

The Rate Controlling Step in the Oxidative Coupling of Methane over a Lithium-promoted Magnesium Oxide Catalyst

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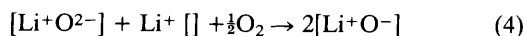
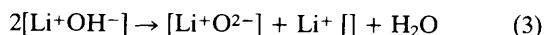
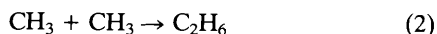
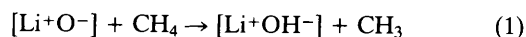
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The rate of conversion of CH₄ in the oxidative coupling reaction over a Li/MgO catalyst at 750 °C is 1.5 times greater than that of CD₄ demonstrating that C–H bond breaking is the rate determining step in this reaction.

The partial oxidation of methane to form C₂ and higher hydrocarbons is an interesting alternative to conversion of methane into synthesis gas by steam reforming or partial oxidation and subsequent reaction of the synthesis gas as a means of producing refinery or petrochemical feedstocks.

Recently a number of catalytic systems which produce methane conversions and C₂ hydrocarbon selectivities of practical significance have been reported.^{1–4} The mechanism of equations (1)–(4) for the oxidative coupling reaction over lithium-doped magnesium oxide (Li/MgO) has been proposed



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by Lunsford and co-workers.³ These workers also argued³ that since both equations (3) and (4) require high temperatures then one or other was the rate-determining step in the catalytic production of CH_3 . However, given the C–H bond strength in CH_4 (435 kJ mol^{-1})⁵ it seems at least as likely that C–H bond breaking would be rate controlling in this system.

This proposition can be tested by substituting CH_4 with an exactly equal pressure of CD_4 and determining whether the overall conversion rate is affected. A significant reduction in methane conversion means that the rate determining step is C–H bond breaking. Calculations based on the prediction of the rate constant ratio from molecular data⁶ show that at 750°C the ratio of the rate with CH_4 to that with CD_4 should be ~ 1.5 if C–H bond breaking is rate determining.

The Li/MgO catalyst used in this experiment was prepared by slurring Li_2CO_3 and MgO (atomic ratio Li : Mg 0.12), and heating to a thick paste which was air-dried overnight at 170°C . Analysis of the catalyst showed levels of other metals to be less than 350 p.p.m. except for Sr (1230 p.p.m.) and Al (1300 p.p.m.). After calcination at 900°C for 4 h in air the catalyst was crushed and the $-1.2 + 0.6 \text{ mm}$ fraction was separated for use. Ultra-high purity CH_4 (99.9% min.), high purity N_2 (99.99%), and industrial O_2 (99.5% min.) were used without further purification. The CD_4 was supplied by MSD Isotopes (99.4 atom % D).

The activity and selectivity of the catalyst were determined using a flow system and a fixed bed tube reactor (recrystallized alumina 99.7%) packed with 101 mg of Li/MgO. Feed and product gas analyses were made by gas chromatography and Fourier transform i.r. spectroscopy. Analyses of CH_4 and CD_4 at equal concentrations showed no detectable difference in response on the flame ionization detector and identical response factors were also assumed for C_2H_6 and C_2D_6 , and C_2H_4 and C_2D_4 . The catalyst was maintained at 750°C and the feedgas was 10% CH_4 , 7.2% O_2 , and balance N_2 at a total flowrate of 96 ml min^{-1} . The experiment was set up so that either CH_4 or CD_4 could be mixed with O_2 and N_2 at the same methane and total flowrates. Under these conditions methane conversion was small (of the order of 5%) and differential reactor conditions could be assumed.

The methane feed was alternated from CH_4 to CD_4 several times during the course of the experiment to check for irreversibility or slow response of the catalyst to changes in the feedgas. In all, nine measurements were made, six with CH_4 and three with CD_4 . Results for the overall methane conversion rate (calculated by summation of products) and carbon selectivities to the various products are shown as a function of time on stream in Figure 1. It can be seen that the system was stable throughout the course of the experiment. When CD_4 was used in the feedgas the conversion rate was significantly lower than that observed with CH_4 . The results are summarized in Table 1. The ratio of the conversion rate with CH_4 to that with CD_4 is 1.50 ± 0.03 , in good agreement with the predicted value of 1.5 on the assumption that bond breaking in methane is rate determining.

A possible alternative explanation for an effect of this magnitude is that the rearrangement step (3), involving the

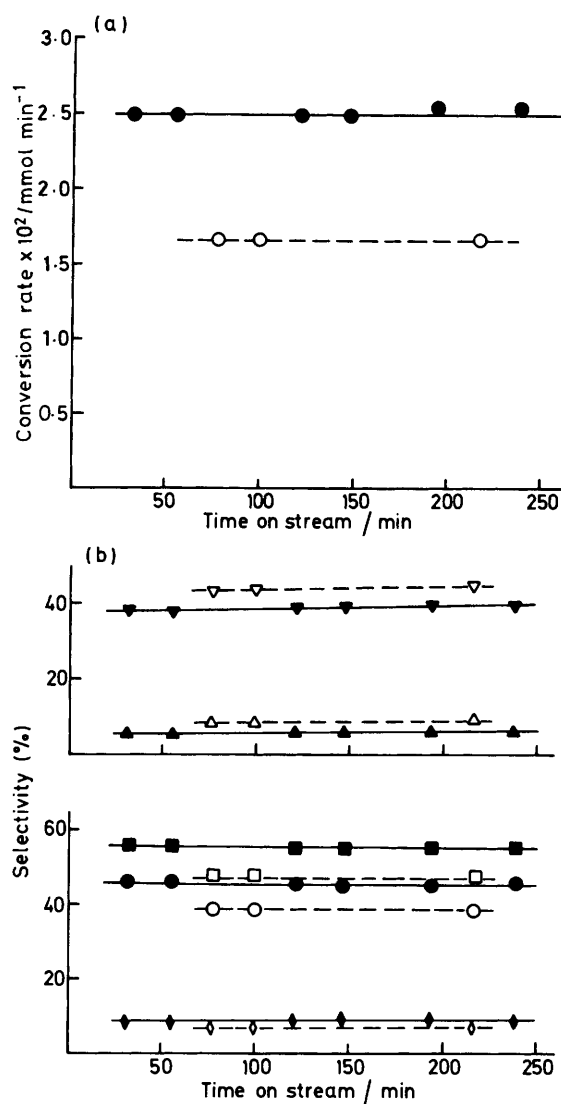


Figure 1. (a) Conversion rates (● CH_4 ; ○ CD_4) and (b) selectivities to major products as a function of time on stream. Li/MgO catalyst (101 mg) at 750°C . Full lines and filled points: CH_4 feed; broken lines and open points: CD_4 feed; ◆ C_2H_4 , ◇ C_2D_4 ; ● C_2H_6 , ○ C_2D_6 ; ■, □ total hydrocarbon; ▲, △ CO; ▼, ▽ CO_2 .

Table 1. Average conversion rates and selectivities.

Conversion rate $\times 10^2$ /mmol min^{-2}	CH_4	CD_4
	2.49 ± 0.02	1.66 ± 0.02
Selectivities (%)		
Ethane	45.6 ± 0.5	38.7 ± 0.3
Ethylene	8.7 ± 0.1	7.1 ± 0.1
Total hydrocarbons	55.3 ± 0.6	47.2 ± 0.3
CO	5.9 ± 0.1	8.8 ± 0.1
CO_2	38.9 ± 0.6	44.0 ± 0.3

reaction of $2 \text{ Li}+\text{OH}^-$ sites and the breaking of an O–H bond, is rate determining. To check this, sequential additions of H_2O and D_2O were made to a feedgas containing CH_4 . The additions increased the concentrations of water by a factor of 2.5–3 above that produced by the catalytic reaction itself, and

H₂O and D₂O should have rapidly exchanged with any surface OH groups present on the catalyst. This is a reasonable assumption as it has been observed that D₂O exchanges with OH groups on MgO at room temperature.⁷ If the rearrangement of the OH(or OD) sites were rate controlling then the conversion rate of CH₄ with D₂O addition would be lower than that with H₂O addition. In fact no discernible difference was observed between these two conditions. Thus this rearrangement is not rate limiting.

Hence C-H bond scission is the rate controlling step in the oxidative coupling of methane over Li/MgO catalysts. Consideration of the selectivities shown in Figure 1 also reveals that the product spectrum changed when CD₄ was present in the feedgas: more CO₂ and CO were produced mainly at the expense of C₂H₆.

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