

## Synthesis of Hydrocarbons from Methanol on Cobalt Catalysts: a Tracer Study

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Tracer experiments using methanol and deuteriated syngas indicate that methyl surface species are formed during the condensation of methanol into hydrocarbons on metallic catalysts.

The reaction of methanol on cobalt catalysts at 200 °C and atmospheric pressure gives rise to a mixture of saturated hydrocarbons whose composition is roughly the same as that obtained with synthesis gas of similar stoichiometric composition.<sup>1,2</sup> This condensation may be due either to a preliminary decomposition of methanol into a CO + 2 H<sub>2</sub> mixture or to another type of reaction in which the methanol (or a part of it) acts as a chain initiator in the polymerisation of C<sub>1</sub> species: it is known from the experiments of Emmett *et al.*<sup>3</sup> using labelled ethanol that alcohols can be incorporated into the carbon chain during the Fischer–Tropsch synthesis. In order to obtain more information on these possible reaction pathways, methanol and deuteriated syngas were used simultaneously and hydrogen repartition in the resulting hydrocarbons was measured.

In a typical experiment, run at 200 °C under atmospheric pressure, the reactor was loaded with 20 g of a Co/Al<sub>2</sub>O<sub>3</sub> catalyst [2 g of Co as Co<sub>2</sub>(CO)<sub>8</sub>] and the molar feed composition adjusted to the ratio CO : D<sub>2</sub> : MeOD = 1 : 2 : 0.1, the hourly space velocity being equivalent to 0.15 dm<sup>3</sup> of carbon monoxide per gram of metallic cobalt per hour. Samples of the light, saturated hydrocarbons (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>) were collected by gas chromatography and the deuterium content was calculated from mass spectrometric analysis. The results obtained are summarized in Table 1.

Methane was obtained in perdeuteriated form only, and was probably produced by reduction of surface carbon species resulting from carbon monoxide dissociative adsorption; the C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> hydrocarbons, however, have a significantly larger hydrogen content than that expected from a random

**Table 1.** Isotopic distribution of light hydrocarbons.<sup>a</sup>

Methane			Ethane			Propane			Butane		
CD <sub>4</sub>	CD <sub>3</sub> H	CH <sub>4</sub>	C <sub>2</sub> D <sub>6</sub>	C <sub>2</sub> D <sub>3</sub> H <sub>3</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> D <sub>8</sub>	C <sub>3</sub> D <sub>5</sub> H <sub>3</sub>	C <sub>3</sub> D <sub>2</sub> H <sub>6</sub>	C <sub>4</sub> D <sub>10</sub>	C <sub>4</sub> D <sub>7</sub> H <sub>3</sub>	C <sub>4</sub> D <sub>6</sub> H <sub>4</sub>
100	—	—	35.7	20.1	44	67	9.2	23.8	42.2	31.1	26.7

<sup>a</sup> Conversions, CO: 50%; MeOD: 50%. Selectivity, C<sub>1</sub>: 30.9%; C<sub>2</sub>: 6.6%; C<sub>3</sub>: 16.6%; C<sub>4</sub>: 12.0%; >C<sub>4</sub>: 34%.

distribution of hydrogen introduced with methanol (10%) where the methanol simply decomposes on the catalyst. For example, the ethane fraction contains amounts of C<sub>2</sub>D<sub>3</sub>H<sub>3</sub> and C<sub>2</sub>H<sub>6</sub>. This result is in agreement with the participation of alkyl groups in the chain initiation and the final step. This is confirmed by analysis of propane and butane which are found to contain a large amount of CH<sub>3</sub> together with some H<sub>4</sub> species indicating the possibility of carbene species originating from the alkyl group. The reverse experiment using CD<sub>3</sub>OH + CO + 2 H<sub>2</sub> in the same ratio as in the above-mentioned runs confirms these results as far as methane is concerned (in this case, the hydrocarbon is obtained as CH<sub>4</sub> only) but unfortunately some interference with residual peaks in the mass spectrum (O<sub>2</sub>, CO<sub>2</sub>, Ar) prohibits a detailed analysis of the deuterium content in the C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> hydrocarbons.

From these results it can be concluded that the condensation of methanol into hydrocarbons on metallic catalysts is not a preliminary retrodecomposition of this alcohol into CO and H<sub>2</sub> followed by a Fischer-Tropsch synthesis but proceeds, at

least in part, through the participation of methyl surface species.

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