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A Low Temperature Reaction Sequence for Methane Conversion

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Surface carbonaceous intermediates produced from methane are shown to produce small alkanes upon hydrogenation below 400 K.

Current practice to convert natural gas to higher hydrocarbons proceeds by the indirect route in which natural gas is first converted to synthesis gas at a high temperature.[1] Subsequently, hydrocarbons are produced in a low temperature exothermic process from synthesis gas.[2,3] Direct methane conversion, like pyrolysis to acetylene and benzene, can only operate at temperatures above 1200 K.[4,5] Oxidative coupling of methane to ethylene has been proposed as a promising alternative route[6–11] and proceeds at temperatures between 850 and 1200 K.

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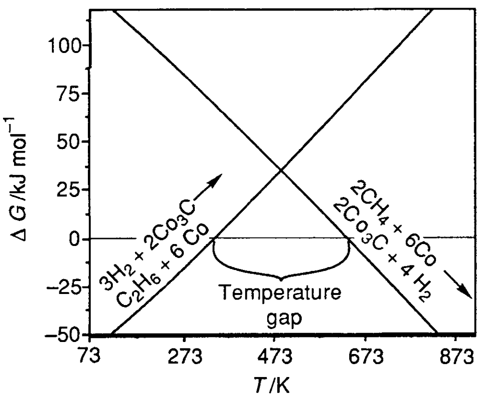

Fig. 1 Gibbs free energies as a function of the temperature for the decomposition of methane on cobalt and the hydrogenation of cobalt carbide to ethane

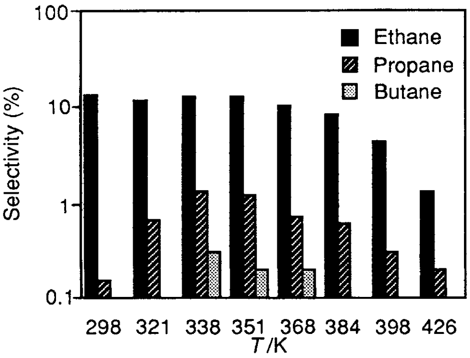

Fig. 2 Product distribution dependence on the hydrogenation temperature of C_α deposited from methane at 763 K on a 5% Ru/SiO$_2$ catalyst

Of interest are recent experiments demonstrating that hydrocarbon formation is possible at low temperature, once methane is activated.[12,13] Here we report the formation of lower alkanes from methane at atmospheric conditions in a two-step route in which methane is thermally activated. At a temperature between 500 and 800 K methane is decomposed by a group VIII metal catalyst into hydrogen and different carbide or graphite surface intermediates.[14–16] Subsequently a particular surface carbonaceous intermediate produces higher hydrocarbons upon hydrogenation at 300–400 K.

The temperature difference between the two reaction steps is a thermodynamic stipulation. This is illustrated in Fig. 1 for the case where the reaction sequence involves bulk cobalt carbide formation. The heat of formation of surface carbide is usually higher which shifts the lines in Fig. 1 to lower temperature. For bulk cobalt carbide the temperature gap between the two reaction steps is 282 K at standard pressure.

The transition metal catalysts studied were prepared by incipient wetness impregnation of silica (Grace 332, surface area = 240 m^2 g^{-1}) from an aqueous solution of their nitrates or chlorides. The catalysts were dried at 383 K. Before each experiment the catalysts were reduced *in situ* between 600 and 800 K in hydrogen.

Methane decomposition was performed on 300 mg of the catalyst in a plug flow reactor, from a pulse of 45 ml min^{-1} of 0.5% methane in helium at temperatures between 473 and 823 K. After methane decomposition the catalyst was cooled in 100 s below 423 K to avoid 'ageing' of the surface carbon species. After cooling surface carbon was hydrogenated to higher hydrocarbons in a flow of 22.4 STP ml min^{-1} of hydrogen around 370 K at 1 atm.

Methane decomposition on reduced transition metal catalyst can result in three different kinds of carbonaceous surface species as identified with NMR[17] and atomic emission spectroscopy (AES).[18,19] They can be distinguished by their different hydrogenation temperatures.[20] Carbidic (C_α) surface carbon can be hydrogenated below 400 K and is most suitable for the formation of C_2^+ hydrocarbons. A less reactive amorphous carbonaceous layer (C_β) is hydrogenated around 500 K and produces only traces of C_2^+ hydrocarbons. Unreactive graphitic carbon (C_γ) reacts above 650 K to produce only methane.

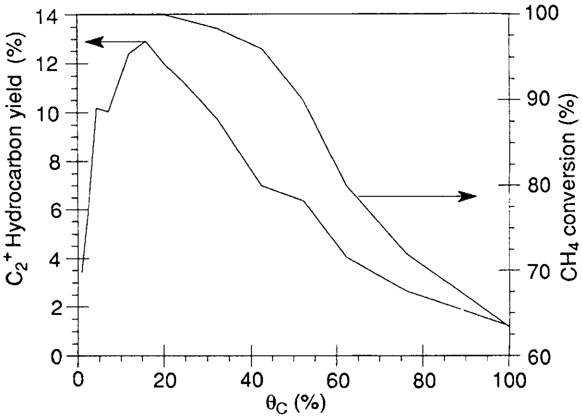

Fig. 3 Methane conversion during decomposition at 730 K and the yield for the formation of C_2^+ hydrocarbons at 368 K as a function of the carbon surface coverage (θ_c) on a 5% Ru/SiO$_2$ catalyst. Different surface carbon coverages were created by varying the methane adsorption time.

Table 1 Chain-growth probability α to form C–C bonds from surface carbon from methane upon hydrogenation at 368 K, as measured for silica-supported catalysts

Fe 0	Co 0.20	Ni 0.09	Cu 0
Ru 0.15	Rh 0.02	Pd 0	Au 0

For C_2^+ hydrocarbon formation it is important to have a high selectivity for C_α carbon formation. This can be achieved at a low carbon surface coverage.

As predicted by thermodynamics the temperature at which C_α is hydrogenated, is an important parameter determining the selectivity for the formation of C_2^+ hydrocarbons (Fig. 2). By raising the temperature from 298 K more surface carbon becomes hydrogenatable which results in an enhanced chain-growth selectivity. At temperatures above 400 K non-selective C_β intermediates are hydrogenated increasing methane selectivity.

The mechanism for C–C bond formation from surface carbon from methane, is thought to be similar to that occurring in the Fischer–Tropsch reaction from surface carbon from CO.[21] Reactivity of the CH$_x$ surface intermediates formed from CO and CH$_4$ appear to be closely related. The chain-growth probability α depends on the metal–carbon bond strength[22] and its maximum at cobalt and ruthenium as shown in Table 1.

As the data for the transition metals of the first row show, the Sabatier principal applies. The metal–carbon bond strength decreases going to the right in the same row of the periodic table.[23,24] An optimum metal–carbon bond strength for carbon–carbon bond formation is found. When the metal–carbon bond strength is too low (Ni, Cu) methanation is rapid. When the metal–carbon bond strength is too high (Fe) no low temperature carbide hydrogenation is possible.

The overall yield for formation of C_2^+ hydrocarbons from methane is controlled by the conversion of methane during decomposition, the selectivity for C_α surface carbon formation and the chain-growth probability upon hydrogenation. These

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parameters are a function of the carbon surface coverage as shown in Fig. 3.

The maximum overall C_2^+ hydrocarbon yield of 13% is obtained at a carbon surface coverage of 18%. Below this carbon surface coverage methane can be converted by 100% into surface carbonaceous species and hydrogen. The overall yield of 13% is of the same order as that obtained with high temperature pyrolysis, while oxidative coupling can result in a yield that is twice as high. However, the low temperature conversion route does not involve the use of oxygen.

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