

Methane Adsorption on a Working Samarium Oxide Catalyst and its Role in Hydrocarbon Formation during High Temperature Partial Oxidation

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Although methane is strongly adsorbed on a samarium oxide catalyst at 700 °C, the adsorbed form does not participate directly in the formation of the hydrocarbon products of the partial oxidation reaction.

The catalysed reaction of methane with oxygen to form higher hydrocarbons represents an intriguing mechanistic problem. Ito *et al.*¹ first observed this reaction using a Li-doped MgO catalyst, and suggested that it involved the production of $\cdot\text{CH}_3$ radicals on Li^+O^- sites, which formed ethane by gas-phase dimerisation. This observation has been extended to a variety of catalysts, some of which (*e.g.* samarium oxide)² are much more active than Li/MgO and which obviously cannot contain these particular centres. Recently, carbene has been sugges-

ted as an intermediate in the reaction,³ but the observation of a CH_4/CD_4 isotope effect for the product formation has again been cited⁴ as supporting the involvement of methyl radicals.

A crucial step in the determination of any catalytic mechanism is the estimation of the extent of adsorption and, if possible, the nature of the adsorbed reactants. Isotope switching techniques, in which one labelled reactant replaces the normal species without disturbing the steady state of the reaction, are effective in obtaining such data.⁵ We have used

such methods to investigate the adsorption of methane on samarium oxide catalysts at temperatures required for hydrocarbon synthesis.

The apparatus consisted of a simple flow-through reactor holding 30 mg of Sm_2O_3 catalyst, a conventional gas feed and isotope switching system based on VALCO multiport valves, and a VG-SX200 mass spectrometer. A pulse of the isotopic species (CD_4 or $^{13}\text{CH}_4$) of approximately 14 s duration was used. A switching time of 0.2 s was achieved. All reagents were of high purity and the isotopic purity of the labelled materials was greater than 99%.

Figure 1 shows the transient for CD_4 (m/z 20) following a CH_4 to CD_4 switch at 700°C . It is obvious that CD_4 desorbs from the catalyst for a long time after the return to the normal isotopic form and the almost instantaneous flushing of the CD_4 from the dead volume of the reactor. A simple calculation gave 6×10^{20} for the number of adsorbed CD_4 molecules per g. This was independent of temperature in the range 500 – 700°C and is considered accurate to within a factor of 2. Its temperature independence suggests that the oxide surface is completely covered by adsorbed methane, both CH_4 and CD_4 as the CD_4 pulse cannot replace the entire methane pool. To put this number into perspective, at 750°C the net CH_4 conversion rate for the samarium catalyst was determined as approximately 2×10^{20} molecules $\text{s}^{-1} \text{g}^{-1}$.⁶

The adsorption of such an inert molecule on a low surface area oxide at high temperature is extraordinary, and probably involves partially or even wholly dissociated methane [equa-

tion (1)], the surface acting as a very strong base and the methane as a weak acid. The high temperatures involved are probably instrumental in forming a 'clean,' highly basic oxide surface, which in normal circumstances would be covered with carbon dioxide and water (hydroxyl) acting as comparatively strong acids. Support for this model is also provided by the observation⁶ that the reaction is strongly poisoned by the addition of carbon dioxide; this property is characteristic of strong base catalysts.⁷ An identical mechanism for the adsorption (or chemisorption) of methane and other alkanes has been recently suggested by Kembal *et al.*⁸ in connection with H/D exchange reactions over lanthana.

Amazingly, the appearance of the major products accessible to the technique was essentially instantaneous after the isotopic switches. For example, the data in Figure 1(e) and (f) show that C_2H_6 disappears (and C_2D_6 appears) with no perceptible delay. We make the following comments:

(1) The rate of formation of the species CD_3H [Figure 1(b)] rises instantly to a value which remains constant for the duration of the isotope switch. This result requires the presence of a large pool of [H] (CH_4 , H, H_2O , OH) on the catalyst surface, in a concentration not significantly depleted during the pulse. A lower limit estimate of this pool is 2×10^{19} molecules per g. Similarly, the slow decay of the species after the end of the CD_4 pulse indicates the adsorption of a form of CD_4 during the pulse.

(2) The rate of formation of D_2 reached a constant value immediately after the commencement of the pulse, but the HD formation increased slowly. This is attributed to the slow incorporation of [D] on the catalyst surface already containing [H].

(3) The rates of formation of D_2 and HD showed a delay following completion of the isotopic pulse. This delay represents less than 1.2% of the total D_2 (H_2) formed. This is

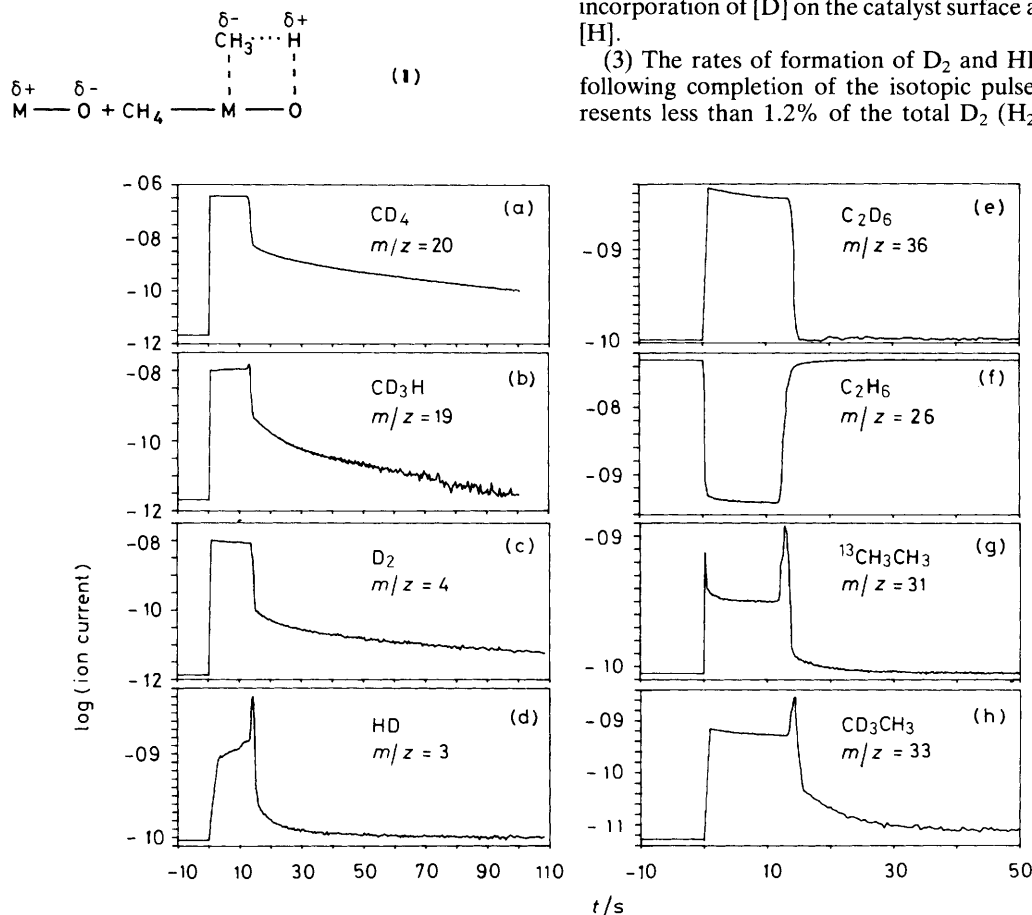


Figure 1. Isotope transients observed at 700°C . The reactant gas flow rate (s.t.p.) was $78 \text{ ml s}^{-1} (\text{g catalyst})^{-1}$ [10% O_2 in CH_4 (CD_4)]. Each curve represents 500–1000 data points. The switch to CD_4 [or $^{13}\text{CH}_4$ for (f) and (g)] occurred at zero time, the switch to the normal isotope approximately 14 s later.

consistent with the presence of a small amount of CD₄ desorbing from the catalyst surface [Figure 1(a)] and entering the gas-phase reaction sequence.

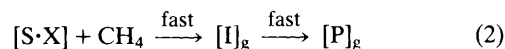
(4) The D₂ formation rate after the commencement of the pulse is approximately an order of magnitude greater than that of HD. If the pool of [H] available on the surface is indeed large as already indicated, this result implies the absence of significant involvement of these [H] species in hydrogen formation. The same comment applies to the formation of the other mixed product forms ¹³CH₃¹²CH₃ and CD₃CH₃ [Figure 1(g) and (h)].

(5) The rates of formation of C₂D₆ (C₂H₆) show no perceptible delay following the termination of the appropriate pulse. This result must mean that the appearance of these species (or their precursors) in the gas phase is not dependent on their desorption from the catalyst surface.

(6) The rates of formation of the mixed dimeric products [HD, ¹³CH₃¹²CH₃, and CD₃CH₃; cf. Figure 1(d), (g), and (h)] show sharp peaks immediately after the end of the pulse of the labelled species. This effect is caused by the reaction of the labelled and normal forms as the partially mixed boundary moves through the reactor. It is important to note that isotope exchange occurs, provided that conditions are such that the two species are present in the reactor.

The interpretation of the foregoing data presents a basic dilemma, *viz.* how can a fully deuteriated species (*e.g.* D₂ or C₂D₆) be formed 'instantaneously' following the isotope switch when the catalyst surface is covered with protium-containing species which are desorbed much more slowly than the deuteriated products are formed? The only plausible answers appear to be either (i) that product formation does not occur on sites which strongly adsorb methane, but that a completely separate pool of sites is present on which reactant adsorption/desorption and product formation are very fast; or (ii) [shown schematically in equation (2)] that there is a very fast interaction between the surface-adsorbed species (S·X) and the gas phase CD₄ (CH₄), resulting in the formation of a gas phase intermediates [I]_g which rapidly react further by

dimerisation or by reaction with molecular methane, to give the stable reaction products [P]_g. In this scheme, the isotopic form of the gas-phase reactants would be instantly reflected in the products.



While substantial evidence exists that the intermediates [I]_g in the foregoing scheme are free radicals (CH₃, H, *etc.*),^{1,9-11} it is likely that ionic species are involved in their formation. The involvement of ions would help to account for the very high catalyst reactivity, which at first sight is difficult to reconcile with a mechanism involving the homolytic rupture of C-H bonds, which would be relatively slow even at these high temperatures. A more detailed analysis of these results, and those of a similar study tracing ¹⁸O₂ to the oxygenated products, will be published elsewhere.

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