Selective Fischer–Tropsch Synthesis of Hydrocarbons over Ruthenium Supported on Silica having a Very Sharp Pore Size Distribution in the Micropore Region

Tadahiro Wakui* and Tadahiko Handa

Research Center of Daido Oxygen Co., Takarazuka, Osaka, Japan

Ruthenium supported on silica having a pore diameter less than 20 Å and a very sharp pore size distribution, exhibits a non-Schulz–Flory plot and a sudden drop of chain growth probability after C_9; thus, the small pore size and sharp pore size distribution of the silica in the catalyst is capable of limiting chain growth.

Fischer–Tropsch synthesis with ruthenium-based catalysts produces several classes of hydrocarbons which range from C_1 to C_{30},[1] and product distributions are usually consistent with the Schulz–Flory formalism.[2] Recent research in Fischer–Tropsch synthesis has been aimed mainly at developing catalysts which do not follow a Schulz–Flory plot. Molecular sieve-supported ruthenium catalysts such as Ru-NaY zeolite[3] are able to produce a non-Schulz–Flory product distribution. Blanchard *et al.*[4] have reported the selective Fischer–Tropsch synthesis of hydrocarbons on $Co_2(CO)_8$–Al_2O_3 with different pore sizes. The selectivity is assigned to an effect exerted by the porosity of the inorganic matrix. We report here that Fischer–Tropsch synthesis from CO and H_2 over ruthenium supported on silica having a pore diameter less than 20 Å and a very sharp pore size distribution[5] produces mainly linear alkanes, whose product distribution shows non-Schulz–Flory kinetics. The sudden drop of chain growth probability occurs in the C_9—C_{11} region.

The silica supports were prepared by the reaction of organic dicarboxylic acid dichlorides such as *p*-phthaloyl chloride, and water glass (SiO_2, 35%; SiO_2/Na_2O, 2.1) in water–tetrahydrofuran (5 : 1) solution.[5] The surface area (525 m^2 g^{-1}), pore volume (0.24 cm^3 g^{-1}), average pore radius (9.16 Å), and pore size distribution of the sample calcined at 450 °C were obtained by nitrogen adsorption–desorption isotherms using a sorptomatic meter. The pore-size distribu-

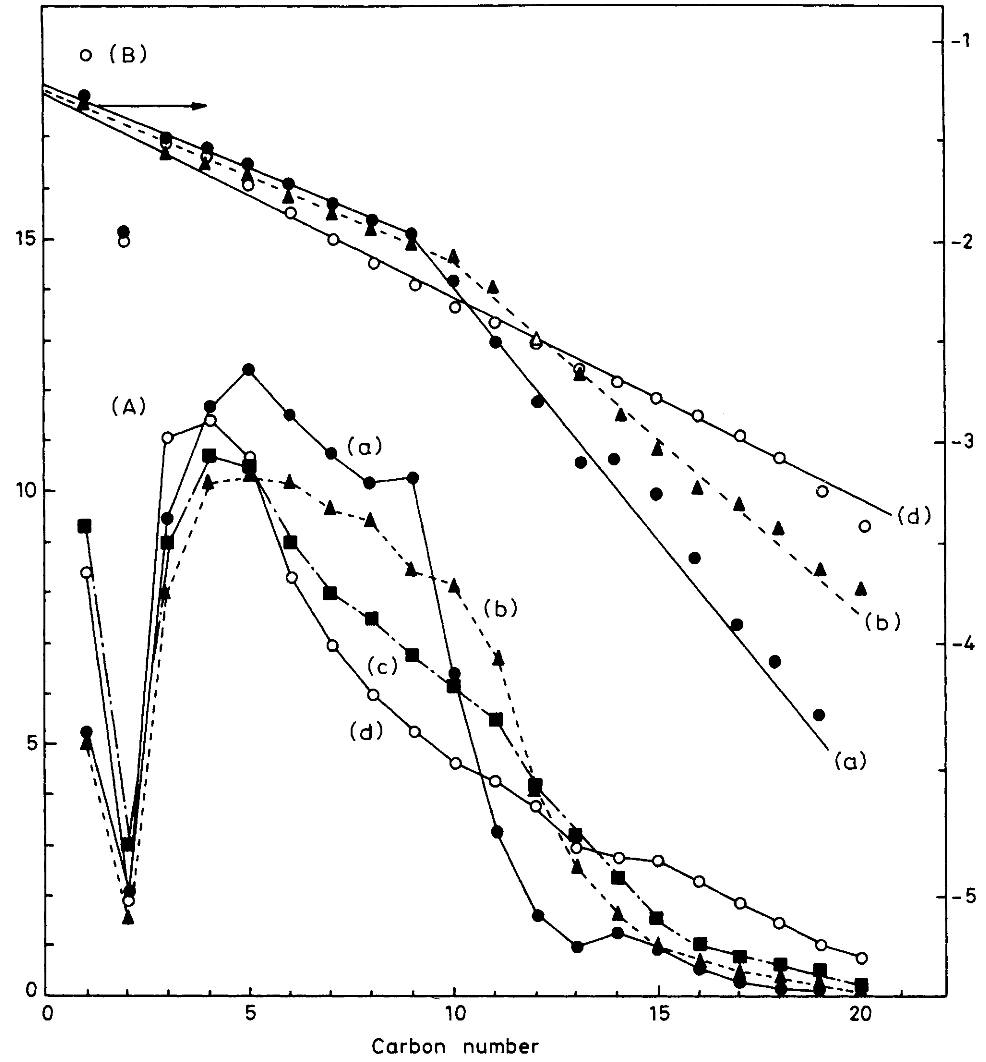

Figure 1. (A) Influence of reaction conditions on product distribution and (B) Schulz–Flory plot over Ru/SiO_2; (a), 235 °C, 18.2% CO conversion, 2.1% CO_2 (α before and after C_9, 0.84, 0.55); (b), 260 °C, 23.2% CO conversion (α before and after C_{10}, 0.83, 0.63); (c), 275 °C, 28.6% CO conversion, 3,2% CO_2 (α before and after C_{12}, 0.81, 0.70); (d), 235 °C, reference Ru/SiO_2 (Davison RD, surface area 446 $m^2\,g^{-1}$, pore volume 0.43 $cm^3\,g^{-1}$, average pore radius 19.6 Å), 13.6% CO conversion (α = 0.78).

tion was within 5 Å in diameter, indicating a very sharp distribution. A solution of $RuCl_3.H_2O$ in water was used to impregnate this calcined silica in order to obtain a 1.5% loading, which was then dried and calcined at 450 °C for 4 h. As reference catalyst, 1.5% Ru on silica was prepared by impregnation of Davison RD type silica with the same salt. The catalyst was charged into a continuous flow reactor and reduced with hydrogen at 300 °C for 2 h before reaction, and operated at a pressure of 10 kg cm^{-2} at 235, 260, 275, and 300 °C with a $CO:H_2$ ratio of 1:1. The space velocity was 750 h^{-1}. Product analysis was by capillary g.l.c. Conversion was measured after 2 h on stream.

In Figure 1 the distribution of the chain lengths of the hydrocarbons and the Schulz–Flory plot obtained by changing the reaction temperature are shown. Fischer–Tropsch experiments on both catalysts were carried out under identical conditions. Using our catalyst, marked deviation from Schulz–Flory kinetics is observed at 235 °C and a pronounced selectivity for C_3—C_{10} hydrocarbons is obtained. The n-alkane is the major product and the isomer distribution of n-C_4 relative to iso-C_4 is 99.0%. The chain-growth probability suddenly drops at *ca.* C_9 for this catalyst and this is analogous to observations reported for the Ru-NaY zeolite.[6] The deviation from Schulz–Flory kinetics is still observed at 260 °C. However, as the reaction temperature is raised to 275 °C, the deviation becomes small and typical Schulz–Flory kinetics are obtained at 300 °C (α = 0.72). The reference catalyst exhibits a broad distribution which perfectly fits a Schulz–Flory distribution (α = 0.78) at a temperature of 235 °C. The ruthenium particle size determined by CO chemisorption is 45 Å and is in good agreement with the relationship between the limits of the size of the products and the metal particle size proposed by Jacobs.[6] However, with 3.8% (Ru particle size 87 Å) or 5.7 (Ru particle size 123 Å), respectively, ruthenium-loaded catalysts using the same silica support, the following hydrocarbon distribution was obtained C_1 5.8, 4.7%; C_2—C_4 17.8, 19.9%; C_5—C_{10} 53.8, 55.6%; C_{11}—C_{15} 20.1, 17.6%; and C_{16}—C_{20} 2.5, 2.2%; at 235 °C. Although the ruthenium particle size on each catalyst is considerably larger than that of a 1.5% Ru catalyst, the product distributions exhibit non-Schulz–Flory kinetics, though the carbon number at which the sudden drop of chain growth probability is seen shifts to *ca.* C_{10}—C_{11}. A similar limit of the chain length in Fischer–Tropsch products with Fe-NaY zeolite having a large particle size of 200—300 Å has been reported.[7] It should be noted that when the ruthenium content was measured by CO chemisorption it was assumed that all the ruthenium existed as metallic particles. Therefore, the possibility remains that ruthenium exists as other than metallic particles.

It is concluded from these experiments that the sudden drop of chain growth probability is related to the small pore size and the very sharp pore size distribution of the silica. However, it is not clear whether this is directly related to the silica cage or to the ruthenium particle size induced by this support silica.

If an appropriate support, with a pore diameter of less than 20 Å and comparable with the pore size in zeolites, and very sharp pore size distribution, is used, this non-Schulz–Flory plot should easily be approached, even with ruthenium–amorphous silica gel.

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