Hydrogen Spillover on Alumina-supported Platinum–Rhenium Catalysts

By Dennis A. Dowden, Ian H. B. Haining, John D. N. Irving, and David A. Whan*
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ, *Scotland*)

Summary An examination of the exchange with deuterium of support-held hydrogen on a series of platinum–rhenium–alumina catalysts has shown that hydrogen spillover does not take place on catalysts where the rhenium content is in excess of 60% of the total metal.

HALL *et al.*[1,2] have described a technique, referred to as differential hydrogen analysis (D.H.A.), in which the hydrogen held by catalysts, both on the metal and on the support, is exchanged with deuterium at steadily increasing temperatures. Their results[2] showed that all of the hydrogen associated with the metal in supported platinum catalysts exchanges at temperatures below 190 K and that higher temperatures are required to cause exchange of hydrogen held in the hydroxy groups of the alumina.

We have investigated by D.H.A. a series of platinum–rhenium catalysts prepared by impregnation of platinum and rhenium onto γ-alumina (surface area 260 $m^2 g^{-1}$, supplied by Condea of Hamburg) from solutions of chloroplatinic and per-rhenic acids in sufficient aqueous ammonia to ensure that any initially formed precipitate had redissolved. Each catalyst had a total metal content of 0·5%, ranging from pure platinum to pure rhenium in 0·1% steps. The catalysts, which were identical to those used in a study of the hydrogenolysis of n-butane,[3] were reduced in flowing hydrogen at 573 K for 45 min and then at 753 K for 16 h before being cooled to 78 K and evacuated. Deuterium (1·33 kN m^{-2}) was then admitted to a sample of the catalyst and the amount of light hydrogen displaced was measured by means of a mass spectrometer, coupled directly to the catalyst vessel by a capillary leak, as the temperature was increased at a rate of 3 K min^{-1}.

The extents of exchange of support-held hydrogen as the temperature was increased were converted by differentiation into plots of rate of exchange dx/dt against temperature, where x is the concentration of hydrogen in the gas phase, and are presented in the Figure.

Although the total numbers of hydrogen atoms exchanged by the support on all catalysts were similar (*ca.* $1{\cdot}5 \times 10^{20}$ g^{-1}), the difference in behaviour between catalysts containing up to 60% rhenium and those with >80% rhenium is striking. As the rhenium content increased from 0 to 60% there was little change, except that the catalyst with composition 60% Re and 40% Pt exhibited a sharper maximum, indicative of less surface heterogeneity; all these catalysts displayed a maximum in the rate at which the exchange of hydrogen on the support took place in the temperature range 260—270 K.

Catalysts with 80 and 100% rhenium had negligible tendency to exchange the hydrogen atoms on the support alumina below 360 K and even at temperatures in excess of this the exchange did not proceed rapidly.

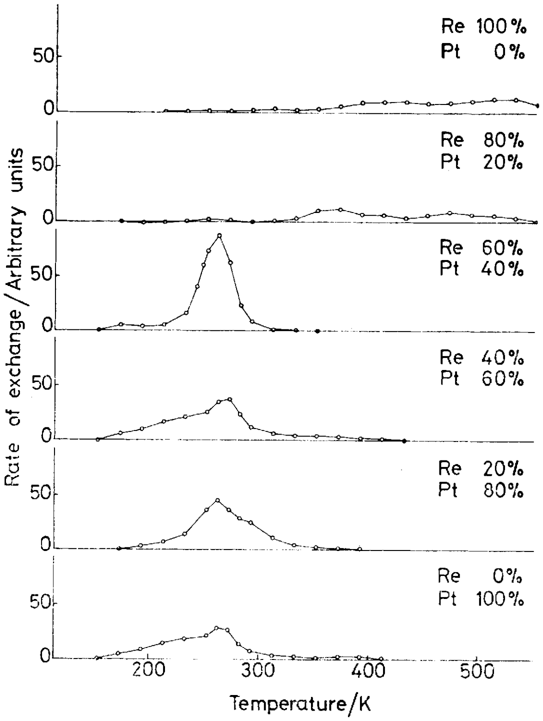

FIGURE. Rate of exchange of support-held hydrogen on a series of platinum–rhenium–alumina catalysts as a function of temperature.

As exchange of alumina-held hydrogen on supported platinum catalysts undoubtedly takes place by a 'spillover' mechanism[4] it would appear that there is a critical Re:Pt ratio, between 60:40 and 80:20, at which point the amount of rhenium is sufficient to prevent spillover from platinum to the alumina. Of the several possible explanations of this phenomenon the simplest would be based on geometric considerations where the critical Re:Pt ratio would be that at which each metal particle consists either of platinum completely enveloped by rhenium or of platinum ensembles isolated in a continuous rhenium matrix thus blocking spillover from platinum to the support. The observation that the critical ratio falls between 60 and 80% of rhenium would be consistent with this explanation.

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