Selective Fischer–Tropsch Synthesis of Hydrocarbons: Particle Size Effect of Ruthenium Metal in Faujasite-type Zeolites

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Summary Selective synthesis of hydrocarbons from CO and H_2 over RuY zeolites shows a drastic decline in chain growth probability after C_5 or C_{10}, depending upon the particle size of the Ru metal.

Recently Nijs *et al.*[1] reported on non-Schulz–Flory (S.F.) kinetics in Fischer–Tropsch (F.T.) synthesis of hydrocarbons over RuNaY-zeolite. The sudden drop of chain growth probability above C_9 was tentatively assigned to an effect exerted by the cage dimensions in the zeolite. This surprising behaviour has been confirmed for iron-loaded Y zeolites.[2] Since non-S.F. distributions are the key to the development of more selective F.T. catalysts, the nature of this 'cage effect' was investigated further.

RuNaY-zeolites reduced in hydrothermal conditions were found to be susceptible to hydrolysis by water.[3] This resulted in the formation of holes in the zeolite crystals, which preferentially filled up with metal. In this way a very narrow metal particle size distribution was obtained,[3] never exceeding 4 nm. A convenient method for characterizing Ru metal particle sizes in zeolites is temperature programmed oxidation (TPO). Ru metal in RuNaY gives a sharp maximum at 593 K in the rate of uptake of oxygen during TPO. When used as a catalyst in F.T. synthesis it is product limiting at a chain length of C_{10}.[1]

In order to restrict the metal particle size to the dimensions of the supercage a steam-stable RuLaY-zeolite was prepared, containing 2·0% by weight of Ru. The maximum in TPO was now found at 496 K, indicating a smaller average size of the Ru metal particles. In a F.T. experiment (space velocity, 0·8 s^{-1}; pressure, 1,420 kN m^{-2}; temperature, 525 K; H_2/CO molar ratio, 1·5) CO conversion was 25%. The product distribution after 60 min on stream is shown in the Figure. In this case, a distinct chain length limitation is observed at C_5, where the chain growth probability drops to zero. This distribution resembles a theoretical product distribution based on the S.F. law with a degree of polymerization of 3·5 and the absence of sites capable of producing chains containing more than 5 carbon atoms.

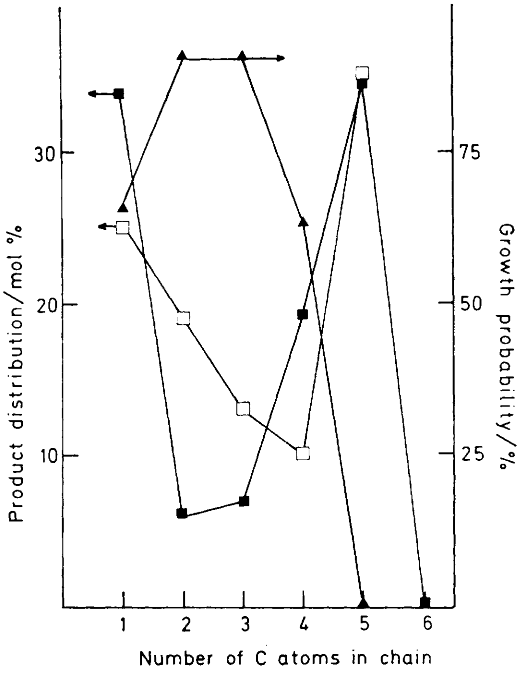

FIGURE. Product distribution on $Ru_{2\cdot0}$LaY zeolite (■). Theoretical product distribution with presumed chain length limitation at C_5 and a polymerisation degree 3·5 (□). Chain growth probability on $Ru_{2\cdot0}$LaY (▲).

It has already been shown[1] for RuNaY that the product limitation cannot be the result of a secondary cracking or hydrocracking reaction. Dec-1-ene was passed over RuLaY (pressure, 338 kN m^{-2}; space velocity 13·5 s^{-1}; temperature, 525 K) since 1-olefins are known to be primary products.[4] Under these conditions dec-1-ene was not cracked but underwent double bond and *cis–trans* isomerization (70%) or skeletal isomerization (20%).

Therefore, the limit imposed by the Y-zeolite on the size of the F.T. products is the result of the particle size of the ruthenium metal in this zeolite. This note definitely shows that the larger the Ru metal particles, the longer the carbon chains desorbing out of the pores. The sudden drop in chain growth probability is most probably related to a very narrow metal particle size distribution which is a specific property of the zeolite. Selective synthesis of F.T. products is expected to be much more difficult on supports where a broad Gaussian distribution of metal particles is obtained.

The key factor in making tailored zeolite based F.T. catalysts seems to be their steam stability which determines the final size of the metal particles and which in its turn fixes the upper size of the product.

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