Analysis of structure-sensitivity in reactions of alkanes: *n*-butane hydrogenolysis on a Ru/Al_2O_3 catalyst

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The rate of *n*-butane hydrogenolysis on 1% Ru/Al_2O_3, the response of the rate to variation of H_2 pressure, and the product selectivities and their alteration with H_2 pressure, change with particle size and with the type of pretreatment used. The generality of particle size effects reported in the literature is rendered uncertain by these results; the predominant factor underlying them may be the strength of H_2 chemisorption.

Keywords: Ru/Al_2O_3; alkane hydrogenolysis; structure-sensitivity

1. Introduction

There is now much evidence to show that in many catalytic systems the turnover frequency (TOF) is dependent on metal particle size. This is particularly so with reactions of alkanes with H_2, although a recent review has highlighted major discrepancies in the literature [1]. There are many possible explanations, such as partial but variable coverage of the surface by "carbonaceous residues", but there is growing evidence to show that the type of pretreatment the catalyst has received has a major effect on TOF: oxidation followed by mild reduction, for example, often gives high values, for which no convincing explanation has yet been advanced [2,3]. A severe limitation to the available literature is the general tendency to measure TOFs for a series of catalysts using a single reactant ratio; indeed the concept of TOF tends to obscure the existence of important experimental variables, such as reactant concentrations. We have recently enquired how the rate of hydrogenolysis of *n*-butane on a 1% Ru/Al_2O_3 catalyst depends on H_2 pressure after various pretreatments, using a procedure which minimises formation of a carbon deposit [4]. The results throw some light on the basis of structure-sensitivity in this system.

2. Experimental

The catalyst was prepared [5] by impregnating γ-Al_2O_3 (Rhône-Poulenc GFC-

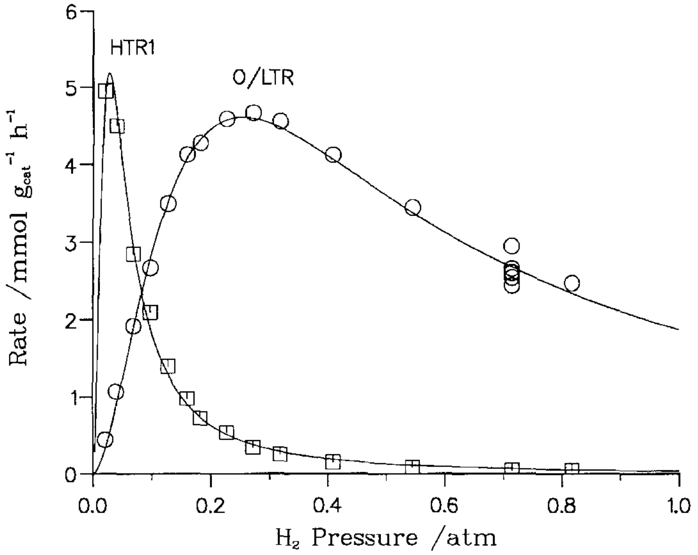

Fig. 1. Dependence of rate of *n*-butane hydrogenolysis on H_2 pressure over 1% Ru/Al_2O_3 at 398 K: effect of HTR1 and O/LTR pretreatments.

200) with a toluene solution of $Ru(acac)_3$; the dried (N_2, 523 K) precursor was reduced in 10% H_2/N_2 at 623 K, and again in situ for 16 h at 753 K (HTR1). After a study of the reaction kinetics, the sample was oxidised (623 K, 1 h) and reduced at only 433 K (O/LTR); after a further kinetic study, there was a second 753 K reduction (HTR2) and a final set of kinetic measurements. Reactions were conducted at 398 K in a continuous flow mode at atmospheric pressure, in an apparatus under microprocessor control: conversion and product selectivity was measured at the end of a short (1 min) reaction pulse, followed by 15 min H_2 flow before the next reaction pulse. This procedure helped to keep the surface clean, but samples reduced at high temperature still suffered some irreversible deactivation when low H_2/*n*-butane ratios were used. H/Ru values were obtained by extrapolating the isotherm measured at 373 K to zero pressure.

3. Results

After HTR1 the average particle size by TEM was 1.2 nm, with most particles between 1.0 and 1.4 nm. The O/LTR treatment resulted in a substantial increase in size (H/Ru, 0.19; by TEM there appeared to be 10–20 nm aggregates of smaller particles), but HTR2 treatment gave little further change to the H/Ru ratio (0.18).

The effect of H_2 pressure on rate following HTR1 (fig. 1) shows the rate to pass through a sharp maximum at ~ 0.04 atm and to be severely inhibited by higher H_2 pressures (order 1.9). The corresponding product selectivities (fig. 2) show scarcely

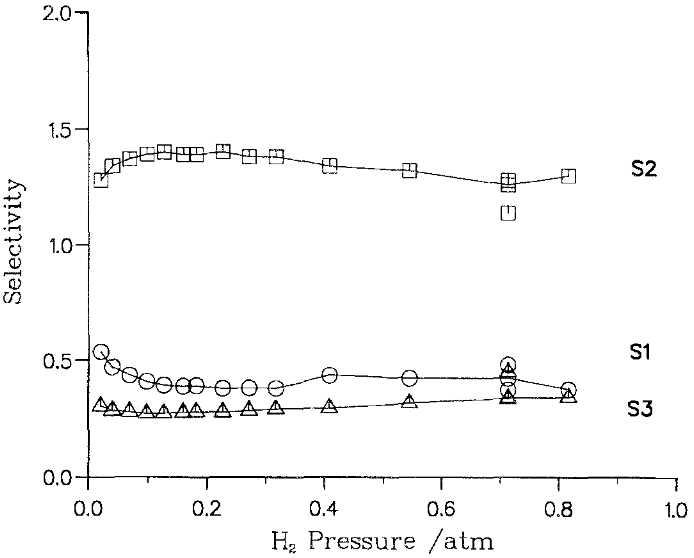

Fig. 2. Product selectivities as a function of H_2 pressure following HTR1 pretreatment.

any variation with H_2 pressure: the ethane selectivity is very high, and the central bond breaking probability is ~ 70%. There is little excess methane formed, so most of the products result from a single bond fission.

The O/LTR treatment leads to striking changes (fig. 1): the rate maximum is at a higher pressure, although the rate at the maximum is about the same as before; however, this treatment leads to faster rates only at H_2 pressures greater than 0.1 atm. At an H_2/*n*-butane ratio of 10 ($P_{H_2} = 0.71$ atm), the rate is ~ 50 times faster than after HTR1. There are equally dramatic differences in the response of product selectivities to varying the H_2 pressure (fig. 3). They now change markedly, and in particular the methane selectivity S_1 increases as the H_2 pressure falls; this is good evidence for the dehydrogenated state of the *n*-butane molecule in the rate-determining step. S_2 is now much smaller (central bond fission probability ~ 20%).

It would be tempting to associate these changes with the decreased dispersion, but to check this possibility the catalyst was subjected to HTR2: while this scarcely decreased the H/Ru value, rates were much slower and the form of the rate dependence on H_2 pressure was much changed (fig. 4). Thus while the rates after HTR1 and HTR2 are about the same at an H_2/*n*-butane ratio of 10, and therefore the TOF for the less well dispersed catalyst is about five times greater, comparison of the maximum rates shows the opposite effect: the TOF of the well-dispersed material is ~ 50% *greater* than that having the lower dispersion. The product selectivities found after HTR2 were much the same as those after O/LTR (fig. 3).

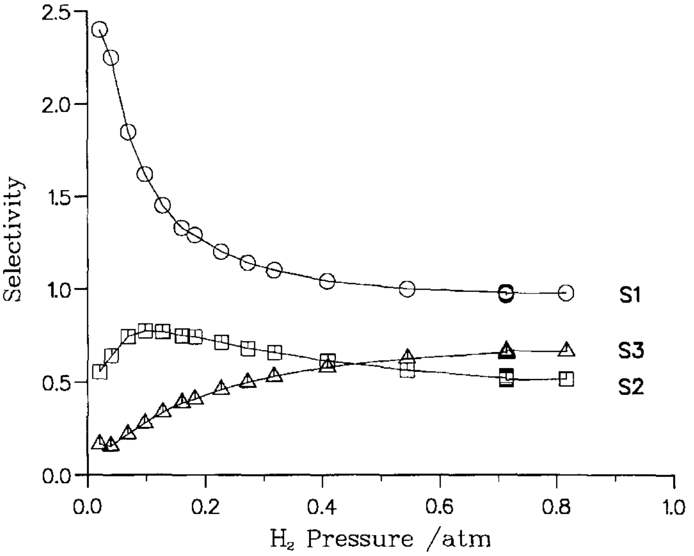

Fig. 3. Product selectivities as a function of H_2 pressure following O/LTR pretreatment.

4. Discussion

The surface structure of the Ru particles is changed in different ways by increasing particle size (comparing HTR1 and HTR2 pretreatments) and by changing the temperature of reduction (comparing O/LTR and HTR2 pretreatments). The latter variable has little effect on product selectivities, but after HTR2 the catalyst

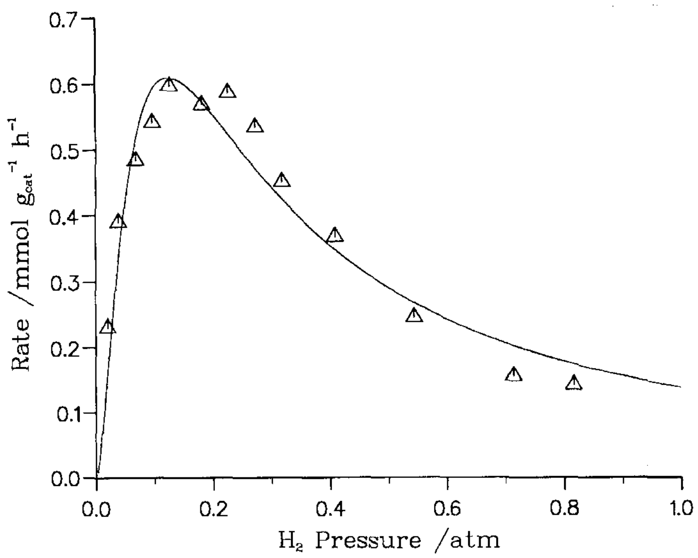

Fig. 4. Dependence of rate on H_2 pressure following HTR2 pretreatment.

is less active (see figs. 1 and 4) and more liable to deactivate. The effects of increasing the particle size alone are to decrease the extent to which H_2 inhibits the rate (fig. 1) and to increase the responsiveness of the product selectivities to H_2 pressure. These two effects are probably linked, and we suggest that H_2 chemisorption is stronger on the small (HTR1) particles than on the large (HTR2) particles: in consequence the H atom coverage is high at all H_2 pressures on the small particles, and this accounts for the negative order in H_2 and the almost constant selectivities which we have observed. H_2 chemisorption being weaker on the larger particles, its inhibiting power is less marked, and the H : adsorbed alkane ratio changes with H_2 pressure, with obvious effects on selectivities.

What is disturbing about these findings is that the magnitude of the effects of particle size and reduction temperature on rate and product selectivities depends so markedly on the H_2 pressure used, and it is now unclear whether many of the effects of these variables reported in the literature [1–3] have any *general* validity. The way forward must be to disentangle their effects on the true rate constant for the slow step from their influence on the adsorption coefficients and related equilibrium constants. We are at present engaged in analysing our results (which are much more extensive than those given here) according to rate expressions found in the literature [4,6], and will report our conclusions in due course.

The more active and stable surface produced by the O/LTR treatment, and destroyed by HTR2, is difficult to explain. Product selectivities seem to be controlled by particle size rather than surface structure. We are considering three possible types of explanation. (i) The O/LTR leaves the surface in an atomically rough state, having a large number of low coordination number atoms; these are annealed out in HTR2. (ii) The O/LTR leaves a number of Ru^{x+} ions on, in, under or around the Ru^0 particles, imparting an electron-deficient character which is removed when reduction is complete in HTR2. (iii) HTR1 leaves some very strongly held and toxic H atoms, which are removed in O/LTR but are restored in HTR2. None of these explanations is wholly sound or convincing, but we expect our further analysis of our results to clarify the situation.

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