Selective Catalytic Synthesis of Linear Paraffins from CO and H_2 over Cobalt Supported Catalysts

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Summary Cobalt catalysts, prepared from cobalt carbonyl and alumina, produce from CO and H_2 linear paraffins whose molecular weights depend on the porosity of the support.

SINCE the early experiments of Fischer and Tropsch, cobalt catalysts have been used to produce linear paraffins from CO and H_2. However, the molecular weight range is large (C_2—C_{20}) when conventional techniques for preparation of the catalysts, such as precipitation and reduction, are used.[1] This molecular weight distribution, whose mathematical expression has been established,[2] was recently compared to that obtained in polymerisation.[3]

We report the preparation and properties of cobalt catalysts which produce mainly linear paraffins, whose molecular weight distribution may be chosen according to the structure of the support. Solutions of octacarbonyldicobalt in pentane[4] were used to impregnate calcined samples of alumina in order to obtain a 2% loading after evaporation of the solvent and decomposition under a slow stream of hydrogen at 200 °C. The support samples used were Spheralite alumina carriers, obtained by dehydration of alumina hydroxides above 450 °C, of known surface area (obtained from the nitrogen adsorption isotherm and the pore size distribution, determined by a picometric method using mercury) (Rhône-Poulenc). All the experiments were carried out at 200 °C with a CO:H_2 ratio of 1:2.

In the Figure the distribution of the chain lengths of the hydrocarbons is shown as obtained with alumina samples of different pore diameter, the $W:F$ ratio being the same for all experiments (W = mass of cobalt, F = molar flow of CO). As a reference, the distribution obtained with a catalyst in which the alumina is the same but the amount of metal is larger is also reported (run 1) in order to present a typical 'Schulz-Flory' distribution; in this case, the conversion is markedly increased but the same selectivities are obtained with lower $W:F$ ratio.

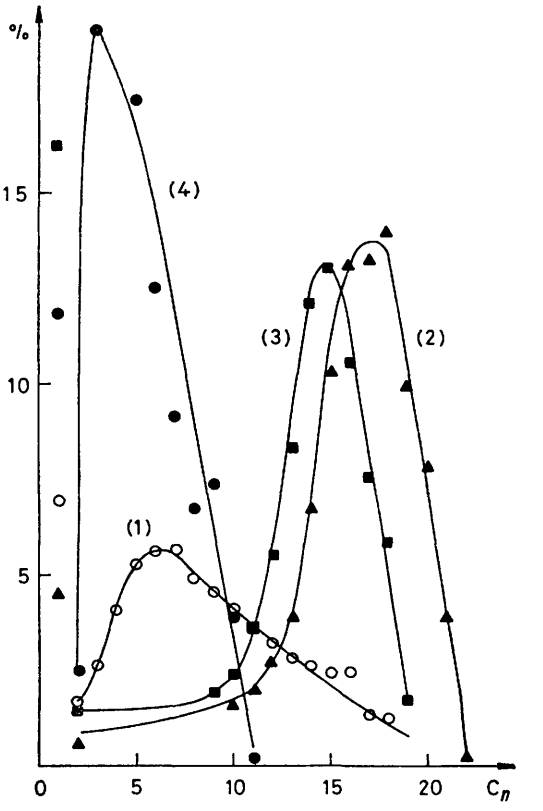

FIGURE. Selectivity of C_n hydrocarbons based on CO conversion: T = 200 °C; W/F = 50 g Co h/mol CO. (1) 5·3% Co on alumina SCS 9, 8 $m^2 g^{-1}$; mean pore radius 3000 Å; 66% CO conversion (identical at 40% CO conversion). (2) 1·9% Co on alumina SCS 9, 17% CO conversion. (3) 2% Co on alumina SCS 59, 90 $m^2 g^{-1}$; mean pore radius 300 Å; 16% Co conversion. (4) 2% Co on alumina SCS 350, 325 $m^2 g^{-1}$; mean pore radius 65 Å; 16% CO conversion. For runs 2—4 the same distributions were observed for higher CO conversions.

It appears that the smaller the pore diameter the lighter the hydrocarbons produced since with alumina SCS 350 (average pore diameter 65 Å) 80% of the linear paraffins obtained were in the C_3—C_{10} range, but with the largest pores this range was C_{14}—C_{21}. When the amount of cobalt is increased the pore size of the support is no longer important and a regular distribution of molecular weights is obtained. This can be explained by diffusion effects which must therefore be as important as other factors in determining selectivity.

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