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Deuterium-Exchange Chromatography on a Nickel/Silica Catalyst

In the course of a detailed gas chromatographic investigation of the hydrocracking reaction on Ni/SiO_2 (*1*), we have made a background study of the catalyst–hydrogen interaction using the method of deuterium-exchange chromatography introduced by Ozaki *et al.* (*2*, *3*). In this method a stream of hydrogen is passed continuously through the catalyst to a thermal conductivity detector. A small sample of deuterium is then injected into the gas stream before the catalyst column. This exchanges with hydrogen on the catalyst surface and emerges from the column (as HD) after a volume of gas has passed which is greater than that which passes between the injection and emergence of a sample of a nonexchanging (and therefore nonretarded) gas such as helium or nitrogen. The difference between these two volumes, which we shall call the deuterium retention volume, is the effective volume of exchangeable hydrogen on the surface. Ozaki *et al.* were primarily concerned with the metal H–D exchange on a Ni–kieselguhr surface at low temperatures, when two kinetically distinct ranges were observed, namely, between −195 and −100°C and between −70 and +60°C. Above these temperatures this direct exchange became very fast [compare also a study on Ni–kieselguhr by Suzuki and Smith using chromatographic peak moments rather than retention volumes (*4*)], but a new exchange mechanism appeared associated with a greater deuterium exchange than could be accounted for by static H_2 adsorption measurements. This discrepancy increased with temperature and appeared to be activated by H_2O molecules. It was suggested that exchange might now involve OH groups on the support. Figueras *et al.* (*5*) have investigated Pt/SiO_2–Al_2O_3 with deuterium-exchange chromatography and similarly find retention values increasing with temperature up to the limit of their measurements at 380°C. Again the values obtained were much greater than could reasonably be explained by exchange with hydrogen adsorbed on the metal surface. Our results confirm and extend these findings.

All the chromatographic work has been carried out using a Pye 104 gas chromatograph with a thermal conductivity detector mounted in an oven separate from that of the catalyst column and kept at 50°C for constant sensitivity. The catalyst was prepared by slurrying the silica support (Porasil A 80–100 mesh, Phase Separations, Ltd., Deeside Industrial Estate, Queensferry, Flintshire) with a 0.05 *M* aqueous solution of nickel nitrate and evaporating to dryness under vacuum with gentle heating and constant agitation. Sufficient nickel nitrate was used to give a catalyst with 2.10% (w/w) nickel. The dry material (22 g) was packed into a 1.5 m × 3 mm glass column fitted with a glass–metal seal at its outlet and was reduced in a current of hydrogen (20 ml/min) at 350°C for 3 hr. When necessary the columns were protected with a short length of MnO/Celite (*6*) to remove oxygen. Oxygen was

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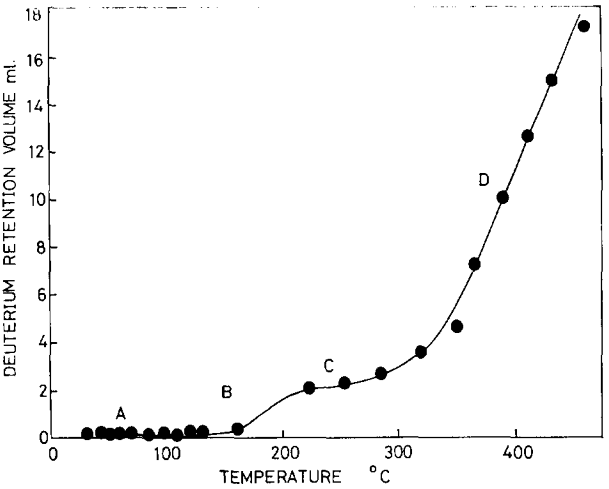

FIG. 1. Deuterium retention volume on Ni/SiO_2 as a function of temperature.

removed from the main carrier gas stream by a larger MnO/Celite tube. Injections of deuterium were made by means of a six-port valve fitted with a loop.

Figure 1 shows the variation of deuterium retention volume (as measured by the peak maximum, see below) as a function of temperature at constant hydrogen gas flow. The curve may be broken down into four main regions: A, B, C, and D. At low temperatures (A, up to 120°C) this volume is very small, difficult (with our low Ni/SiO_2 ratio) to measure precisely, and apparently equivalent to the volume of hydrogen adsorbed on the Ni surface. Values for the latter were obtained by direct hydrogen adsorption measurements, using isotherms calculated from the trailing edges of elution profiles of hydrogen peaks in nitrogen carrier gas and from titration of the surface with aliquots of hydrogen. Above 120°C, B, the deuterium retention volume increases beyond that accounted for by hydrogen adsorption on the surface of the nickel up to a plateau value C. This we believe to be associated with exchange with "loosely bound" water on the SiO_2 surface which is kinetically limited over the region B. Beyond this, D, above 260°C, the retention volume increases considerably and exponentially with temperature over the range which we have studied. This we attribute to kinetically controlled exchange with SiOH groups on the SiO_2 surface.

Kinetic control of these exchange phenomena is demonstrated in a number of ways. In the first place all the chromatographic peaks are asymmetric with trailing rear edges. Second, the position of the peak maximum is a function of flow rate: the retention volume of the peak maximum decreases with increasing flow rate, becoming substantially constant at higher flow rates and presumably corresponding to rapid exchange with the "loosely-bound" water. Third, at the lower temperatures of region B (Fig. 1), it is possible to measure the kinetics of the exchange by stopped-flow chromatography (7), as follows.

A sample of deuterium was injected into the catalyst column and the gas flow was stopped for 30 min. The gas flow was then restarted and the bulk of the deuterium eluted. The flow was then interrupted for further 1-min periods. After each stop the HD liberated during the stop appeared as a peak which was a direct measure of the rate of liberation from the surface during the stop. A plot of log (peak area) versus time is linear and thus corresponds to first-order kinetics. The slope of the plot gives the velocity constant of the desorption process, and from the variation of this with temperature an activation energy of 40 ± 2 kJ mol^{-1} was calculated. If we make the possibly oversimplified assumption that the upper part of Fig. 1 is also controlled only by an $e^{-E/RT}$ term related to exchange rates, we obtain an E value of 39 ± 2 kJ mol^{-1}.

The effect of the "loosely bound" water was investigated further by measuring the rise and fall of the deuterium retention volume when H_2O was injected into the hydrogen gas stream and passed through the column. This increases rapidly after the H_2O is introduced and falls rapidly after the H_2O is eluted from the catalyst. Above 250°C the increase in retention volume corresponds quantitatively to complete exchange with all the H atoms of the injected sample of H_2O, but below this temperature (see Fig. 2), the retention volume increase is controlled by the rate of the exchange process. From adsorption isotherms derived from the trailing edge of the elution profile for water, the H_2O adsorption energy is calculated as 28 kJ mol^{-1} compared with about 40 kJ mol^{-1} for the activation energy of the exchange (see above).

The rate of the exchange may also be measured conveniently using an injection of D_2O rather than D_2. A sample of D_2O is injected and stopped on the column for 20 min at temperatures corresponding to the lower part of region B in Fig. 1. During the stop a substantial amount of deuterium exchange takes place onto the column, and on restarting the gas flow this slowly exchanges back into the carrier gas and is measured by stopped-flow chromatography. The kinetics of this reaction appear to be slightly more complex than the kinetics of the equivalent exchange measured by stopping deuterium on the column (see above) in that the rate of desorption rises initially before falling onto a first-order kinetic plot, but the activation energy calculated from the linear portion of the log (peak area) versus time plots is 35 ± 5 kJ mol^{-1} and therefore the same as that for the exchange using deuterium gas, within the limits of experimental error.

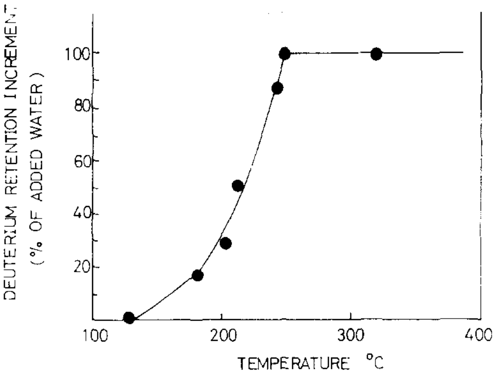

FIG. 2. Effect of added H_2O. Increment in deuterium retention volume on Ni/SiO_2 as a function of temperature.

Drying the hydrogen gas with freshly activated molecular sieve gives rise to a related drop in deuterium retention volume corresponding to the small amount of water vapor in cylinder hydrogen. At higher temperatures the effect of drying the column with carrier gas is only observed to take place slowly, suggesting that this removal of water is associated with slow reactions of the SiOH groups.

The deuterium exchange was also observed by infrared spectroscopy which readily distinguishes bands due to OH around 3600 cm^{-1} from those due to OD around 2600 cm^{-1}. At low temperatures any exchange between molecular D_2O and the Ni/SiO_2 surface is readily removed on drying, the infrared spectrum of a $Ni–SiO_2$ sample treated with D_2O (0.5 g/g) and then dried at 350°C showing no absorption due to OD. Exchange with deuterium gas at 350 and 500°C for 3 hr produced a significant OD band increase but this corresponded to only about 10% of the total OH band intensity.

Under hydrogen gas, extensive hydrocracking of straight-chain hydrocarbons occurs from about 170°C, the rate of reaction increasing extremely sharply with temperature so that 170°C may be regarded as a "switch-on" temperature for the reaction (*1*). The hydrocracking of cyclohexane similarly switches on at about 215°C. It is therefore of some interest to see how far the deuterium retention volume is increased when (a) *n*-heptane or (b) cyclohexane is introduced to the catalyst column as a constant feed in hydrogen gas. In each case the surface concentrations of the various hydrocarbons have been calculated from gas chromatographic retention data for the injected hydrocarbon and the cracked products and from the kinetics of the hydrocracking reactions which we have determined separately (*1*).

(a) With *n*-heptane the extra deuterium retention volume is negligible below 140°C, but rises to a maximum value at about 215°C, and, above this temperature, it falls rapidly to zero. This behavior can be satisfactorily accounted for by (i) an extra kinetically controlled exchange with hydrogen atoms of the adsorbed hydrocarbon molecules, which increases with temperature in a manner quantitatively parallel to the exchange observed in the absence of hydrocarbon; and (ii) the onset of hydrocracking limiting this exchange. Methane produced in the hydrocracking reaction presumably does not exchange significantly at these temperatures.

(b) With cyclohexane which only begins to hydrocrack at 215°C, it is possible to make measurements of the extra deuterium retention volume at 215 and 226°C. As a result the effects are now much larger than those observed with *n*-heptane. The experimental values correspond to an exchange of deuterium with an average of about one hydrogen atom per C_6H_{12} molecule.

WO_3 can be reduced to the blue tungsten bronze (H_xWO_3) by hydrogen at 20°C when the oxide is intimately mixed with a small percentage of Pt/SiO_2 catalyst, although reduction of the pure oxide is not observed under 500°C. This has been attributed by Levy and Boudart (*8*) to the "spillover" of active hydrogen from the metal along the silica surface to the WO_3 which is not directly in contact with the metal. We have found a similar experimental result with our Ni/SiO_2 catalyst, but the temperature of reaction is higher as is normally the case in a comparison of nickel and platinum catalysis. An amount of Ni/SiO_2, 24% by weight, was ground with WO_3 (produced by heating ammonium tungstate at 750°C for 24 hr) in a mortar for 30 min. It was then packed in a small tube on top of some pure WO_3 and heated in a current of hydrogen which had been saturated with water vapor at 18°C. The temperature was then raised slowly, allowing 2 hr at each the following temperatures: 20, 100, 200, 300, and 400°C. No color change was observed below 300°C, but at and above this temperature the pale yellow color of the WO_3 changed to grey-blue, but only in the region where there was Ni/SiO_2.

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