

The Synthesis of High Molecular Weight Polymethylenes

NEW RUTHENIUM CATALYSTS OF EXCEPTIONAL ACTIVITY

Among the earliest reports concerning the reaction of carbon monoxide with hydrogen over ruthenium catalysts was Pichler's, which appeared in 1938 when he produced paraffins of high melting points using pressures up to 100 atmospheres and temperatures up to 195°C (1). The melting points of the products were about 132°C and their average molecular weights around 8000. The ruthenium dioxide employed as catalyst was prepared by a method originally described in 1905 (2) and was reduced to metallic ruthenium during the first stages of reaction.

Since 1938 a number of papers has been published describing investigations into the effect of pressure and temperature on the reaction products, in particular, their effects on the distribution of molecular weights and melting points. It was found that at reaction temperatures below 140°C the yield of products was very low and as this temperature is only just above the melting point of the highest-melting products it was assumed that these compounds may be responsible for reducing catalyst activity by blocking the active centres on its surface. The latest report by H. Pichler and B. Firnhaber (3), from the Carl Engler and Hans Bunte Institute for Petroleum and Coal Research of the Karlsruhe Technical Highschool, describes the reaction of carbon monoxide with hydrogen over two novel types of ruthenium catalysts when the latter are suspended in nonane, a solvent likely to keep in solution the reaction products suspected of blocking catalyst activity.

The tests were conducted in a copper-lined autoclave with a synthesis gas having a CO:H₂ ratio of 1:2. Catalyst activity was

assessed by measuring the drop in pressure per unit of time from a starting pressure of 1000 atmospheres. Ruthenium dioxide, prepared by precipitation by methyl alcohol from potassium ruthenate solutions, was dried and irradiated in air with gamma-radiation from a Co⁶⁰ source. On additions to nonane it reacted violently, becoming reduced to ruthenium and converting part of the nonane to carbon dioxide and water. A second ruthenium catalyst was prepared by the reaction of ruthenium (VIII) tetroxide with nonane, where also ready reduction of the oxide to the metal occurred. Both types of ruthenium suspensions were assessed as catalysts and showed exceptionally high activities, enabling the CO:H₂ reaction to commence at a temperature as low as 100°C. Their activities per unit weight of metal were very similar.

Employing a pressure of 1000 atmospheres at 120°C, the reaction product contained 33 per cent by weight of a (CH₂)_n polymer of mean molecular weight 108,000, compared with molecular weights of 50,000 to 100,000 for commercially available polyethylenes. The reaction mechanism postulated involves the formation of ruthenium carbonyl-hydrocarbon complexes the composition of which varies with the reaction conditions employed and of which several have been isolated and analysed.

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References

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- 2 A. Gutbier, C. Trenkner, *Z. anorg. Chem.*, 1905, **45**, 166
- 3 H. Pichler and B. Firnhaber, *Brennstoff-Chemie*, 1963, **44**, (2), 33-37