An Oxygen Species for the Oxidative Coupling of Methane at Lower Temperatures

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The formation and reactivity of a stable oxygen species which is effective in the production of hydrocarbons from methane at lower than normal temperatures is described.

Current interest in methane activation encompasses intensive work on the application of oxides to the heterogeneously catalysed oxidative coupling of methane to higher hydrocarbons.¹ So far, all the materials which have been investigated as potentially useful catalysts require operation at rather high temperatures (\geq 970 K); this constitutes a significant drawback to their implementation.

We have already reported on the performance of a promising class of mixed metal oxide catalysts which all possess the rock salt structure.² Under conventional O_2/CH_4 feed conditions, two of these (LiNiO₂ and LiYO₂) exhibit activities and selectivities which are at least equal to those of the best catalysts described so far. This communication describes how the use of N₂O with LiNiO₂ can lead to the formation of an oxygen surface species which is effective for methane coupling to C₂ hydrocarbons at significantly reduced temperatures.

Samples of the LiNiO₂ catalyst were prepared by solid state reaction between $LiNO_3$ and NiO (573 K for 1 h then 873 K for 1 h followed by calcining in air at 1073 K for 15 h). Surface species and catalytic activity were evaluated by temperature programmed desorption (TPD) and temperature programmed reaction (TPR) measurements using $\hat{0.5}$ g of catalyst in a quartz tube microreactor whose temperature was varied linearly at 30 K/min to a maximum value of 1073 K. Analysis of the effluent flow was by means of a multiplexed quadrupole mass spectrometer. Oxygen TPD spectra from the fresh catalyst reproducibly exhibited a desorption fingerprint characterised by the onset of O₂ evolution at 770 K (Figure 1A). This material is especially active and selective in the oxidative coupling of methane,^{2,3} apparently by means of a redox reaction which involves sacrificial use of lattice oxygen atoms (reaction 1). A catalytic cycle can be maintained by supplying gaseous oxygen to regenerate the original mixed oxide



Figure 1. Oxygen TPD spectra. (A) from fresh LiNiO₂; (B) after treatment with N_2O at room temperature; (C) after treatment with N_2O at 873 K. Vertical dashed line indicates the point at which the temperature ramp was stopped.



Figure 2. Catalytic decomposition of N_2O over LiNiO₂ as a function of temperature showing signals due to N_2O depletion (m/z 30, 44), O_2 evolution (m/z 32), and N_2 evolution (m/z 28 a.m.u.).



Figure 3. (A) CH₄/He TPRS spectra for LiNiO₂ pre-oxidised in O₂ at 873 K. (B) CH₄/He TPRS spectra for LiNiO₂ pre-oxidised in N₂O at 873 K.

(reaction 2). The efficiency of this second step therefore plays a vital role in determining overall steady state activity of the catalyst. Reoxidation of the used LiNiO₂ catalyst in O₂ (1073 K, 30 min) followed by oxygen chemisorption (873 K) gave rise to a TPD fingerprint which was essentially identical to that characteristic of the fresh material.

$$2\text{LiNiO}_2 + 2\text{CH}_4 \rightarrow \text{Li}_2\text{O} + 2\text{NiO} + \text{C}_2\text{H}_6 + \text{H}_2\text{O} \quad (1)$$

$$Li_2O + 2NiO + \frac{1}{2}O_2 \rightarrow 2LiNiO_2$$
 (2)

In contrast with this, it was found that pretreatment of the catalyst with N2O at temperatures in excess of 673 K gave rise to enhanced oxygen uptake which manifested itself in TPD spectra as a very significant increase in oxygen desorption to lower temperatures(Figure 1C); treatment with N₂O at lower temperatures was ineffectual in this respect (e.g. 293 K, Figure 1B). Furthermore, this oxygen population could not be generated by treatment with O_2 under any experimentally accessible conditions. Control experiments (Figure 2) demonstrated that the 700 K temperature threshold for the onset of measurable catalytically induced N₂O decomposition (depletion of gaseous N_2O and the appearance of gaseous N_2 and O_2) corresponded closely with that for catalyst oxygenation by N_2O (673 K). Indeed an actual maximum in the N_2O decomposition rate was observed at ~900 K (Figure 2), close to the temperature which was found to be most effective for catalyst oxygenation by N_2O (873 K, Figure 1).

These N₂O-activated catalysts exhibited significantly improved activity for C_2 hydrocarbon production in subsequent TPR experiments in which CH₄/He was passed over the

N₂O pre-oxidised catalyst. Figure 3B illustrates the behaviour of the signals at m/z 26 (C₂H₂⁺, predominantly ethene), m/z28 (C₂H₄⁺, ethene + ethane), and m/z 30 (C₂H₆⁺, ethane) which show the onset of C_2 production at ~850 K followed by an actual rate maximum at ~ 950 K which is just the temperature regime over which the N₂O-induced oxygen species are still present on the catalyst (Figure 1). By contrast, corresponding CH_4/He TPR measurements on an O_2 activated catalyst reveal a C₂ threshold at a substantially higher temperature (~980 K), and no low temperature C_2 peak whatever (Figure 3A). It is important to note that the m/z 28 and 30 signals observed here cannot be due to N₂ or NO evolved from the catalyst as a result of the N₂O pretreatment. Firstly, the m/z 28 and 30 signals follow the m/z 26 signal which is unambiguously diagnostic of C₂ hydrocarbons. Secondly, control experiments in which the N_2O pretreated catalyst was heated to 1080 K in He showed no detectable signals at m/z 28 and 30 over the whole temperature range.

The implication of these observations is that N_2O is capable of supplying a form of oxygen to the catalyst which cannot readily be supplied by O_2 itself. This oxygen species is stable to high temperatures and appears to be particularly active for the oxidative coupling of CH₄ to C₂ hydrocarbons. The result is that LiNiO₂ catalysts working with N₂O as oxidant are effective for the oxidative coupling of methane at temperatures which are very significantly lower than when O₂ is the gaseous oxidant. Other work^{4.5} has suggested that more than one kind of surface oxygen species can induce oxidative coupling of CH₄, and it has also been reported⁶ that the use of N₂O with Li-doped MgO catalysts can lead to the formation of an O⁻ species which is selective for coupling at lower temperatures but not at higher temperatures. Experiments are in progress to determine whether in the present case one is dealing with what might be principally a kinetic effect due to different dissociative chemisorption efficiencies, or whether different oxygen surface species are deposited by O_2 and N_2O .

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- 1 J. S. Lee and S. T. Oyama, Catal Rev. Sci. Eng., 1988, 30, 249.
- 2 R. K. Ungar, X. Zhang, and R. M. Lambert, *Appl. Catal.*, 1988, **42**, L1.
- 3 M. Hatano and K. Otsuka, Inorg. Chim. Acta, 1988, 146, 243.
- 4 D. J. Driscoll, W. Martir, J.-X. Wang, and J. Lunsford, J. Am. Chem. Soc., 1985, 107, 58.
- 5 K. Otsuka, A. A. Said, K. Jinno, and T. Komatsu, Chem. Lett., 1987, 77.
- 6 G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, J. Chem. Soc., Chem. Commun., 1987, 1388.