Chain Limitation of Fischer–Tropsch Products in Zeolites

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Summary Fischer-Tropsch synthesis on RuY-molecular sieves shows a non-linear Schulz–Flory plot and a drastic decline in chain growth probability after C_{10}; thus, pure dimensions in zeolite-based catalysts are capable of limiting reaction product chain growth.

Recent research in Fischer–Tropsch synthesis has been aimed mainly at improving product selectivity. It appears that the molecular weight distribution of the products is dominated by a chain growth mechanism, which can be described by a Schulz–Flory equation.[1] Attempts to restrict the size of the Fischer–Tropsch products over catalysts exhibiting Schulz–Flory kinetics result in a dramatic increase in C_1 products. Molecular sieve supported metals are able to produce a non-Schulz–Flory product distribution.

It occurred to us that zeolite cages should be very efficient in limiting the size of the Fischer–Tropsch products. In order to verify this, Ru metal was encaged in zeolite Y. Ruthenium metal is known to show excellent Fischer–Tropsch activity and an extraordinary capacity to induce hydrocarbon chain growth.[2] Moreover, ruthenium appears to be the only Fischer–Tropsch active metal that can be easily kept in the zeolite cages. This is necessary since Ru metal outside the zeolite is expected to behave as on classical supports, forming high molecular weight products. In this way a possible 'cage effect' exerted by the zeolite would not be detected.

A RuNaY zeolite, with 5·79% Ru by weight on NaY zeolite, was prepared by ion exchange with $Ru(NH_3)_6Cl_3$. A reference catalyst, 15·55% Ru by weight on SiO_2, was prepared by impregnation of Aerosil type silica with the same complex. The zeolite was dehydrated *in situ* and reduced with hydrogen at 573 K. The silica catalyst was calcined at 1023 K and reduced under the same conditions as the zeolite. Hydrogen chemisorption gave H : Ru ratios of 0·50 : 1 and 0·06 : 1 for the zeolite and silica catalysts, respectively. The repartition of the metal between the zeolite pores and its external surface could be determined using a modification of the temperature-programmed reduction method published earlier.[3] It was confirmed that all of the Ru metal was encaged in the zeolite.

On both catalysts, Fischer–Tropsch experiments were carried out in identical conditions. The catalyst was diluted with quartz and charged into a continuous flow reactor operating at a pressure of 1420 kN m^{-2} at 525 K. Hydrogen and carbon monoxide were present in the feed in a ratio of 3 : 2. The contact time for CO was 0·4 s^{-1}. Product analysis was done by capillary g.l.c. and g.l.c.-mass spectrometry was used for product identification. Conversion was measured after 1 h on stream.

The turnover numbers (TON = molecules of CO transformed per surface Ru atom per second) for the zeolite and silica catalysts were $14{\cdot}4 \times 10^{-3}$ s^{-1} and $42{\cdot}6 \times 10^{-3}$ s^{-1}, respectively. It seems, therefore, that the reaction is slower over the zeolite catalyst. It is not clear whether this is due to (i) a cage effect of the zeolite, (ii) a particle size effect of the Ru metal,[4] the size of the particle on the zeolite being much smaller than that on the silica surface, or (iii) the apparent value of TON in zeolites [≡ the accessibility of the Ru surface to the reactants ($3CO : 2H_2$)] may be different from the one measured by H_2 adsorption and used in TON calculations.[5]

Regardless of the exact mechanism of chain initiation, propagation, and termination, a Schultz–Flory distribution is obtained by plotting the natural logarithm of the mole concentration against the carbon number. The chain growth probability corresponds to the percentage of a hydrocarbon chain of a given length which grows to a longer chain. For the calculations, Pichler's method was used.[6] The results for both catalysts are shown in the Figure.

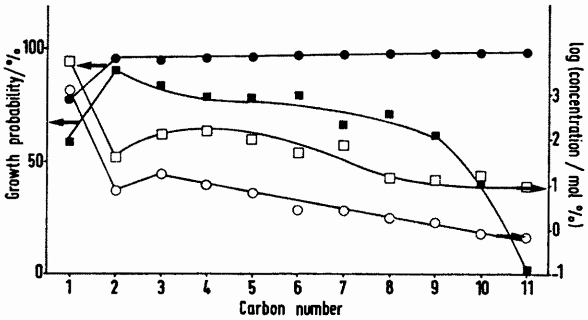

FIGURE. Schulz-Flory distribution and probability of chain growth of Fischer–Tropsch products over Ru–zeolite (□, ■) and Ru–silica (○, ●).

The actual conversions obtained under the conditions used are 11 and 12% for silica and zeolite, respectively. For Ru on silica, 60% of the products are in the C_{12}^+ range. For RuY, $< 1\%$ is in the C_{11}^+ product range.

The Ru on silica catalyst exhibits a nearly constant chain growth probability. The slight increase with increasing carbon number suggests an increased stabilisation of the adsorbed alkyl chain. A similar behaviour was found for cobalt on amorphous supports.[6] This growth ratio results in products, the concentration of which perfectly fits a Schulz–Flory distribution.

On RuY zeolite, the chain growth probability gradually declines from C_2 to C_9 and then suddenly drops to very low values. This results in a much less satisfactory Schulz–Flory fit. It is clear that the zeolite cages impose a restriction upon the size of the Fischer–Tropsch products by destabilizing longer, adsorbed alkyl chains. The mechanism involved in this destabilization requires further investigation.

This 'cage effect' is not due to secondary hydro-isomerisation or hydro-cracking on acid sites in the zeolite generated as in equation (**1**). Indeed, the relative concentration of

$$Ru^{3+} + 3\,H_2 \longrightarrow Ru^0 + 3H^+ \qquad (1)$$

isomers at all carbon numbers is very similar in both catalysts.

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