

## Comparison of Ethene and Ethane Primary Selectivities with Li/MgO and MgO Catalysts for Oxidative Coupling of Methane: Comments on the Role of Lithium

Graham J. Hutchings,<sup>a</sup> Michael S. Scurrell,<sup>b</sup> and Jeremy R. Woodhouse<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of the Witwatersrand, 1 Jan Smuts Avenue, Johannesburg, 2001, South Africa

<sup>b</sup> Catalysis Division, NICER-CSIR, P.O. Box 395, Pretoria, 0001, South Africa

The catalysts in the title demonstrate significantly different primary selectivities for ethene and ethane which indicates that Li inhibits the oxidative dehydrogenation activity of MgO.

The oxidative coupling of methane to form ethene and ethane continues to receive considerable research attention. To date most of this research effort has been directed at the identification of suitable catalytic materials, and the mechanism of ethene and ethane formation has received only limited attention. A large number of oxide catalysts have been proposed for this reaction,<sup>1,2</sup> and high C<sub>2</sub> selectivities have been observed with catalysts based on MgO<sup>3-5</sup> and rare earth oxides,<sup>6-8</sup> particularly Sm<sub>2</sub>O<sub>3</sub>.<sup>9</sup> Recently MnO based catalysts<sup>10</sup> have been shown to give very high yields of C<sub>2</sub> hydrocarbon products. The C<sub>2</sub> selectivity of these catalysts is enhanced significantly by the addition of alkali promoters,<sup>11</sup> but the specific catalytic role of such promotion has not yet been delineated, although it has been proposed<sup>4</sup> that Li<sup>+</sup>O<sup>-</sup> centres are the active and selective methane activation centres for Li-promoted MgO catalysts. We have now addressed this problem and in this communication we present our initial findings concerning the role of Li promotion in MgO catalysts as revealed by comparison of primary selectivity data.

MgO was prepared as previously described<sup>12</sup> and 5% Li/MgO was prepared using the method of Lunsford.<sup>4</sup> Catalysts were calcined (24 h, 500 °C) prior to use for partial methane oxidation with O<sub>2</sub> as previously described.<sup>11</sup>

Experiments were conducted for a wide range of reactant flowrates at 710 °C using a fixed CH<sub>4</sub>/O<sub>2</sub> molar ratio of 3.5. Variation of ethene and ethane selectivity with increasing reactant feedrates demonstrated significantly different behav-

**Table 1.** Specific activity data, 710 °C, GHSV 2400 h<sup>-1</sup>.

Catalyst	10 <sup>4</sup> Specific activity/mol product m <sup>-2</sup> h <sup>-1</sup>						
	H <sub>2</sub>	CO <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	Total C <sub>2</sub>	Total C
Li/MgO	7.7	16.1	1.3	2.5	8.0	10.5	27.9
MgO	3.7	4.5	1.3	0.8	0.8	1.6	7.4

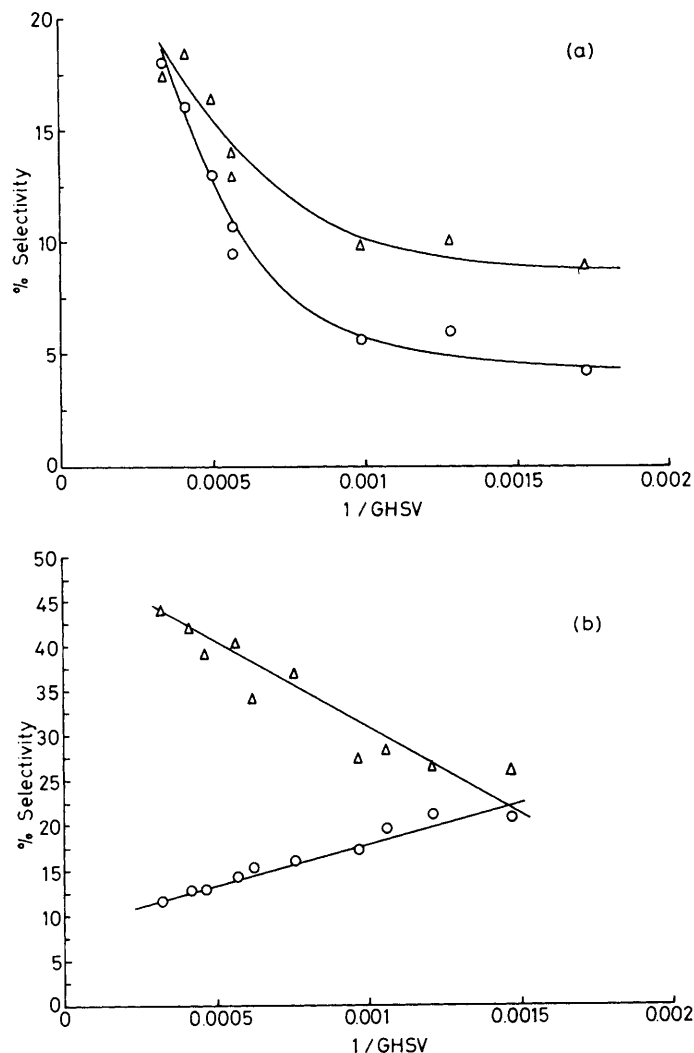


Figure 1. Selectivity vs. reciprocal GHSV: (a) MgO; (b) Li/MgO;  $\Delta$  ethane;  $\circ$  ethene.

ior for Li/MgO compared to MgO, as shown in plots of selectivity vs. reciprocal gas hourly space velocity (GHSV = volumetric gas flow rate/unit catalyst volume/h). With MgO as catalyst (Figure 1a) both ethene and ethane selectivities increase with decreasing reciprocal GHSV, and extrapolation indicates similar primary selectivity (selectivity extrapolated to zero conversion) for both products. Addition of Li (Figure 1b) dramatically changes this behaviour and now ethene selectivity decreases with decreasing reciprocal GHSV. Hence, Li/MgO catalysts demonstrate high ethane primary selectivity but significantly lower ethene primary selectivity when compared to the unpromoted MgO. However, Li addition significantly enhances total  $C_2$  hydrocarbon selectivity (Figure 2) at all reaction conditions investigated as has been previously noted.<sup>11</sup> Further experimental evidence can be obtained from comparison of the specific activity data for the two catalysts (Table 1). Addition of Li to MgO significantly enhances the specific activity for all observed products, and also enhances the formation of selective oxidation products. In particular, the specific activity for ethane formation is enhanced by a factor of ca. 3 compared to the enhancement of ethene formation.

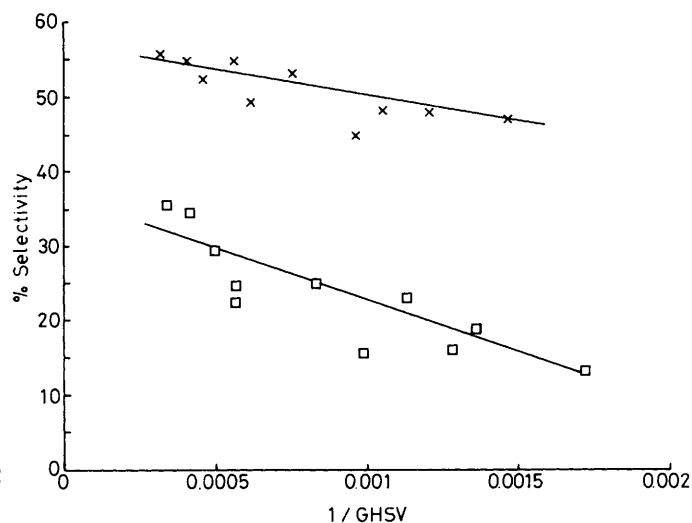


Figure 2. Selectivity to total  $C_2$  hydrocarbon vs. reciprocal GHSV:  $\times$  Li/MgO;  $\square$  MgO.

It is clear from these data that addition of Li to MgO significantly promotes specific activity in addition to enhancing selectivity to partial oxidation products. The specific role of Li would appear to be the inhibition of oxidation activity of MgO in two ways: (a) by suppressing the activity for the oxidative dehydrogenation of ethane as evidenced by higher primary ethane selectivity for Li/MgO; and (b) by reducing the extent of total oxidation of both ethene and ethane as evidenced by a less pronounced loss of  $C_2$  selectivity with increasing reciprocal space velocity (Figure 2). This is unfortunate, with respect to the industrial application of this catalyst system, since ethene is the more desired reaction product. Studies are now in progress to determine if this is a general feature of alkali addition to active oxide catalysts, and if this is observed then it is apparent that further catalyst modifications will be required to enhance ethene formation.

We thank the Richard Ward Foundation, University of the Witwatersrand, and the FRD, CSIR for financial support.

Received, 7th July 1987; Com. 961

## References

- 1 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.
- 2 I. T. A. Emesh and Y. Amenomiya, *J. Phys. Chem.*, 1986, **90**, 4785.
- 3 T. Ito and J. H. Lunsford, *Nature (London)*, 1985, **314**, 721.
- 4 D. J. Driscoll, W. Martir, J-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1985, **107**, 58.
- 5 T. Moriyama, N. Takasaki, E. Iwamatsu, and K-I. Aika, *Chem. Lett.*, 1986, 1165.
- 6 K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.*, 1986, **100**, 353.
- 7 K. Otsuka, Q. Liu, M. Hatano, and A. Morikawa, *Chem. Lett.*, 1986, 467, 903.
- 8 K. Otsuka and K. Jinno, *Inorg. Chim. Acta*, 1986, **121**, 237.
- 9 K. Otsuka and T. Nakajima, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1315.
- 10 K. Otsuka and T. Komatsu, *J. Chem. Soc., Chem. Commun.*, 1987, 388.
- 11 G. J. Hutchings, M. S. Scurrill, and J. R. Woodhouse, *J. Chem. Soc., Chem. Commun.*, in the press.
- 12 M. Boudart, A. Delbouille, J. A. Dumesic, S. Khammouma, and H. Topsoe, *J. Catal.*, 1975, **37**, 486.