

## High Molecular Weight Hydrocarbons from the Fischer–Tropsch Process with a Pre-oxidized Ruthenium Zeolite Catalyst

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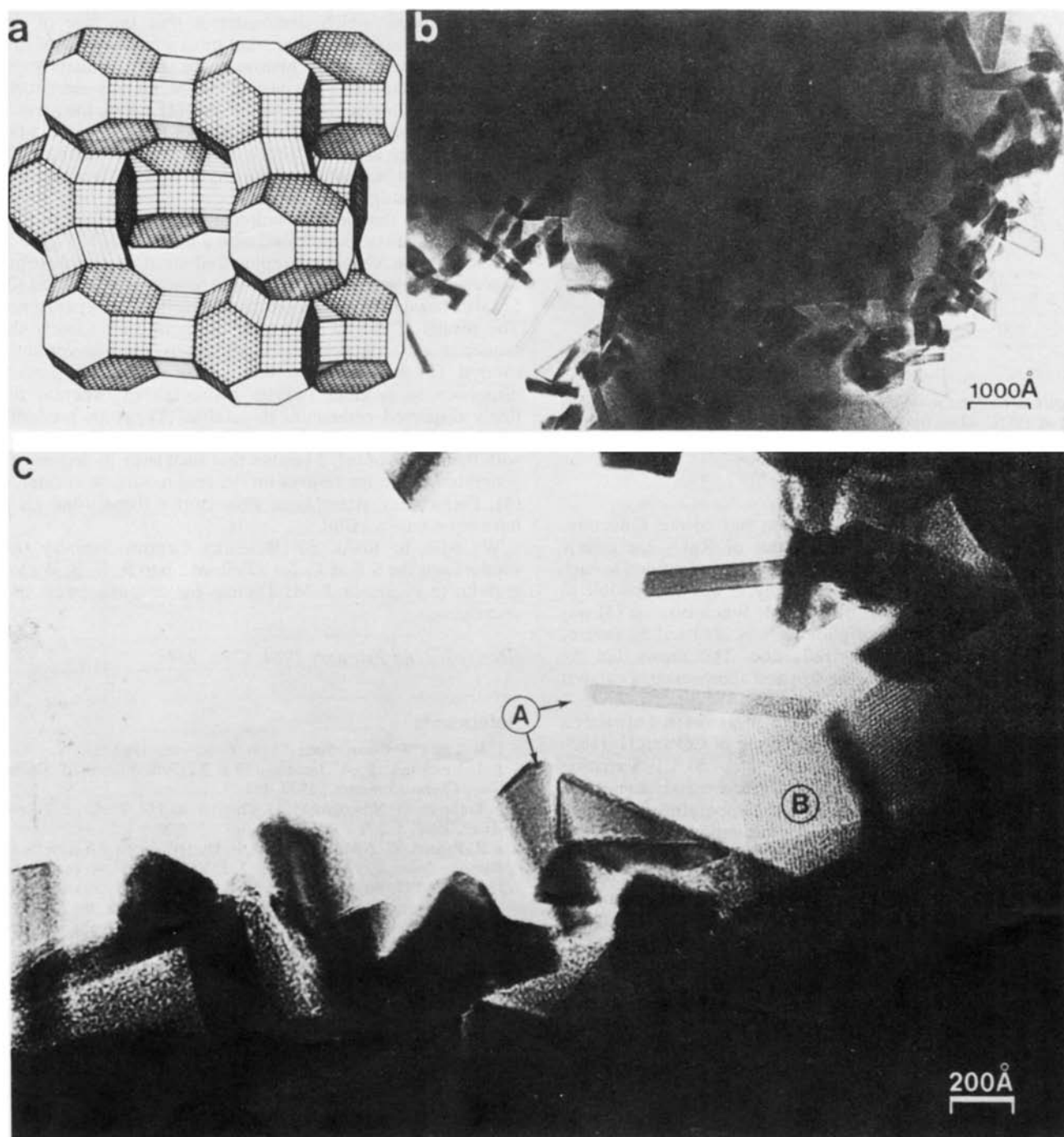
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The catalytic performance of zeolite-based ruthenium catalysts in the Fischer–Tropsch reaction depends on the sequence of oxidations/reductions to which they are subjected: with finely divided Ru particles obtained by reducing  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -exchanged synthetic faujasitic zeolite, methane is the predominant product; but when the zeolite is first oxidised in air at 400 °C forming crystallites of  $\text{RuO}_2$  which can then be reduced, longer-chain hydrocarbons are produced at low reaction temperatures (155 °C).

Zeolites impregnated with transition metals are among the most widely investigated catalytic systems, and the high catalytic activity of ruthenium-based catalysts for the Fischer–Tropsch and water gas shift reactions is of particular interest when the Ru is encapsulated in zeolites.<sup>1,2</sup> Ruthenium may be introduced by ion exchange of water-soluble  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  halide salts.  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  itself may be readily reduced to metallic Ru under hydrogen, or even by heating in an inert atmosphere when auto-reduction of  $\text{Ru}^{3+}$  to  $\text{Ru}(0)$  takes place by the  $\text{NH}_3$  ligands.<sup>3</sup> A similar reaction takes place in  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ -exchanged zeolite Y where, depending upon the reduction conditions, there may be formed atomically dispersed  $\text{Ru}(0)$ , particulate  $\text{Ru}(0)$  of various degrees of

dispersion mostly located in faujasitic supercages, or metallic Ru on the zeolite surface.<sup>4</sup> The catalytic activity of such products depends on the degree of dispersion. The properties of zeolite Na-Y partly exchanged with  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  ('NaRuY') and its reactions with small molecules such as CO and  $\text{H}_2\text{O}$  have been extensively investigated.<sup>5</sup>

Aliquots of zeolite Na-Y (Si/Al 2.61) were exchanged with a degassed aqueous solution of the salt for 24 h, washed with water, and dried under vacuum. A yellowish powder was obtained which slowly turned purple on exposure to air.<sup>5</sup> Heating in air, for instance by an i.r. beam, produced highly dispersed  $\text{RuO}_2$  which has a sloping i.r. spectrum<sup>6</sup> superimposed on that of the zeolite. We were interested in the



**Figure 1.** (a) The structure of zeolite Y. (b) and (c) High-resolution electron micrographs of catalyst (2) particles (after oxidation but before reduction) at different magnification. (A)  $\text{RuO}_2$  Crystal. (B) Zeolite crystal.

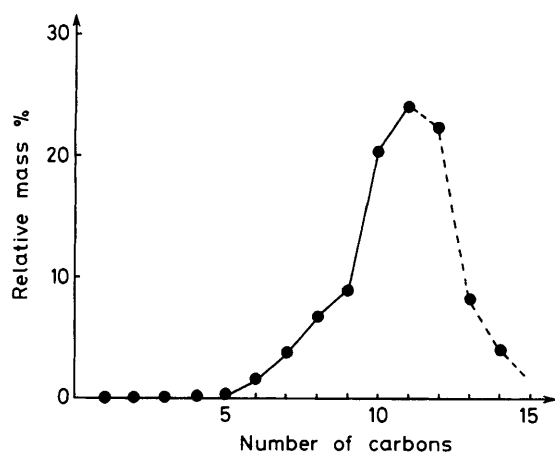
possibility of full oxidation of zeolite-based Ru with a view to selective production of hydrocarbons.

Catalytic tests were carried out in an automated Fischer-Tropsch reaction chamber. Hydrocarbons  $\text{C}_1$ — $\text{C}_8$  were analysed on a gas chromatograph with a hydrated alumina column,  $\text{C}_5$ — $\text{C}_{20}$  with an SE30 column, and the analysis of the  $\text{H}_2/\text{CO}/\text{CO}_2/\text{N}_2/\text{CH}_4$  mixture was carried out with a silica gel column.

1.0 g of catalyst on a quartz support was taken for each experiment and a 64 : 36  $\text{H}_2$  : CO mixture was used at  $3.3 \text{ l h}^{-1}$ . Temperatures were increased from 150 to 230 °C in 5 °C steps, then up to 350 °C in 30 °C steps. Three different catalysts were

investigated: Catalyst (1). NaRuY directly reduced at 300 °C under flowing hydrogen. Catalyst (2). NaRuY oxidised at 400 °C in air and subsequently reduced at 300 °C under flowing hydrogen. Catalyst (3). This was prepared from catalyst (1) which had already been used in Fischer-Tropsch synthesis and then oxidised in air at 400 °C and finally reduced at 300 °C under hydrogen.

Catalysts were examined by high-resolution electron microscopy (HREM). In catalyst (1) ruthenium is very highly dispersed, so much so that HREM does not detect individual particles. The product appears identical to the original zeolite, which means that the size of the clusters must be less than *ca.*



**Figure 2.** Molecular weight distribution for the reaction with catalyst (3) at 155°C. Data for C<sub>1</sub>–C<sub>8</sub> hydrocarbons were obtained with an alumina column; those for C<sub>5</sub>–C<sub>14</sub> hydrocarbons with the SE30 column (see text).

5 Å. In catalyst (2) after oxidation but before reduction, characteristic well-developed crystals of RuO<sub>2</sub> are clearly visible by HREM (see Figure 1). They were identified as such by electron diffraction. Unfortunately, it was not possible to observe reduced catalysts by HREM. When catalyst (3) was re-oxidized in air, its morphology was identical to that of oxidized catalyst (2) before reduction. This shows that the oxidation step determines the size and appearance of catalyst particles.

The total activity of catalyst (1) is higher than that of catalyst (2), as measured by total transformation of CO and H<sub>2</sub> (15% vs. 12% at 200°C and 22% vs. 15% at 250°C). Variation of H<sub>2</sub> transformed, CO transformed, and the ratio (H<sub>2</sub>: hydrocarbons) transformed with temperature is approximately the same for both catalysts, but important differences appear in the selectivity, *i.e.* the composition of the product. Catalyst (1) produces a very high proportion (40–50%) of CH<sub>4</sub> while (2) is selective for alkanes higher than methane. At 250°C the selectivity of (2) towards higher alkanes is lost and only methane is produced owing to hydrogenation of heavier alkanes at this temperature. Catalyst (3) has overall activity about the same as (1), but is much more selective towards

higher alkanes, which demonstrates that the size of the particles is responsible for the molecular weight of the product. Longer chain hydrocarbons must evidently be produced on the larger Ru particles on which they chemisorb. This is impossible in the case of catalyst (1), where the particle size is very small. At 155°C over 80% of the product is in the form of higher alkanes, with less than 10% of methane. It is certain that maximum yields occur at C<sub>11</sub>; however, an SE30 chromatographic column can measure only semi-quantitatively the yield of hydrocarbons higher than *ca.* C<sub>11</sub> and these results are indicated with a dotted line in Figure 2.

Nevertheless, chromatographic analysis of product distribution clearly demonstrates important selectivity of catalyst (3) towards heavier hydrocarbons at relatively low temperatures. The results at 155°C are especially significant. Clearly the sequence of reductions and oxidations used to produce catalyst (3) has achieved the correct degree of particle dispersion to produce heavier hydrocarbons, whereas the finely dispersed ruthenium in catalyst (1) results predominantly in the formation of C<sub>1</sub>–C<sub>3</sub> hydrocarbons. Comparison with the results of ref. 1 implies that such large molecules are generated at the Ru centres on the zeolite surface in catalyst (3). Preliminary attempts to characterize these using *e.s.r.* have been unsuccessful.

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