J. Chem. Soc., Faraday Trans. 1, 1989, **85**(2), 199–206

The Oxidative Coupling of Methane on Lithium Nickelate(III)

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Kinetic studies and isotopic exchange measurements (CH_4–CD_4 and $^{16}O_2$–$^{18}O_2$) of the oxidative coupling of methane over stoichiometric $LiNiO_2$ indicate a redox mechanism involving lattice oxygen atoms. The formation of C_2 products is second-order in methane, both in the presence and absence of gaseous oxygen. Methane is dissociatively adsorbed on Ni^{3+}—O^{2-} sites, and the rate-determining step is the coupling of adsorbed CH_3. Reduction of the catalyst by methane forms NiO, over which deep oxidation occurs. Adsorbed oxygen or gaseous oxygen is responsible for the deep oxidation.

The oxidative coupling of methane is a potentially attractive method for the production of ethylene from natural gas. Since Keller and Bhasin[1] reported the synthesis of C_2 compounds ($C_2H_6+C_2H_4$) by partial oxidation of methane over metal oxides, many groups have published preliminary results on catalytic activity and C_2 selectivity for this reaction.[2]

We have shown that Li-doped NiO gives fairly good yield of C_2 compounds and C_2 selectivity.[3] The reaction was suggested to proceed *via* the redox of surface lattice oxygen atoms of the oxides.[3,4] However, the fundamental studies carried out so far are not sufficient to clarify the mechanism of methane activation on solid surfaces. We now report kinetic studies on the oxidative coupling of methane over a stoichiometric solid solution of lithium and nickel oxide, $LiNiO_2$. The picture of methane activation and the detailed reaction mechanism will be discussed.

Experimental

The $LiNiO_2$ used was prepared by means of the impregnation method using powder NiO and aqueous solution of $LiNO_3$ (Ni : Li = 1 : 1). The Li-impregnated NiO was calcined in air at 673 K for 2 h and subsequently at 1073 K for 20 h. X.r.d. analysis for this sample showed the transformation to the homogeneous solid solution of Li and NiO, which is written by the formula $Li_x(Ni^{2+})_{1-2x}(Ni^{3+})_xO$.[4] Lattice parameters of this sample, $a = 2.900$ Å and $c = 14.25$ Å, assuming rhombohedral structure, suggested the formation of LiNiO (1 : 1) solid solution $Li^+Ni^{3+}O_2$.[5,6] The surface area of the sample was 0.33 $m^2\ g^{-1}$.

Kinetic studies were carried out using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure using helium as a carrier gas. The amount of catalyst used in the reactor was between 0.01 and 1.00 g. The volume of the reactor was 15.3 cm^3. The range of reactant flow rate was 20–150 cm^3 (s.t.p.) min^{-1}. The gas–solid reaction of methane with the catalyst and the CH_4–CD_4 exchange and oxygen tracer experiments were carried out using a closed gas-circulation apparatus of *ca.* 360 cm^3 dead volume. A small quantity of the gas in the system was sampled during the reaction and the relative quantities of the isotope-exchanged products were measured using a quadrupole mass spectrometer. The total amounts of isotopic methanes (CH_4+CH_3D+

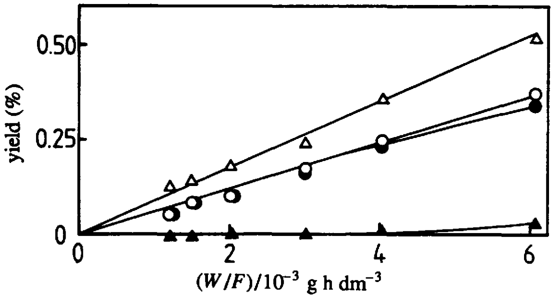


Fig. 1. Yields of products as functions of W/F. △, CO_2; ○, C_2 total; ●, C_2H_6; ▲, C_2H_4. $T = 973$ K, CH_4 pressure = 40.5 kPa, O_2 pressure = 20.3 kPa.

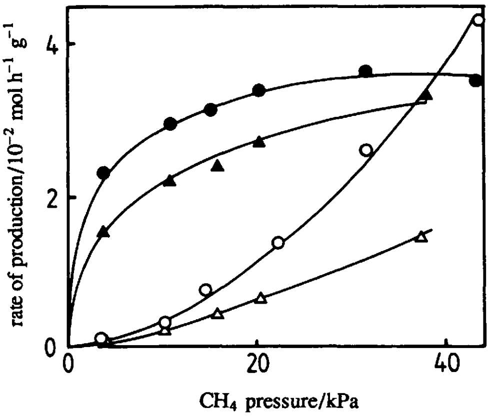


Fig. 2. Formation rates of C_2 and CO_2 as functions of CH_4 pressure. ●, CO_2 (973 K); ○, C_2 (973 K); ▲, CO_2 (953 K); △, C_2 (953 K). O_2 pressure = 5.01 kPa, $W/F = 1.67 \times 10^{-3}$ g h dm^{-3}.

$CH_2D_2 + CHD_3 + CD_4$) and oxygens ($^{18}O^{18}O + {}^{16}O^{18}O + {}^{16}O^{16}O$) were measured by gas chromatography. Thus the absolute amounts of each product were evaluated. The conversion of methane, the rates of formation of the products, the selectivities and the yields of the products were calculated on the basis of the carbon number of the reacted methane.

Results and Discussion

Kinetic Studies on Oxidative Coupling of CH_4 over $LiNiO_2$

The oxidation of methane over $LiNiO_2$ in temperature range 873–1023 K produced C_2H_6, C_2H_4, CO_2 and H_2O. Kinetic studies on this reaction were carried out using a fixed-bed reactor with the gas flow apparatus under the conditions where the conversion of O_2 was $< 5\%$.

Fig. 1 shows a plot of the yields of C_2 compounds and CO_2 as functions of W/F (= weight of catalysts/flow rate of reactants). The formation of ethylene was detected only at the $W/F > 3 \times 10^{-3}$ g h dm^{-3}. It is clear from the curves for C_2H_6 and C_2H_4 formation that C_2H_4 is formed successfully from C_2H_6 ($2CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4$). The straight lines from the origin for the yields of CO_2 and C_2 suggest that the formation of CO_2 is not ascribed to the oxidation of C_2 compounds, but to the oxidation of methane itself.

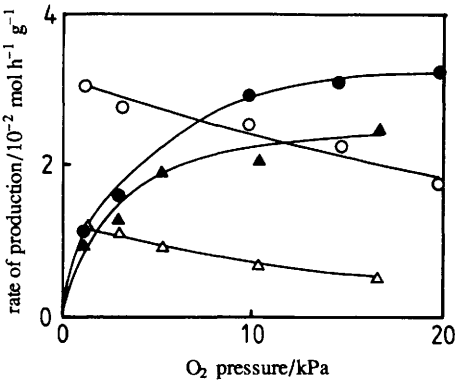


Fig. 3. Formation rates of C_2 and CO_2 as functions of O_2 pressure. ●, CO_2 (973 K); ○, C_2 (973 K); ▲, CO_2 (953 K); △, C_2 (953 K). CH_4 pressure = 40.5 kPa, $W/F = 1.67 \times 10^{-3}$ g h dm^{-3}.

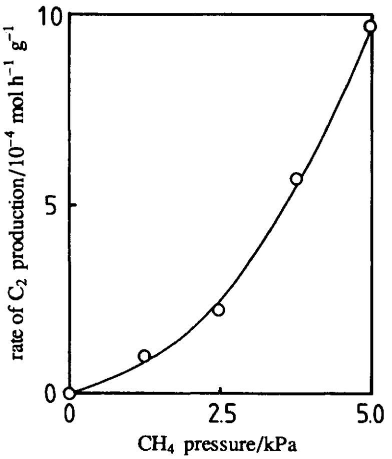


Fig. 4. Initial rate of formation of C_2 as a function of CH_4 pressure (gas–solid reaction at 973 K). $W = 1.00$ g.

Fig. 2 shows the rates of C_2 and CO_2 formation as functions of CH_4 pressure. The experiments were carried out at 953 and 973 K and at a constant pressure of oxygen (5.0 kPa). The results in fig. 2 show that the rate of formation of C_2 compounds depends roughly on the square of the CH_4 pressure. However, the rate of CO_2 formation does not change appreciably at pressures > 10 kPa. Thus the selectivity to C_2 hydrocarbons increases sharply with increasing methane pressure.

Fig. 3 shows the effect of oxygen pressure on the rates of formation of C_2 and CO_2. The rate of C_2 formation decreases gradually on increasing the oxygen pressure, but the rate of CO_2 formation increases with pressure. The decrease in the rate of formation of C_2 cannot be ascribed to the deep oxidation of C_2 because the latter reaction was not appreciable under the experimental conditions applied in this work (fig. 1). Rather, it may be ascribed to competitive adsorption of methane and oxygen on the active sites for C_2 formation.

It was shown previously[3] that the reaction of methane with the lattice oxygen atoms of $LiNiO_2$ produced C_2 compounds selectively. Therefore, the effect of methane pressure on the rate of the gas–solid reaction has been examined at 973 K in the absence of

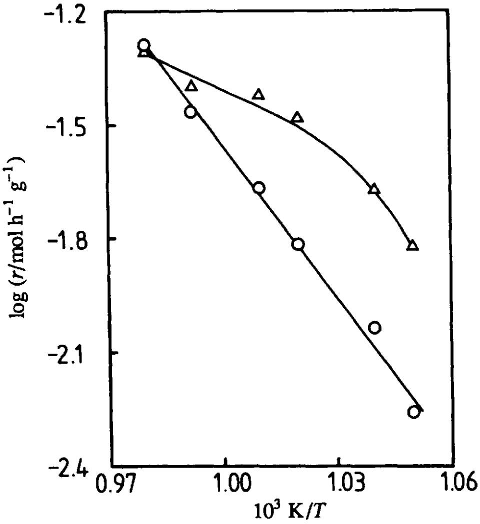


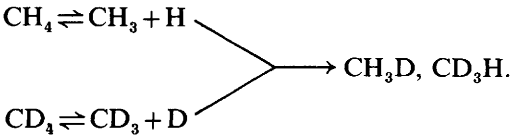
Fig. 5. Temperature effects on the formation rates of C_2 and CO_2. ○, C_2; △, CO_2. CH_4 pressure = 40.5 kPa, O_2 pressure = 20.3 kPa, $W/F = 1.67 \times 10^{-3}$ g h dm^{-3}.

gaseous oxygen. The C_2 compounds were produced very selectively (> 95%) in the early stages of the reaction (< 5 min). The initial rate of C_2 formation is plotted as a function of methane pressure in fig. 4; the results show that the rate depends on the square of methane pressure, similar to the results shown in fig. 2. Moreover, note that the rates of C_2 formation in the presence (fig. 2) and absence (fig. 4) of gaseous oxygen are approximately the same at the same methane pressure. These observations strongly suggest that the oxidative coupling of methane over $LiNiO_2$ proceeds *via* the reaction of CH_4 with surface lattice oxygen atoms.

Temperature effects on the rates of CO_2 and C_2 formation are shown in fig. 5. The straight line for the formation of C_2 compounds give an apparent activation energy of 250 ± 10 kJ mol^{-1}. The results in fig. 5 show that the C_2 selectivity increases sharply with a rise in temperature.

CH_4–CD_4 Exchange

Hydrogen exchange between CH_4 and CD_4 (1:1) on $LiNiO_2$ has been examined at 973 K. The kinetic curves for the distribution of deuterated methane are shown in fig. 6. The progress of the exchange reaction as indicated in fig. 6 suggests that methane is dissociatively adsorbed on the catalyst. Moreover, the kinetic curves suggest that the exchange occurs stepwise, because CHD_3 and CH_3D predominate over CH_2D_2:



$$\begin{tikzcd} CH_4 \rightleftharpoons CH_3 + H \arrow[dr] & \\ & CH_3D,\ CD_3H. \\ CD_4 \rightleftharpoons CD_3 + D \arrow[ur] & \end{tikzcd} \qquad (1)$$

The isotope effect by which CD_3H is formed in preference to CH_3D is not easily explained. The observation might be ascribed either to a higher surface concentration of CD_3 than CH_3 or to a higher concentration of H than D. Moreover, the formation of H_2O, HDO and D_2O may further complicate the situation.

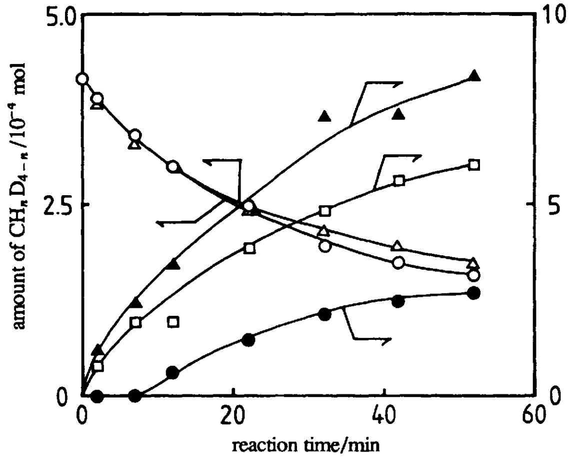


Fig. 6. CH_4–CD_4 exchange at 973 K. Initial pressure CH_4 = CD_4 = 2.7 kPa. ○, CH_4; △, CD_4; □, CH_3D; ●, CH_2D_2; ▲, CD_3H.

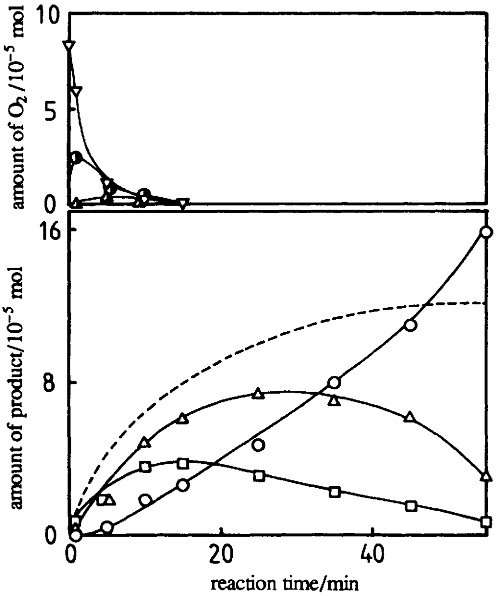


Fig. 7. Oxygen tracer experiments at 973 K. Initial reactants: CH_4 (5.3 kPa), $^{18}O^{18}O$ (0.53 kPa), $LiNiO_2$ (1.00 g). Upper plot: Changes in the amount of gaseous oxygen isotopes. ▽, $^{18}O^{18}O$; ◐, $^{16}O^{18}O$; ▲, $^{16}O^{16}O$. Lower plot: Changes in the amount of CO_2 isotopes. ○, $C^{16}O^{16}O$; △, $C^{16}O^{18}O$; □, $C^{18}O^{18}O$. Dotted curve: amount of C_2 formed.

Oxygen Tracer Experiments

The distribution of ^{18}O in the oxygen-containing products, *i.e.* CO_2 and H_2O, has been followed during the oxidative coupling of methane (5.3 kPa) with $^{18}O_2$ (0.53 kPa) as the initial gas mixture at 973 K using a closed gas-circulation apparatus. The ratio of the amount of gaseous oxygen to that in the catalyst at the starting point was roughly 6×10^{-3}. The kinetic curves of the $C^{16}O^{16}O$, $C^{16}O^{18}O$ and $C^{18}O^{18}O$ formed are shown in fig. 7. Since a considerable amount of CO_2 was captured in the catalyst,[4] the amounts

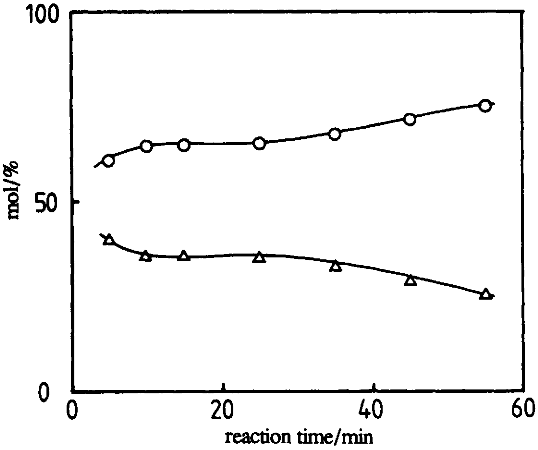


Fig. 8. Changes in the mole fractions of $H_2{}^{16}O$ and $H_2{}^{18}O$ formed during oxidation in fig. 7. ○, $H_2{}^{16}O$; △, $H_2{}^{18}O$.

of CO_2 isotopes shown in fig. 7 include both CO_2 on the catalyst and that in the gas phase, assuming the same isotopic compositions of CO_2 in both phases. Changes in the amounts of the gaseous oxygen isotopes are shown in the upper part of fig. 7. The dotted curve in fig. 7 shows the kinetic curve of the C_2 compounds produced. C_2H_6 was the main C_2 product in the early stages of the reaction. The results in the upper part of fig. 7 show that oxygen exchange between gaseous O_2 and $LiNiO_2$ occurs rapidly. All the oxygen in the gas phase was consumed in the oxidation of methane within 15 min. However, the rate of total CO_2 in the gas phase still increased after 15 min owing to the reaction of CH_4 with lattice oxygen atoms of the catalyst.

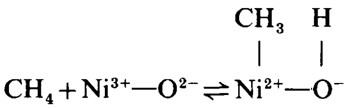
Fig. 8 shows the changes in the mole fractions of $H_2{}^{16}O$ and $H_2{}^{18}O$ in the gas phase measured at the same time during the oxidation of CH_4 in fig. 7. We confine our attention to the early stages of the reaction, at which point the products and the reduction of the catalyst do not seriously complicate the situation. Note that the ^{18}O-containing CO_2 ($C^{18}O^{18}O$ and $C^{18}O^{16}O$) are the main products in the early stages of the reaction (fig. 7). This observation clearly shows that the adsorbed or gaseous oxygen is responsible for the deep oxidation of methane to CO_2. On the other hand, the results in fig. 8 show the preferential contribution of lattice oxygen atoms to the formation of H_2O in comparison with the contribution of adsorbed oxygen (or gaseous oxygen).

Reaction Mechanism

As suggested earlier with regard to the results in fig. 1, C_2 compounds and CO_2 are produced concurrently from methane. The quite different pressure effects on the rates of formation of C_2 and CO_2 observed in fig. 2 and 3 strongly suggest that both reactions proceed *via* different reaction intermediates or on different active sites.

The observation that the rate of formation of C_2 products is second-order in methane pressure has not been reported previously.[2] This observation implies that the coupling of methyl groups adsorbed is the rate-determining step in the oxidative coupling of methane. On the basis of the kinetic results described earlier, we propose the following reaction mechanism.

The CH_4–CD_4 exchange experiments have suggested the dissociative adsorption of methane on $LiNiO_2$ (fig. 6). Therefore, let us hypothesize that this adsorption occurs readily on a pair of sites comprising $Ni^{3+}—O^{2-}$ on $LiNiO_2$ as follows:



$$CH_4 + Ni^{3+}—O^{2-} \rightleftharpoons \overset{CH_3}{\overset{|}{Ni^{2+}}}—\overset{H}{\overset{|}{O^-}} \qquad (2)$$

$$CH_3 + CH_3 \rightarrow C_2H_6. \qquad (3)$$

It is generally suggested that the vacant d-orbital of a transition-metal cation should make electrophilic attachment on the σ_{CH} orbital of methane, resulting in the breaking of the C—H bond. This C—H activation on $LiNiO_2$ must be promoted by the resulting formation of OH with the partner lattice oxygen anion of Ni^{3+}.

The initial rates of adsorption and desorption of CH_4 [eqn (2)] can be roughly estimated from the initial slopes of the kinetic curves in fig. 6, neglecting the isotopic effect of H and D. Assuming a steady-state concentration of methyl groups in the early stages of the reaction, the rates of adsorption and desorption were estimated to be 2.6×10^{-3} and 1.7×10^{-3} mol g^{-1} h^{-1}, respectively. The initial rate of C_2H_6 formation [eqn (3)] was 9.1×10^{-4} mol g^{-1} h^{-1} from the dotted curve in fig. 7. Note that the rates of the forward and reverse steps in eqn (2) are faster than the rate of C_2H_6 formation. When the migrations of CH_3 and H on the surface are slower than the adsorption and desorption rates in eqn (2), the true values of the latter two cannot be estimated by $CH_4—CD_4$ exchange experiments because the observable exchange rate cannot exceed the rates of migration of CH_3 (or CD_3) and H (or D). The adsorption and desorption rates estimated above are the lower limits for the rates of the both steps. Therefore, it seems reasonable to assume that reaction (2) is in equilibrium and the coupling reaction (3) is the rate-determining step. This assumption explains the observation that the rate of formation of C_2 compounds depends on the square of the methane pressure (fig. 2 and 3).

The large activation energy for the formation of C_2 compounds (fig. 5) implies that the bond dissociation energy of $CH_3—Ni^{2+}$ is fairly large, and so the surface migration of CH_3 groups must be restricted.

Oxygen Species Responsible for the Formation of C_2H_6 and CO_2

On the basis of the results of the oxygen-isotope experiments (fig. 7 and 8) we can comment further on the oxygen species responsible for the reaction. As described earlier, the selective formation of C_2H_6 occurs through reactions (2) and (3). Here, the lattice oxygen atoms of $LiNiO_2$ play an important role in the activation of methane on eqn (2). The formation of OH in eqn (2) would facilitate the forward reaction by lowering the activation energy. The OH formed in eqn (2) must be desorbed as water as follows:

$$2O^*H \rightarrow H_2O^* + O^* \qquad (4)$$

where O* is a lattice oxygen atom or oxygen originating from the lattice oxygen atoms. This is one reason why the mole fraction of $H_2{}^{16}O$ observed was greater than that of $H_2{}^{18}O$ in fig. 8. However, the amount of H_2O accompanied by deep oxidation of CH_4 was at least twice as large as the amount of H_2O from which hydrogen atoms had arisen through the initial abstraction from CH_4 in reaction (2). The abundance of $H_2{}^{16}O$ observed in fig. 8 can be explained by the assumption that the lattice oxygen atoms also oxidize the methane hydrogen during deep oxidation. However, we will not discuss this further, since the situation may be complicated by the possible occurrence of hydrogen migration on the surface.

The results in fig. 7 clearly indicate that CO_2 is generated *via* the reaction with adsorbed or gaseous oxygen. Thus C_2 compounds are produced with 100% selectivity in the absence of gaseous oxygen in the early stages of the reaction.[4]

The reduction of $LiNiO_2$ by CH_4 inevitably generates NiO according to the following stoichiometric reaction:[4]

$$2LiNiO_2+2CH_4 \rightarrow Li_2O+2NiO+C_2H_6+H_2O. \qquad (5)$$

The presence of gaseous oxygen is indispensable for regenerating $LiNiO_2$:[4]

$$Li_2O+2NiO+\tfrac{1}{2}O_2 \rightarrow 2LiNiO_2. \qquad (6)$$

We believe that the deep oxidation of methane occurs on a different active site, *i.e.* on NiO present on the surface under steady-state reaction conditions. In fact, NiO catalysed only the deep oxidation of methane under the experimental conditions applied in this work.

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Paper 7/2247; *Received* 23*rd December*, 1987