

OXIDATIVE DIMERIZATION OF METHANE OVER LITHIUM-PROMOTED
ZINC OXIDE

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INTRODUCTION

The heterogeneously catalyzed oxidative dimerization of methane has received considerable attention in recent years. A variety of materials have now been examined which include the main group oxides (1,2), the rare-earth oxides (3,4) and a number of doped transition (5) and main group metal oxides (6). Work in this laboratory has focused primarily on the latter materials, and in particular Li-doped MgO (7,8). Over this material it is postulated that methane is activated via hydrogen atom abstraction by $[\text{Li}^+\text{O}^-]$ centers which are present under reaction conditions on the surface of the catalyst. Subsequent steps in the mechanism involve the release of these radicals from the surface into the homogeneous gas phase where they then undergo coupling reactions to produce the selective C_2 products.

The formation of $[\text{Li}^+\text{O}^-]$ centers has also been reported on Li-doped ZnO (9,10). This material is considered to be a non-basic semiconductor, whereas, MgO is considered to be a basic insulator. Li-doped ZnO was chosen for examination not only because of its ability to produce potentially active centers, but also to determine the effect of basicity on the catalytic properties. Recent work by Matsuura *et al.* (11) has shown that this material is indeed active for the oxidative dimerization of methane. In the present study, this material will be examined in further detail in an effort to identify the active site on the catalyst surface and to determine the overall mechanism for final product formation.

EXPERIMENTAL

The catalysts were prepared by adding zinc oxide (ZnO) and lithium carbonate (Li_2CO_3) to deionized water and evaporating the water, while stirring, until only a thick paste remained. The paste was dried in air at 140°C overnight. This material was then pressed, broken into small chips, loaded into the reactor and preconditioned at 750°C for 4 h under a flow of oxygen before exposure to the reactant gases. The unpromoted ZnO catalyst was prepared and pretreated in the same manner, except for the addition of Li_2CO_3 .

The catalytic studies were carried out in a conventional fused-quartz flow reactor operated at atmospheric pressure. Typical reactant feeds consisted of a 2:1 methane:oxygen feed diluted with a helium carrier gas at a total flow of 50 ml/min. Reaction temperatures ranged from 600 to 770°C . Product analysis was accomplished by conventional GC techniques. Further details on this system can be found in previous papers by Lunsford and co-workers (3,7).

The EPR spectra were obtained using a Varian E-6S spectrometer at 77 K. Quenching studies were carried out using the technique previously developed in this laboratory by Wang *et al.* (12). In this

work, the samples were quenched into liquid oxygen after exposure to 180 torr of gaseous oxygen at 730°C for 1 h.

RESULTS

Catalyst Preconditioning

The method used to pretreat the catalyst was found to have a strong influence on the reaction stability. Samples preconditioned for 3 h at 650°C in air rapidly deactivated, regardless of the reaction temperature, methane/oxygen ratio or the sample purity. However, by increasing the pretreatment temperature to 750°C and employing a 50 ml/min oxygen flow a steady state could be rapidly attained. In this case, a steady state reaction was achieved after only 2.5 h and was maintained even after 130 h on stream. Therefore, to ensure that all results were obtained after steady state had been reached, samples were pretreated at 750°C for 4 h under an oxygen flow and measurements were not begun until after 12 h on line.

Catalytic Studies

In order to gain insight into the overall reaction mechanism the effects of temperature, Li-doping levels and reactant partial pressures on reactivity were examined in detail. The effect of temperature is considered first and the results are illustrated in Figure 1. Methane conversion continually increased with increasing temperature over the entire range examined. The C₂ selectivity slowly increased to a maximum at a temperature of approximately 675°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 (7). The activation energy determined for this reaction, over the temperature range of 550 to 700°C was 51 kcal/mol.

The effect of lithium doping was examined and a plot of methane conversion, C₂ selectivity, C₁ selectivity and C₂ yield (which is defined as the product of conversion and selectivity) vs lithium doping into ZnO is presented in Figure 2. Methane conversion reached a maximum over the pure oxide; however, selectivity to C₂ products was extremely low. Addition of lithium resulted in a decrease of methane conversion, but the C₂ selectivity rapidly increased and eventually leveled off at a doping level of approximately 1.0 wt% Li. A corresponding decrease in the C₁ was also observed. The major component in the C₁ fraction was CO₂ (>90%) while the C₂ portion consisted of a mixture of ethane and ethylene at a constant ratio of C₂H₄/C₂H₆ = 0.85. The surface areas of these used materials decreased from 0.5 m²/g over the pure oxide to a constant value of ~0.1 m²/g over all of the lithium-doped samples.

In one experiment a used catalyst was thoroughly washed to remove any residual Li₂CO₃ from the surface. This material exhibited an activity for C₂ formation which was comparable to the original catalyst; however, the rate of C₁ product formation increased considerably.

The variation of reactivity with respect to oxygen partial pressure is presented in Figure 3. This data was obtained over a 0.9 wt% Li/ZnO catalyst at 720°C; however, similar behavior was also observed at a reaction temperature of 660°C. As the oxygen partial pressure was increased, methane conversion continued to increase. At low oxygen partial pressures the formation of selective C₂ products

was favored whereas, as expected, high oxygen partial pressures tended to promote the production of non-selective CO and CO₂.

Maximum C₂ Yields

In order to obtain the maximum C₂ yields catalytic runs were carried out over 4 g of a 0.9 wt% Li/ZnO catalyst at several different temperatures and these results, along with some typical conversion and selectivity data, are summarized in Table I. A maximum C₂ yield of 15% was obtained at a temperature of 750°C. Higher yields apparently could be obtained at higher temperatures; however, at these temperatures the catalyst appeared to enter a molten phase. It is of value to compare these yields with those previously obtained over the Li/MgO catalysts (7). At 720°C under similar reactant feed conditions a C₂ yield of 18% was observed. The value of 11% obtained here at 720°C is obviously lower, but still within the range of the more active methane conversion catalysts thus far reported.

Table I.

MAXIMUM C₂ YIELD

Temperature(°C)		650	700	720	750
Selectivity(%)	CO ₂	44.0	39.6	42.4	43.7
	CO	4.9	1.4	0.0	3.0
	C ₂ H ₄	10.4	22.2	26.9	28.7
	C ₂ H ₆	40.7	36.8	30.7	24.6
	Total C ₂	51.1	59.0	57.6	53.3
Conversion(%)	CH ₄	5.1	13.9	18.7	28.2
	O ₂	11.7	25.3	35.2	55.5
C ₂ Yield(%)		2.6	8.2	10.8	15.0

Catalyst: 4g 0.9 wt% Li/ZnO; Flow rates: He = 42.5 ml/min, CH₄ = 5.0 ml/min, O₂ = 2.5 ml/min.

EPR Studies

Quenching of all of the doped materials from high temperature in the presence of oxygen resulted in the detection of [Li⁺O⁻] centers. No [Li⁺O⁻] signal, or O⁻ signal, was detected over pure ZnO. The variation of [Li⁺O⁻] concentration with respect to lithium doping is presented in Figure 2 along with the selectivity and conversion data obtained under steady state reaction conditions.

DISCUSSION

To simplify presentation of the mechanism it is best to divide the discussion into two sections: (1) methane activation and (2) stable product formation.

Methane Activation

The presence of [Li⁺O⁻] centers in the quenched samples once again suggests that this site is most likely responsible for the initial methane activation. Although the [Li⁺O⁻] concentration curve

does not correlate well with the conversion curve in Figure 2, relatively good agreement is observed with the C_2 yield curve, and there is even better agreement with the C_2 selectivity curve. Furthermore, in the absence of these centers (i.e. over the pure oxide) the formation of both ethane and ethylene is negligible which provides additional support for the fact that $[Li^+O^-]$ centers are required to promote selective C_2 product formation. In accord with the earlier work over Li-doped MgO catalysts it is proposed that methane is activated via hydrogen atom abstraction by $[Li^+O^-]$ centers to produce the methyl radical (7).

Stable Product Formation

The conversion and selectivity data presented in Figure 2 clearly show that selective C_2 product formation is not favored on the pure oxide surface. In addition, as C_2 selectivity increased the surface area of the catalyst fell by a factor of approximately 5. This further suggests that the catalyst surface is not entirely responsible for the selective product formation. In agreement with the earlier Li/MgO work, it is once again proposed that ethane and ethylene are formed via coupling of the radicals in the gas phase and not on the surface (7).

The formation of the non-selective products, CO and CO_2 , is also briefly considered. As mentioned above, reaction on the catalyst surface appears to be a major source for these products. In addition, the data of Figure 1 indicates that the selectivity for these products increases at temperatures greater than approximately 700°C. This is believed to be due to the further oxidation of the C_2 products. This route apparently is only important at these elevated temperatures. High oxygen partial pressures also tends to promote complete oxidation products (Figure 3), but it is not possible to determine whether this is promoted on the surface or in the gas phase from this data.

Lithium carbonate on the surface appears to moderate the non-selective activity of the zinc oxide, but it has no effect on the selective oxidative dimerization reaction. When the carbonate was removed only the non-selective reactions were affected. Since zinc oxide itself is not a strongly basic oxide, one may conclude that basicity is not a prerequisite for the selective 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 $[Li^+O^-]$ centers. Gas phase coupling reactions provide the primary route for the formation of the selective C_2 products. Non-selective C_1 product formation is most likely promoted on the pure oxide surface. A strongly basic oxide is not required for the selective oxidative dimerization of methane.

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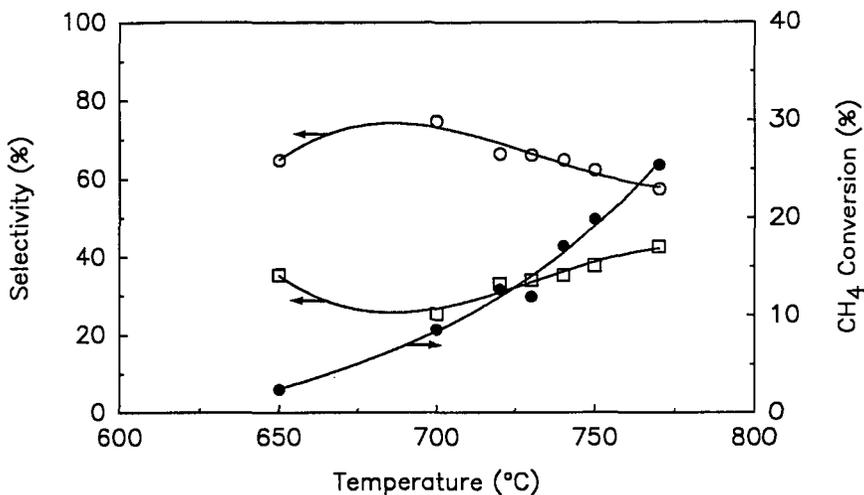


Figure 1. Methane conversion and product selectivity as a function of temperature: ● methane conversion; □ C₁ selectivity; ○ C₂ selectivity. Catalyst: 0.9 wt% Li/ZnO.

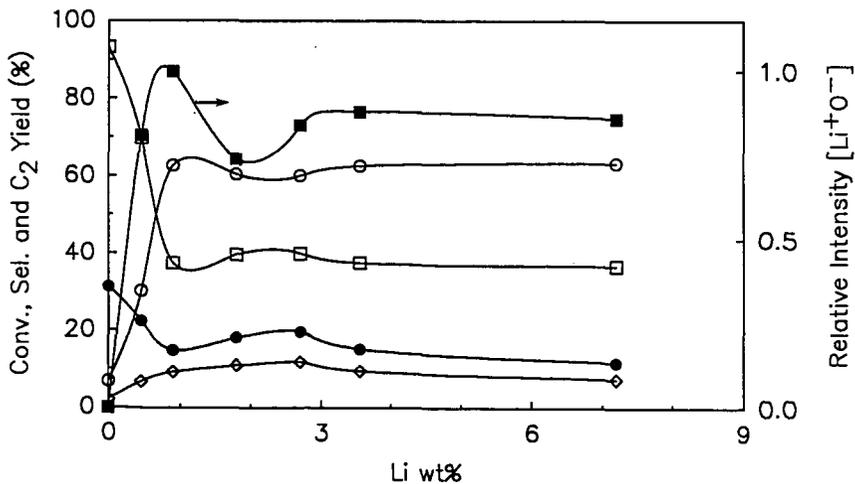


Figure 2. Methane conversion, product selectivity and C₂ yield as a function of Li-doping into ZnO: ● methane conversion; □ C₁ selectivity; ○ C₂ selectivity; ◇ C₂ yield; ■ [Li⁺O⁻] concentration. Temp: 750°C.

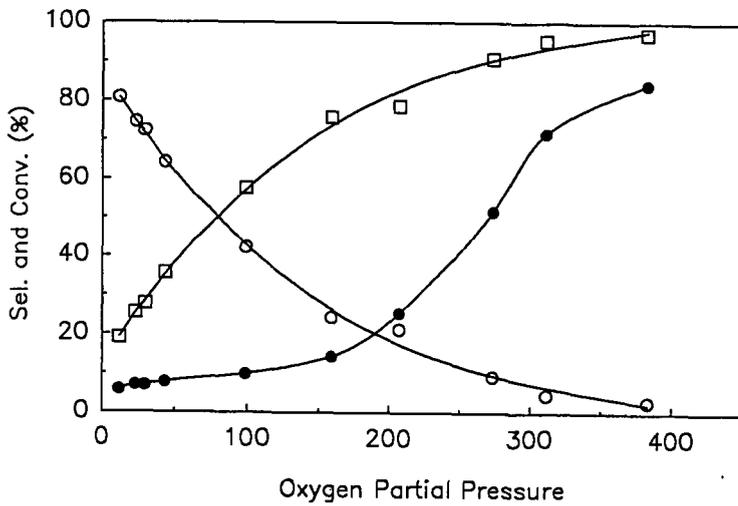


Figure 3. Methane conversion and product selectivity as a function of oxygen partial pressure: ● methane conversion; □ C₁ selectivity; ○ C₂ selectivity. Catalyst: 0.9 wt% Li/ZnO; Temp: 720°C.