

## Cobalt Catalysts for the Liquid Phase Synthesis of Light Olefins from CO and H<sub>2</sub>

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**Summary** Methane and a C<sub>2</sub>—C<sub>6</sub> cut containing up to 75% olefins are synthesized from CO and H<sub>2</sub> at 199 °C and under atmospheric pressure with a catalyst prepared by the reduction of cobalt(II) acetylacetonate with triethylaluminum with an alkylterphenyl solvent

SUPPORTED cobalt catalysts are efficient for the synthesis, in the gas phase, of hydrocarbons from CO and H<sub>2</sub>. The products are n-alkanes whose molecular weight range is large, except if the porosity of the support is controlled and if the amount of cobalt is not too high.<sup>1</sup>

We report the preparation of a highly dispersed cobalt catalyst for the synthesis of light hydrocarbons in the liquid phase. Moreover, with this catalyst, large amounts of olefins are obtained which is unusual for cobalt catalysts. Up to now, good selectivities for low molecular weight olefins have been reported, in the main, only with iron-based catalysts prepared either by conventional techniques<sup>4</sup> or by decomposition of iron carbonyls<sup>5,6</sup>

In a typical experiment cobalt(II) acetylacetonate (2.182 g) was treated with triethylaluminum<sup>3</sup> (0.7 g) in dry benzene (50 cm<sup>3</sup>) under a stream of hydrogen, after addition of Et<sub>3</sub>Al, the H<sub>2</sub> stream was replaced for a few minutes by a stream of butadiene and finally the reactor was filled with the synthesis gas (CO, H<sub>2</sub>). The alkylterphenyl (75 cm<sup>3</sup>)† was introduced and the benzene and the products of reduction were slowly distilled off by heating up to 190 °C. Synthesis gas was then circulated through the liquid phase in the closed reactor and water continuously evacuated. In order to restore the vessel to atmospheric pressure, a measured quantity of either N<sub>2</sub> or fresh synthesis gas was introduced so that the rate of consumption of the gas could be measured. Analyses were performed in the gas phase by g.c. and the carbon balance was estimated using an internal standard. A blank experiment with H<sub>2</sub>(N<sub>2</sub>:H<sub>2</sub> = 1:2) shows that hydrogenolysis appears, in fact, to be negligible when using an alkylterphenyl solvent [2.4 × 10<sup>-5</sup> g-atom C h<sup>-1</sup> (g Co)<sup>-1</sup>]

† The alkylterphenyl used was obtained by alkylation of a mixture of terphenyl isomers by ethylene with aluminum chloride (R. Ouliac, thesis, University of Poitiers, 1971)

TABLE. Rates of formation and yields of olefins (only n-olefins are produced) for various compositions of synthesis gas. ( $T$  193—199 °C,  $P$  1 atm, mass of catalyst 0.5 g of cobalt, reaction time 1 h.)

Synthesis gas	Rate of formation [g atom C h <sup>-1</sup> (g Co) <sup>-1</sup> ]		Yield/%					% Olefins in C <sub>2</sub> —C <sub>6</sub> hydrocarbons
	Hydrocarbons	Olefins	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>12</sub>	
1 CO, 1 H <sub>2</sub>	4.4 × 10 <sup>-4</sup>	2.00 × 10 <sup>-4</sup>	3.2	16.1	13.2	8.6	4.3	74.7
1 CO, 2 H <sub>2</sub>	5.6 × 10 <sup>-4</sup>	1.94 × 10 <sup>-4</sup>	1.9	13.6	9.9	6.5	2.6	63.4

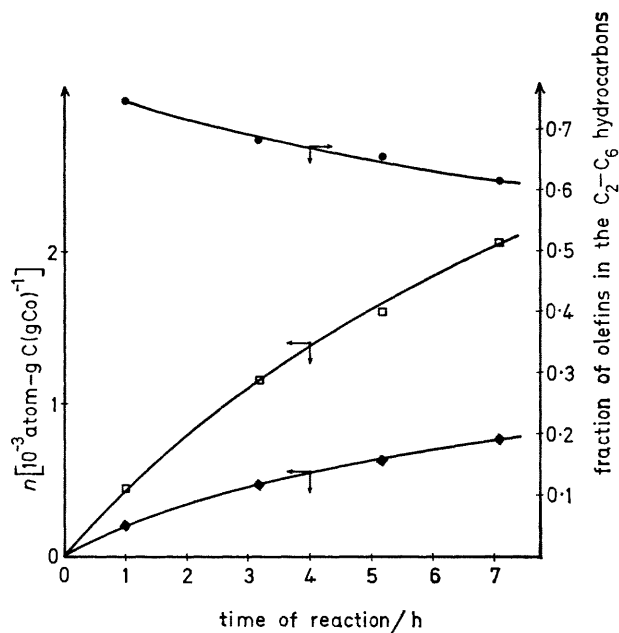


FIGURE. Amounts  $\{n$ , expressed as converted CO [atom-g C (g Co)<sup>-1</sup>]} of hydrocarbons (□) and olefins (◆) produced and the fraction of olefins in the C<sub>2</sub>—C<sub>6</sub> hydrocarbons (●) vs. time of reaction. (CO:H<sub>2</sub> 1:1,  $T$  199 °C,  $P$  = 1 atm, mass of catalyst 0.5 g of cobalt in suspension.)

Typical values of the activities and the selectivities are given in the Table and the variation of the amounts of products vs. time are given in the Figure.

No hydrocarbon with a molecular weight above C<sub>6</sub> was detected as in previous experiments with supported catalysts,<sup>3</sup> which appears to be an effect of the use of a solvent, but the selectivity towards the production of olefins is a property of this type of catalyst. The activity remains stable after a number of runs and the selectivity in olefins remains high even after many hours of reaction with the same mixture.

The alkylterphenyl is a good solvent compared to others such as decalin, for which the rate of hydrogenolysis is too high, or trichlorobenzene, which inhibits the reduction of CO.

These new catalytic properties of cobalt obtained by the reduction of a complex could be due to the high dispersion of the catalyst. The nature of the cobalt species is not yet well defined (metallic cobalt or cobalt-alumina), but a decrease in the dispersion could explain the slight decrease of the activity.

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