Cobalt Catalysts for the Liquid Phase Synthesis of Light Olefins from CO and H_2

By MICHEL BLANCHARD and DOMINIQUE VANHOVE
(*Laboratoire de Chimie XI, E R A* 371, *Faculté des Sciences*, 40, *Avenue du Recteur Pineau*,
86022 *Poitiers Cédex, Poitiers, France*)

and FRANCIS PETIT and ANDRE MORTREUX
(*Laboratoire de Chimie Organique Appliquée, E R A* 458, *E N S C L B P* 40, 59650 *Villeneuve d'Ascq, France*)

Summary Methane and a C_2—C_6 cut containing up to 75% olefins are synthesized from CO and H_2 at 199 °C and under atmospheric pressure with a catalyst prepared by the reduction of cobalt(II) acetylacetonate with triethylaluminium with an alkylterphenyl solvent

SUPPORTED cobalt catalysts are efficient for the synthesis, in the gas phase, of hydrocarbons from CO and H_2 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 [1]

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[4] or by decomposition of iron carbonyls [5,6]

In a typical experiment cobalt(II) acetylacetonate (2·182 g) was treated with triethylaluminium[2] (0·7 g) in dry benzene (50 cm^3) under a stream of hydrogen, after addition of Et_3Al, the H_2 stream was replaced for a few minutes by a stream of butadiene and finally the reactor was filled with the synthesis gas (CO, H_2) The alkylterphenyl (75 cm^3)† 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_2 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 $H_2(N_2:H_2 = 1:2)$ shows that hydrogenolysis appears, in fact, to be negligible when using an alkylterphenyl solvent [$2·4 \times 10^{-5}$ g-atom C h^{-1} (g Co)$^{-1}$]

---

† The alkylterphenyl used was obtained by alkylation of a mixture of terphenyl isomers by ethylene with aluminium chloride (R. Oulіac, 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.)

	Rate of formation [g atom C h^{-1} (g Co)$^{-1}$]		Yield/%					% Olefins in C_2—C_6 hydrocarbons
Synthesis gas	Hydrocarbons	Olefins	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	
1 CO, 1 H_2	$4·4 \times 10^{-4}$	$2·00 \times 10^{-4}$	3·2	16·1	13·2	8·6	4·3	74·7
1 CO, 2 H_2	$5·6 \times 10^{-4}$	$1·94 \times 10^{-4}$	1·9	13·6	9·9	6·5	2·6	63·4

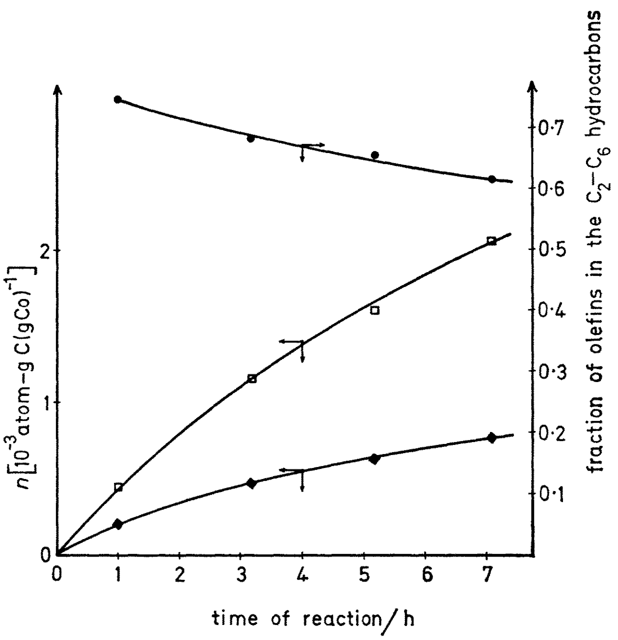

FIGURE. Amounts {*n*, expressed as converted CO [atom-g C (g Co)$^{-1}$]} of hydrocarbons (□) and olefins (◆) produced and the fraction of olefins in the C_2—C_6 hydrocarbons (●) *vs.* time of reaction. (CO : H_2 1 : 1, *T* 199 °C, *P* = 1 atm, mass of catalyst 0·5 g of cobalt in suspension.)

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_6 was detected as in previous experiments with supported catalysts,[3] 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.

(*Received*, 20*th June* 1980; *Com.* 669.)

[1] D. Vanhove, P. Makambo, and M. Blanchard, *J. Chem. Soc., Chem. Commun.*, 1979, 605.
[2] M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, 1963, **85**, 4014.
[3] M. Blanchard, D. Vanhove, and A. Derouault, *J. Chem. Res.* (*S*), 1979, 404; (*M*), 1979, 4756.
[4] B. Bussemeier, C. D. Frohning, and B. Cornils, *Hydrocarbon Process.*, 1976, **55**, 105.
[5] H. H. Storch, *Adv. Catal.*, 1948, **1**, 115.
[6] D. Commereuc, Y. Chauvin, F. Hugues, and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 1980, 154.