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SUSTAINED HYSTERESIS IN A CATALYSED REACTION: HYDROGENOLYSIS OF ALKANES ON Re/Al_2O_3 CATALYSTS

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Alkane hydrogenolysis on Re/Al_2O_3 catalysts has been studied by a thermal cycling procedure. Because deactivation occurs during heating and is then reversed at higher temperatures, rates are much faster during cooling than during heating. Rates during subsequent thermal cycles are reproducible. Re is 10^4 times more active than Pt for hydrogenolysis.

1. Introduction

Although Re is a vital component of one class of petroleum reforming catalysts [1], little information is available in the literature concerning its own behaviour in hydrocarbon transformations. Re/SiO_2 shows [2] high activity for ethane hydrogenolysis, but lower than that of SiO_2-supported Ru and Os. More recently a number of groups [3–7] have cursorily examined Re/Al_2O_3 catalysts as part of studies on the Pt-Re/Al_2O_3 system. The consensus [3,5–7] is that Re has higher activity than Pt for alkane hydrogenolysis, although the contrary is sometimes found [4]. Methane is the principal product and little skeletal isomerisation is observed [3,5–7]. There is however a paucity of reliable and quantitative information on the behaviour of Re catalysts in hydrogenolysis, and we have carried out a further study, with somewhat unexpected results.

2. Experimental

We have used Re/Al_2O_3 catalysts (1.5, 2.2 and 2.75% Re) prepared [8] in the laboratory of Professor M. Che (Université P. et M. Curie, Paris) by impregnating γ-Al_2O_3 with aqueous NH_4ReO_4 solutions, drying and calcining at 490 °C; they were reduced in the reactor at the same temperature for 1 h before use. Tpr measurements [8] indicated that this schedule should achieve complete reduction to Re°; lower concentrations of Re were less easily reduced by reason of the strong interaction between Re^{7+} and Al_2O_3 [9], and although such catalysts were tested the results will not be reported here.

The hydrogenolysis of propane, n-butane and isobutane was studied in a continuous flow mode at atmospheric pressure, using a 10 : 1 H_2 : alkane mixture; products were analysed by gas-chromatography, but in this paper we are mostly concerned with rates of reactant removal. For an earlier study [10] of Pt/Al_2O_3 and $Pt\text{-}Re/Al_2O_3$ catalysts, we evolved a procedure to assess rapidly their initial deactivation and the consequential changes in product mix, and have applied it here: it is briefly described as follows. The furnace temperature was programmed to increase from the chosen initial temperature (here 60 ° C) in a stepwise manner, the steps being 15 ° and the isothermal periods 20 min. A sample was extracted at each temperature after 18 min and was analysed while the following temperature change was under way. On reaching the maximum desired temperature, completing stage 1, the process was reversed (stage 2), products being analysed again at 15 ° intervals. This cycle was repeated one or more times. In the conditions used, the rate in mmol g_{cat}^{-1} h^{-1} is about 1.2 times the percentage conversion; at the highest temperatures, conversions of about 60–65% were achieved.

3. Results

An example of the results obtained with the Re/Al_2O_3 catalysts is shown in fig. 1 (n-butane hydrogenolysis on 1.5% Re/Al_2O_3). In stage 1, normal Arrhenius behaviour was found between 100 and 140 ° C, but thereafter the rate passed through a maximum before increasing again in a second normal phase. However, most surprisingly, this course was not re-traced on cooling, but only a single Arrhenius phase (190–100 ° C) was observed. In the second heating stage, a similar phenomenon was encountered, but the maximum occurred at a lower temperature and conversion; the second cooling stage however exactly reproduced the first. When a further cycle was carried out, the results were closely similar to those in the second cycle. The activation energy in the cooling stages was ~ 100 kJ mol^{-1}.

Related patterns of behaviour were found with the other alkanes and the other catalysts. Results for the n-butane reaction on the 2.2% Re/Al_2O_3 catalyst resembled those shown in fig. 1, but with 2.75% Re/Al_2O_3 there was no distinct rate maximum during either of the heating stages, but only inflexions in the Arrhenius plots at higher temperatures than those at which the maxima are shown in the figure. In the case of n-butane, with each catalyst the temperature of the rate maximum or point of inflexion fell from the first to the second heating stage, although the coordinates of the maximum were not well reproducible from sample to sample, especially in the second cycles. Three cycles were performed with the isobutane reaction using 1.5% Re/Al_2O_3, and here the second and third cycles quite precisely reproduced the first. In the reaction of propane on the same catalyst, the rate maxima occurred at such low conversions that their positions could not be accurately defined. The phenomena occurring in the heating stages

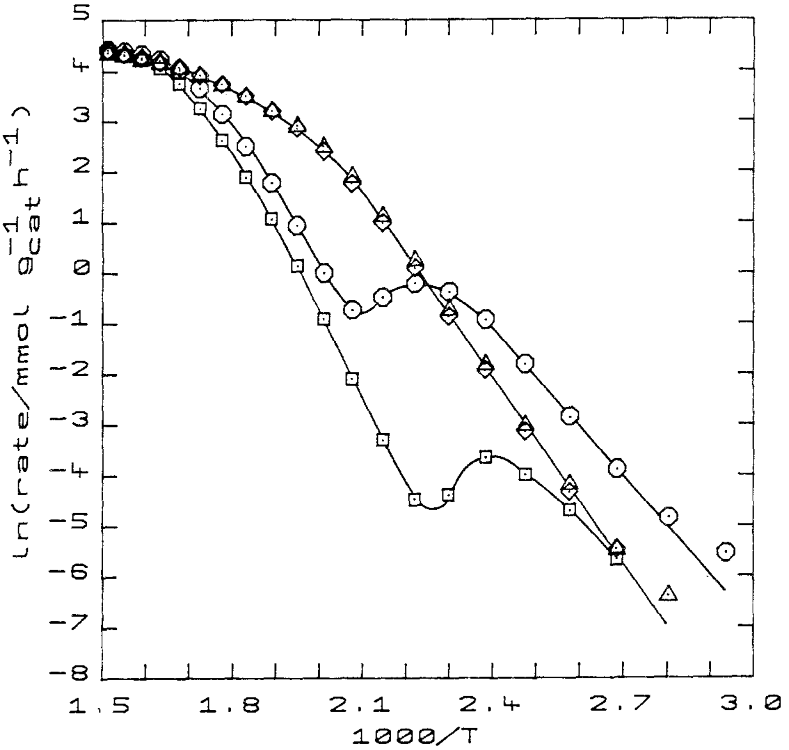

Fig. 1. Arrhenius plots for the hydrogenolysis of n-butane on 1.5% Re/Al_2O_3. Circles, stage 1; diamonds, stage 2; squares, stage 3; triangles, stage 4.

are clearly responsive to the structure of the alkane and to the Re content of the catalyst. No such phenomena were found with Pt-Re/Al_2O_3 catalysts [10].

Table 1 gives values of the rates observed at 242 ° C in the heating stages and at 117 ° C in the cooling stages. These demonstrate (i) the decline in rate at 242° C between the heating stages 1 and 3, especially marked in the case of n-butane, and the lack of further change where a third heating stage (5) was recorded, and

Table 1
Rates of alkane hydrogenolysis (mmol g_{cat}^{-1} h^{-1}) in heating stages at 242 ° C and in cooling stages at 117 ° C

Alkane	% Re	Rate at 242 ° C Stage			Rate at 117 ° C Stage		
		1	3	5	2	4	6
n-C_4H_{10}	1.5	1.84	0.98	–	0.031	0.028	–
	1.5 [a]	2.81	1.15	1.12	0.018	0.021	0.018
	2.2	4.18	1.66	–	0.035	0.034	–
	2.75	–	4.14	–	0.062	0.068	–
iso-C_4H_{10}	1.5	1.14	0.96	1.00	0.013	0.011	0.010
C_3H_8	1.5	0.54	0.41	0.37	–	–	–

[a] Repeat measurement.

(ii) the very close similarities in the rates at 117 °C in each cooling stage. For n-butane hydrogenolysis on 0.3% Pt/Al_2O_3 [10], the rate extrapolated to 117 °C is about 6×10^{-6} mmol g_{Pt}^{-1} h^{-1}, so that on a weight basis Re is at least 10^4 times more active for this reaction than is Pt. In view of the unusual behaviour of Re/Al_2O_3 catalysts in hydrogenolysis, it is little wonder that the literature reports discordant findings.

4. Discussion

We now attempt an outline explanation of what we believe is happening. In the early part of the first heating stage, the Re surface is clean and the reaction proceeds normally (see fig. 1), but at about 100 °C deactivation sets in, due perhaps to incipient carbon deposition. However at about 200 °C the toxic species begin to be removed by H_2 and a second normal Arrhenius phase is observed: cleansing of the surface however appears not to be complete. It appears that operating the catalyst at high temperatures and conversions may almost complete the cleansing process, for, on cooling, faster rates are found, rates moreover that are only a little smaller than those at the beginning of stage 1. In the second heating stage, deactivation sets in sooner, triggered by the residual carbon deposit left from the first cycle. This second toxic deposit is however removed at about 170 °C, after which it is possible to perform thermal cycles showing quite reproducible rates (see table 1). The stability of the catalysts' behaviour, and the dependence of the rate on the direction of the temperature change, justify the use of the term hysteresis in the title of the paper. The 2.75% Re/Al_2O_3 catalyst is distinctly less prone to suffer deactivation, so that the toxic deposits may form preferentially on the smaller Re particles, although this is not the case with other metals [11]. Carbon residues from propane are removed more easily (at 150 °C) than those from n- or isobutane (at 200 °C), suggesting that the toxic species are extensively dehydrogenated forms of the alkane.

Curvature of the Arrhenius plots at conversions greater than about 7% are undoubtedly due to our using rates rather than rate constants; changes in kinetics and in the concentrations of adsorbed species, as well as the onset of diffusion limitation, would account for what is seen.

In agreement with previous work [3–7], we find that methane is the most abundant product under all conditions, although significant amounts of intermediate products are found, particularly in the lower temperature range. A fuller account of these observations will be submitted for publication elsewhere.

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