so, these ions react by abstracting a hydrogen atom from CH_4 , which would not normally be viewed as an acid-base reaction.

CONCLUSIONS

The mechanism for the oxidative dimerization of methane over Li-doped ZnO is similar to that previously proposed for the same reaction over Li-doped MgO. Surface-generated gas-phase methyl radicals are produced from the interaction of methane with $[\text{Li}^+\text{O}^-]$ centers. Gas-phase coupling reactions provide the primary route for the formation of the selective C_2 products. Nonselective C_1 product formation is most likely promoted on the pure oxide surface.

ACKNOWLEDGMENTS

We thank Dr. Janos Szanyi for assistance with the EPR quenching studies and Mr. Carl McAfee for conducting the Particle Desorption Mass Spectrometry experiments. This work was supported by the National Science Foundation under Grant CHE-8617436.

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