Hydrogenolysis of Alkanes

Part 2.—Hydrogenolysis of n-Butane over Variously Treated Ru/TiO₂ Catalysts

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The hydrogenolysis of n-butane has been studied on 1 and 5% ruthenium/titania catalysts pretreated in hydrogen at various temperatures and in air at 623 K. Increasing the temperature of reduction of impregnated ruthenium trichloride from 623 to 758 K gives an increase in activity attributed to removal of chloride, but the low activities associated with a strong metal-support interaction (SMSI) are not found until a reduction temperature of 893 K is used. Subsequent oxidation followed by low-temperature reduction gives much higher activities: this is ascribed to spreading of ruthenium oxide over the support, reduction of which affords more highly dispersed metal which easily succumbs to SMSI on a further high-temperature reduction. This interpretation receives some support from temperature-programmed-reduction results.

Product distributions are interpreted according to the scheme devised by Kempling and Anderson. The oxidation treatment and low-temperature reduction creates a new type of active site which appears to favour terminal bond splitting in adsorbed n-butane and has greater reactivity for bond splitting in adsorbed C_2 and C_3 species. This analysis also leads to the conclusions that a second reduction at 623 K does not wholly convert the well dispersed metal to the SMSI state and that not quite all of the oxide formed at 623 K spreads over the support. The strange behaviour of this system is contrasted with that of ruthenium and of platinum supported on silica.

The nature of the interactions which occur between the metal particles and the support in a supported metal catalyst is the subject of much current research.¹ It is now well established that the reduction of metal precursors on certain transition-metal oxides, notably titania, in hydrogen at *ca*. 770 K leads to the loss of chemisorption capacity and of catalytic activity for reactions regarded as structure sensitive, but the origin of this so-called 'strong metal-support interaction' (SMSI) is still shrouded in mystery. One of the more curious features of the work reported so far is that the susceptibility of metals to the SMSI effect appears to vary considerably: thus in the hydrogenolysis of ethane the activities of palladium and of platinum supported on titania after high-temperature reduction are reported to be much less than on silica, while that of ruthenium is almost the same.^{2, 3} However, in another less well publicised report⁴ the activity of ruthenium on titania after high-temperature reduction was stated to be some thousand-fold less than that of ruthenium on silica. Since both observations cannot be valid simultaneously, it is possible that the development of the SMSI state may depend on the pretreatment.

A further shortcoming of the work performed so far is that reactions containing a selectivity element have been neglected: their value in describing the character of the active site is in no doubt. We have therefore studied the hydrogenolysis of n-butane

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on ruthenium/titania catalysts containing 1 and 5% metal, reduced at various temperatures and pretreated in various ways, with the following objectives: (1) to see whether the SMSI effect is indeed exhibited with ruthenium or whether it is resistant to it and (2) to see if there is any variation in the product distribution with pretreatment conditions, such as may betoken a change in the character of the active site. The results have been interpreted using the formalism of the Kempling-Anderson scheme,⁵ the advantages of which have been described previously.6

EXPERIMENTAL

Catalysts were prepared by impregnation to incipient wetness of Degussa P-25 titania, which had been previously dried at 383 K for 16 h, with solutions of ruthenium trichloride (Johnson Matthey plc) to give 1 and 5% ruthenium by weight: the products were dried at 373 K. The 1% ruthenium/silica catalyst was prepared similarly, using Davison 70 silica gel as support.

Temperature-programmed reduction was performed in an apparatus of the type described by Robertson et al.7 using 6% hydrogen in nitrogen (45 cm³ min⁻¹) as reductant and a heating rate of 2 K min⁻¹.

Procedures for preparing or pretreating samples for transmission electron microscopy and for measuring hydrogen chemisorption were as described in Part 1:6 outgassing conditions are mentioned later in the text and in table 1. Hydrogenolysis of n-butane was also carried out as described in Part 1.

RESULTS AND DISCUSSION

HYDROGEN CHEMISORPTION AND PARTICLE-SIZE ESTIMATION

Portions of each catalyst were first reduced in flowing hydrogen at 473 K for 1 h at the same temperature within the volumetric apparatus before outgassing. After measurement of the isotherms, they were reduced for a second time at a higher temperature (1% Ru at 823 K, 5% Ru at 773 K) for 1 h before outgassing. The same samples were subsequently examined by transmission electron microscopy. The results are summarised in table 1.

The hydrogen isotherms were approximately linear between *ca*. 10 and 90 Torr[†] but the slopes were much greater than found for example with platinum.⁶ This can be deduced from the differences between the amounts adsorbed extrapolated to zero pressure and at 80 Torr (see table 1). It is also evident that the average particle sizes estimated from the supposed monolayer volume (*i.e.* extrapolated to zero pressure) are much greater than those shown by electron microscopy. There are several possible explanations for these differences. (1) The low outgassing temperature (473 K) was insufficient to remove all the chemisorbed hydrogen, thus giving an artificially low monolayer volume. (2) Even at 473 K there may have been some incipient SMSI effect, bearing in mind the small size of the particles: however, results presented below make this unlikely. (3) Insufficient time may have been allowed for the adsorption equilibrium to be attained: we have previously observed a slow rate of adsorption of hydrogen onto ruthenium particles on and in zeolite NaY.⁸ (4) The low-temperature reductions might not have succeeded in removing all the chloride from the catalysts, which might therefore have been partially poisoned by it.9 Morris et al.10 have also reported apparently low dispersions for various supports when starting with the chloride; the higher dispersions recorded after the use of these catalysts for carbon monoxide hydrogenation can be attributed to the effect of the water produced in lowering the chloride concentration.

† 1 Torr = $(101 \ 325/760)$ Pa.

		$V_{\mathrm{H}_2}/\mu\mathrm{H}_2$	mol g ⁻¹				
catalyst	final T _{red} /K	at $P = 0$ Torr	at $P = 80$ Torr	H/Ru ^a	$\frac{d_{\mathrm{sph}}}{\mathrm{nm}^{a, b}}$	$d_{ ext{TEM}}/ n m^c$	
1% Ru/TiO	473	9.4	14.7	0.19	ca. 7.5	_	
1% Ru/TiO	823	3.7	7.2	0.07	ca. 15	0.7 (0.5–0.8)	
5% Ru/TiO	473	29.8	50.0	0.12	ca. 11		
5% Ru/TiO	773	23.1	35.5	0.09	ca. 14	1.2 (0.5-2.8)	

 Table 1. Hydrogen chemisorption after low- and high-temperature reductions and particle-size estimates by electron microscopy

^{*a*} Based on $V_{\rm H_2}$ extrapolated to zero pressure. ^{*b*} Estimated assuming all particles are spheres of uniform size. ^{*c*} The first figure is the most frequent size, those in parentheses are the lower and upper limits.

Some confirmation of the retention of chloride was obtained by X.p.s. measurements. With 5% ruthenium, the height of the $Cl 2p_{3/2}$ peak in a sample reduced by temperature programming to 473 K was approximately one-half of that in the material dried after impregnation. After reduction for 3 h at 758 K it was *ca.* 15% of the original value.

There is no doubt from the electron micrographs that the ruthenium remains very well dispersed even after high-temperature reduction. Equally it is clear from table 1 that this treatment further decreases the capacity for chemisorption. The H/Ru ratios after both low- and high-temperature reduction are very close to the values originally reported¹ (*i.e.* 0.23 and 0.06, respectively, for 2% Ru). In view of the ambiguity in the areas active in the catalytic reaction, rates are expressed simply on the basis of unit weight of metal.

TEMPERATURE-PROGRAMMED REDUCTION

The reduction profile for 1% ruthenium trichloride on titania (fig. 1A) shows the principal peak to be at 355 K; with the 5% loading its maximum is raised to *ca*. 380 K (fig. 1B). These values are much lower than those reported⁹ for unsupported ruthenium trichloride hydrate (*ca*. 480 K), but are closer to those given¹¹ for 3% ruthenium trichloride supported on alumina or silica (broad peaks having maxima at *ca*. 400 K).

In connection with the various pretreatments applied to the catalysts before making rate measurements (see below), we were interested to see the effect of oxidation on a second reduction profile. Following the first reductions (fig. 1 A and B), each sample was oxidised in air for 1 h at 473 K and the reduction profile remeasured: the cycle was repeated with oxidation at 573 and 623 K. The results are also shown in fig. 1 A and B. Oxidation at 473 K affords a more easily reducible oxide phase, reduction of which starts at *ca*. 273 K. At the 1% loading, the process is split into two parts designated α and β in fig. 1 ($T_{max} = 318$ and 342 K), but these are not clearly distinguishable at the 5% loading, where the α -phase is the predominant one. The slight shoulder may be due to a contribution from the β -phase, the T_{max} for which is lowered by spillover catalysis by the reduced α -phase. With the 1% loading, a portion of the chloride may have become oxidised to the β -phase during drying, and the shape of the profile for the 5% material implies this also. Reoxidation at the higher temperatures clearly produces a less easily reducible δ -phase ($T_{max} = 408 \pm 6$ K):

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Fig. 1. Temperature-programmed reduction of 1% (···) and 5% (---) ruthenium/titania: A, after drying at 373 K; B, after 1 h oxidation at 473 K; C, after reduction and reoxidation for 1 h at 573 K; D, after reduction and reoxidation for 1 h at 623 K.

oxidation at 573 K leaves some of the β -phase unchanged, while at 623 K there is also a γ -phase of intermediate stability ($T_{max} \approx 365$ K). A little of the δ -phase may be formed in the 473 K oxidation. These temperatures are all lower than those quoted⁹ for ruthenium dioxide, unsupported ($T_{max} = 475$ K) or supported at 5% loading on silica ($T_{max} = 450$ K). Similar effects of oxidative treatments on reducibility have been reported in the case of rhodium on alumina.¹² None of the events we have observed falls within the range of temperature where reduction of Ti⁴⁺ to Ti³⁺ is likely to occur in the absence of a hydrogen-activating metal.¹

PRETREATMENTS

Samples of each catalyst (130-200 mg) were first reduced in flowing hydrogen at 623, 758 or 893 K for 16 h, this procedure being coded as R623(16) *etc.*: the temperature dependence of the rate and product distribution was then studied over a range of 15-40 °C between 388 and 518 K. Each was then oxidised in flowing air

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Table 2. Effect of	of reduction t	emperature and	of oxidation	on the activi	ties of rutheni	ium/titania
and ruthenium,	/silica catalys	sts for n-butane	hydrogenoly	sis at 433 K	(rates in mm	ol $g_{Ru}^{-1} h^{-1}$)

					set				
catalyst	Α	В	С	D	E	F	G	Н	Ι
1% Ru/TiO,	38	254	62	584	1610	18	6	1240	2
5% Ru/TiO ₂	262	744	199	365	3090	22	76	3070	53
1% Ru/SiO ₂	173	143	131						

at 623 K for 1 h [code O623(1)] and the reaction parameters remeasured in the same way, without further reduction except that effected by the reactants within the temperature range employed (388-443 K). This treatment was included partly because it is known¹ that in other systems the SMSI effect is reversed by oxidation and partly because we had previously found¹³ with a 1% ruthenium/silica catalyst that such a treatment produces a marked change in the product distribution. Finally each sample was again reduced under the original conditions and the kinetic parameters again measured to see whether any effects produced by the oxidation were reversible. These treatments, performed on three different samples of both the 1 and 5% catalysts, generated eighteen sets of activity measurements: for ease of reference each set is defined by a number giving the metal content and a letter denoting the sample and its pretreatment, as follows:

R623(16)1A, 5A	R758(16)1D, 5D	R893(16)1G, 5G
O623(1)1 B, 5 B	O623(1)1E, 5E	O623(1)1H, 5H
R623(16)1C, 5C	R758(16)1F, 5F	R 893(16)1 I, 5I.

Thus for example sets 1 A, 1 B and 1 C were obtained by successive reduction, oxidation and reduction treatments on the same sample of the 1% catalyst. The treatments of the 1% ruthenium/silica at 623 K generate sets 1SA, 1SB and 1SC.

EFFECTS OF PRETREATMENTS ON RATES AND ARRHENIUS PARAMETERS FOR THE HYDROGENOLYSIS OF n-BUTANE

Table 2 gives the rates of n-butane removal measured at or extrapolated to the common temperature of 433 K for 1 and 5% ruthenium/titania catalysts after the pretreatments described above. They are expressed per unit mass of metal. Comparable results for 1% ruthenium/silica after reduction and oxidation at 623 K are also shown.^{13, 14} The various pretreatments produce dramatic changes in the rate. A preliminary account of these results has already been published¹⁵ and the previously suggested interpretation can now be developed.

Reduction of the 1% titania-supported catalyst at 623 K leads to only a modest rate in comparison with the 1% ruthenium/silica. Increasing the temperature of the first reduction to 758 K gives a fifteen-fold increase in rate for the 1% ruthenium/titania (compare sets 1 A and 1 D), but only a much smaller increase for the 5% analogue (sets 5A and 5D). The higher reduction temperature is in the range in which the SMSI phenomenon is expected to appear,¹ so these rate increases are at first sight very surprising: they appear to constitute an inverse SMSI effect. We believe, however, that the effect is more apparent than real and that (as the above-mentioned X.p.s. results imply) 623 K is not a sufficiently high temperature to effect complete removal of the

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chloride, especially in the case of the 1% catalyst. Both catalysts are probably substantially free of chloride after 16 h reduction at 758 K (sets 1 D and 5 D). We shall discuss further the differences between sets 1 A and 5 A at a later stage. In view of the very large differences in activity observed (a factor of *ca.* 1500), we feel it is unnecessary to speculate on the reasons for changes of less than a factor of three.

The first reduction at 893 K finally achieves the lower activities characteristic of the SMSI state. The change in rate is greatest with the 1% catalyst, suggesting that particle size may determine the ease with which the SMSI condition is attained. Perhaps also the development of the SMSI is inhibited by traces of chloride, complete removal of which demands the highest reduction temperature (*i.e.* 893 K).

The effects of oxidation are even more striking. It is very likely that this raises the ruthenium's oxidation state to $+4^{9,14}$ as a consequence of which some or all the chloride is removed from the surface through the agency of traces of water formed in the oxidation. We have shown by an X.p.s. measurement that a 1 h oxidation at 623 K following t.p.r. to 473 K lowers the chloride content by a factor of ca. 4. It is equally certain from our t.p.r. results (fig. 1) that the mild reduction effected by the reactants will regenerate the metal, even from the δ -phase. Oxidation of both the titania-supported catalysts at 623 K after a first reduction at the same temperature leads to a marked increase in rate (compare sets 1A and 1B and 5A and 5B), but oxidation after first reduction at 758 K produces yet further increases. While the effects at 623 K might be at least partly ascribed to a decrease in the chloride content, those at 758 K cannot if we suppose that the first 758 K reduction removes most of it. We have therefore postulated¹⁵ that oxidation at 623 K forms ruthenium(IV) oxide which then spreads in an extremely thin layer over the titania surface, and that this, after reduction by the reactants, gives either very small and active ruthenium particles or rafts of monatomic thickness. This process also appears to occur even after reduction at 893 K when the metal is initially in the SMSI state (compare sets 1 E and 1 H and 5 E and 5 H). This spreading seems to take place to a lesser extent during oxidation after the 623 K reduction, perhaps because of an inhibiting effect of residual chloride.

We look next at the effect of the second reductions. At 623 K, final rates are approximately four times less than after oxidation, but comparable to those found after the first reduction (compare sets 1 A, 1 B and 1 C and 5 A, 5 B and 5 C). The second reduction at 758 K induces SMSI in both catalysts, the transition being easier than during the first reduction because of the highly dispersed state of the metal at the outset. The second reduction at 893 K also regenerates the SMSI, most thoroughly in the case of the 1% catalyst.

Oxidation of reduced 1% ruthenium/silica at 623 K does not give a similar increase in activity. Although it may well lower the chloride content,¹³ this may be more than compensated for by some particle growth. It thus appears that ruthenium(IV) oxide cannot spread on silica; platinum oxide is believed to spread on alumina but not on silica.¹⁶ The second reduction gives little further change, as expected. The contrast between the behaviour of the two supports is very marked, although the final activities only differ by a factor of *ca*. 2.

These various pretreatments also lead to effects on the Arrhenius parameters; activation energies are given in table 3, from which, with the rate measurements in table 2, the pre-exponential factors may be calculated. The activation energies for the two ruthenium/titania catalysts after each treatment are remarkably alike, confirming that the responses of both to a given treatment are similar. Increasing the temperature of the first reduction causes a progressive rise in activation energy; oxidation always gives a decrease, but the second reduction restores the original values except at the highest temperature.

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Table 3. Activation energies $(kJ \text{ mol}^{-1})$ for n-butane hydrogenolysis over various	siy
pretreated ruthenium/titania and ruthenium/silica catalysts	

					set				
catalyst	A	В	С	D	E	F	G	Н	I
1% Ru/TiO ₂ 5% Ru/TiO ₂ 1% Ru/SiO ₂	124 ± 2 124 ± 2 124 ± 2 124 ± 2	90 ± 3 117 \pm 3 110 \pm 2	118 ± 1 122 ± 3 141 ± 4	149 ± 4 149 ± 7	129 ± 5 128 ± 4	163 ± 11 154 ± 4 	157 ± 11 182 ± 4	142 ± 3 133 ± 4	132 ± 6 151 ± 4



Fig. 2. Compensation-effect plot of the Arrhenius parameters for the variously pretreated ruthenium/titania and ruthenium/silica catalysts. The code against each point is that of the relevant data set as defined in the text.

The Arrhenius parameters are also displayed as a compensation-effect plot in fig. 2, where it is possible to detect certain regularities. Notwithstanding the twelvefold range of rates (see table 2), the points for all the oxidised catalysts lie on or close to the same line. Those for sets 1 D and 5A, 5C and 5D, which correspond to what we may term the normal reduced state, lie on a second, lower line to which all three points for the variously treated ruthenium/silica catalysts adjoin. The points for sets 1 A and 1C, where activity is low (see table 2), perhaps because of chloride poisoning, are below this line. Finally the low-activity systems (sets 1F, 1G and 1I and 5F, 5G and 5I) lie on a quite distinct line to the right of the others.

The root cause of compensation effects is still a matter for discussion.¹⁷⁻²⁰ However, it has been noted previously¹⁷ with several bimetallic catalysts and with silica-supported ruthenium–copper catalysts pretreated in various ways¹⁴ that there are abrupt movements from one distinguishable line to another, rather than a continuous transition. Similar behaviour has also been seen with single metal catalysts which fall into groups according to the magnitude of their activities.²⁰ In ref. (14) and (20) we

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have advanced two alternative concepts to account for the phenomenon. According to the first, there may be two or more types of active site, differing in the number of atoms involved and in their coordination numbers, and hence in their activities: catalysts whose Arrhenius parameters adhere to the same line share the same type of active site. The alternative view is that, because of constraints imposed by moving to a high concentration of an inactive element or to a less favourable electronic configuration of the active atom, there may be a sudden change in the class of surface atoms able to fulfil the requirements for membership of an active centre and hence in the proportion of surface atoms able to participate. The groupings identified in fig. 2 coincide with defined pretreatments and thus are of at least empirical value in confirming the similar consequences of like treatments. However, we may now enquire as to whether analysis of the product distributions can assign any more fundamental significance to these groupings or can help to distinguish between the two alternative interpretations outlined above.

PRODUCT SELECTIVITIES IN n-BUTANE HYDROGENOLYSIS

Measurement of the yields of the products methane, ethane and propane over a range of temperature for both catalysts after all nine pretreatments has led to a body of information which greatly assists identifying the physical processes produced by the pretreatments, but which also poses problems of presentation. As explained in detail in Part 1,⁶ the product yields are expressed as selectivities S_i , defined as the number of moles C_i of product *i* formed from each mole of n-butane converted. Thus

number of moles of n-butane reacted = $A = (c_1 + 2c_2 + 3c_3)/4$ $S_i = c_i/A$.

and

Selectivities almost always fall in the sequence
$$S_1 > S_2 > S_3$$
 (but $S_2 < S_3$ under some conditions), indicating immediately that methane formation by complete cracking of the n-butane during one residence on the surface is always important. We continue to employ the kinetic scheme of Kempling and Anderson,⁵ described fully in Part 1,⁶ to understand the basis of the changes of product yields. This straightforward but comprehensive scheme contains three disposable parameters: *F*, which is the fractional probability of a central rather than a terminal C—C bond in an adsorbed n-butane molecule undergoing fission, and T_i ($i = 2$ or 3), defined as

$$T_i = k'_i / (k'_i + k^*_i)$$

where k'_i and k^*_i are, respectively, the rate constants for an adsorbed species containing *i* carbon atoms desorbing as ethane or propane and suffering further reaction.

Unfortunately the equations relating the selectivities to these parameters cannot be rigorously solved because only two of the selectivities are truly independent. In the absence of ancillary results on either propane or isobutane to provide unambiguous values of T_2 and T_3 we have to resort to assuming a numerical value for one of the parameters to solve for the others. We have therefore set T_2 equal to unity on the grounds that over reduced ruthenium catalysts the hydrogenolysis of propane affords values of T_2 close to unity,¹³ that T_2 is expected to exceed T_3 because the C—C bond in ethane is stronger than in propane and that if an arbitrary assumption has to be made, this is as convenient as any. However, as we shall see, difficulties arise with oxidised catalysts, where this assumption is patently unsatisfactory. Values of F and T_3 obtained on the basis that T_2 is unity (or has some other arbitrary value) are denoted as F' and T'_3 .

The most frequently observed pattern of behaviour is that S_1 and S_2 increase with increasing temperature, but S_3 decreases (fig. 3): S_2 sometimes passes through a

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Fig. 3. Product selectivities and values of F' as a function of temperature for sets 1 H and 51. The parameter T'_3 is shown as the function $\ln [(1/T'_3) - 1] = \ln (k_3^*/k'_3)$ as a function of reciprocal absolute temperature in the lower part of the diagram.

maximum. This behaviour requires both F' and T'_3 to decrease also. In some situations, however, the variation with temperature of both F' and T'_3 (particularly the former) is small (see below and fig. 4). The product selectivities respond more sensitively to changes in the experimental conditions than do the kinetic parameters: this is simply an artefact of the algebra. For this reason it is not always adequate or satisfactory to describe the product yields in terms of these parameters, so a selection of product selectivities is presented in table 4.

We may begin analysing the results by comparing selectivities and the derived parameters at fixed temperatures. For first and second reductions of both catalysts, a convenient temperature is 433 K; only for sets 1G and 1I, where the rates are very small, is it necessary to use the higher temperature of 473 K. The oxidised catalysts, being more active (table 2), are compared at 403 K, but, for the 1% catalyst, values at 433 K are also given for direct comparison with reduced catalysts. The results are shown in table 4, together with some values for the 1% ruthenium/silica.

To a first approximation the values observed with sets 1 A and 1 D and 5 D and 5G,



Fig. 4. Parameters F' as a function of temperature for the data sets 1G-I and 5G-I: \Box , 1G; \triangle , 1H; \bigcirc , 1I; \blacksquare , 5G; \triangle , 5H; \bigcirc , 5I.

after first reductions, are broadly similar ($F' \approx 0.35-0.43$ and $T'_3 \approx 0.56-0.66$). However the results for set A differ considerably, both F' and T'_3 being lower, while for set 1 G the value of T'_3 is close to unity, although F' has the normal value. Turning next to the oxidised catalysts, comparison of the 1% catalyst at 433 K shows higher S_1 values, lower S_2 values and similar or slightly higher values of S_3 . For the very active 5% oxidised catalysts, selectivities at 403 K are similar to those for the 1% catalysts at this temperature. These effects of oxidation are caused by much lower values of F' (0.03-0.16), which do not vary greatly with temperature. There is therefore no doubt that the physical changes effected by oxidation give a marked lowering of F' and relatively smaller changes in T'_3 .

We consider next the effects of the second reductions. With both catalysts, reduction at 758 and 893 K gives at 433 K values of F' which are higher than before (*ca.* 0.30), but not quite as high as after the first reductions: values of T'_3 are again 0.55–0.63 (compare sets 5D and 5F and 5G and 5I). However, with both catalysts after second reductions at 623 K F' retains the low values characteristic of the oxidised catalysts (*ca.* 0.10) and T'_3 also remains low (compare sets 1 B and 1 C and 5 B and 5 C). Evidently the effect of oxidation is not reversed by reduction at 623 K despite the four-fold drop in rate (table 2).

One set of results is anomalous. The 5% catalyst after a first reduction at 623 K (set 5A) shows low values of both F' and T'_3 as well as quite high activity. We note from the t.p.r. results above the possibility that oxidation might occur to a limited extent during drying, with the same consequences as given by the 1 h oxidation at 623 K. This might explain the rather unusual behaviour of this sample.

Under certain circumstances it is quite clear that the assumption that T_2 equals unity throughout cannot possibly be valid: for example, when the 1% catalyst after oxidation and second reduction (sets 1 B and 1 C) shows negative values of F' (above 443 and 453 K, respectively). The most negative value of F' observed (-0.14) requires T_2 to be 0.85 to give a minimally positive value of F'. The parameters for set 1 C at 433 K were recalculated assuming T_2 to be 0.80: this raised F' from 0.10 to 0.33 and T'_3 from 0.28 to 0.37. Thus it is possible that the effects attributed above to changes in F' are more likely to be associated with changes in T_2 . However, as remarked above on the basis of the available information further speculation would be unwarranted and more work is needed to remove the uncertainty.

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Table 4. Product selectivities and derived parameters for n-butane hydrogenolysis variously pretreated on ruthenium/titania and ruthenium/silica catalysts

		G.	C. BOND AN	ND XU YIDE	
$T_3'$	0.56 0.66 0.49	0.36 0.57 0.64 0.69	(0.68) 0.31 0.71 0.56	0.83 0.53 0.75 0.75 0.75	0.28 0.55) 0.87 0.24 0.63 0.63
F,	0.36 0.43 0.31	0.23 0.35 0.48 0.48	(0.15) 0.034 0.13 0.13	0.12 0.11 0.10 0.16 0.16	-0.05 0.10 0.30 0.30 0.30 0.30 0.30 0.30
S ₃	0.36 0.38 0.34	0.27 0.37 0.41 0.36	(0.58) 0.30 0.62 0.49	0.73 0.47 0.51 0.63 0.63	0.26 0.25 0.62 0.62 0.40 0.43 0.43
$S_2$	0.99 1.05 0.97	0.96 0.98 0.95 1.11	(0.57) 0.73 0.51 0.64	0.39 0.64 0.53 0.53	0.67 0.86 0.87) 0.67 0.87 0.87 0.86
S1	0.92 0.77 1.03	1.26 0.93 0.86 0.67	(1.18) 1.63 1.12 1.25	1.03 1.30 1.28 1.05 1.05	1.84 1.54 (1.01) 0.78 0.97 0.97 0.96
T/K	433 433 473	433 433 433 433	403 433 403 433	403 403 403 403 403	433 473 473 473 433 433 433 433 433 433
set	1 1 1 1 G	5A 5D 5G 1SA	18 15 15 15 18	1H 1H 5B 5H	1SB 11 55 55 51 1SC
pretreatment	lst reduction, 623 K lst reduction, 758 K lst reduction, 893 K	lst reduction, 623 K lst reduction, 758 K lst reduction, 893 K lst reduction, 623 K	oxidation oxidation oxidation oxidation	oxidation oxidation oxidation oxidation oxidation	oxidation 2nd reduction, 623 K 2nd reduction, 758 K 2nd reduction, 893 K 2nd reduction, 758 K 2nd reduction, 758 K 2nd reduction, 893 K 2nd reduction, 623 K
catalyst	1% Ru/TiO ₂ 1% Ru/TiO ₂ 1% Ru/TiO ₂	5% Ru/TiO ₂ 5% Ru/TiO ₂ 5% Ru/TiO ₂ 1% Ru/SiO ₂	1% Ru/TiO ₂ 1% Ru/TiO ₂ 1% Ru/TiO ₂ 1% Ru/TiO ₂	1% Ru/TiO2 1% Ru/TiO2 5% Ru/TiO2 5% Ru/TiO2 5% Ru/TiO2	1% Ru/SiO ₂ 1% Ru/TiO ₂ 1% Ru/TiO ₂ 1% Ru/TiO ₂ 5% Ru/TiO ₂ 5% Ru/TiO ₂ 5% Ru/TiO ₂ 1% Ru/SiO ₂

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Values in parentheses are extrapolated.

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While oxidation at 623 K scarcely changes the activity of the 1% ruthenium/silica, the product distribution is altered in the same way as for the titania-supported catalyst (compare sets 1A and 1SA and 1B and 1SB). Our previous work,¹³ which included parallel work with propane, showed that at 433 K this treatment decreased  $T_2$  from 0.95 to 0.73,  $T_3$  from 0.81 to 0.34 and F from 0.54 to 0.19. The effect of oxidation on the reaction parameters is thus more marked with ruthenium/silica than with ruthenium/titania.

### DEPENDENCE OF PRODUCT SELECTIVITIES ON TEMPERATURE

We have placed little emphasis thus far on the way in which product selectivities and the derived parameters change with temperature. The normal form of variation has been stated above and some of the entries in table 4 provide confirmation (e.g. sets 1 E and H). The greater part of the results was obtained in the rising-temperature mode, but in a number of instances spot-checks were made as the temperature fell: in most cases the results appear on the same curves.

We consider first the temperature dependence of F'. In approximately half the cases (sets 1A, 1D, 1E and 1G and 5A, 5B, 5C, 5D and 5H) F' changes very little; this is usually so with the oxidised catalysts (except set 1 B). With the other half, F' falls at an increasing rate as the temperature rises. Examples of these behaviours are shown in fig. 3 and 4. We may then treat  $k_4^*$  F and  $k_4^*(1-F)$  as rate constants and apply the Arrhenius equation to their ratio [i.e. to F'/(1-F')] to give an activation energy difference  $\Delta E_F$ . With the first group the average value of  $\Delta E_F$  is 3 kJ mol⁻¹ (from -7 to  $+14 \text{ kJ mol}^{-1}$ ; for the second group the average is 20 kJ mol}^{-1} (from 13 to 37 kJ mol⁻¹). We discount the values derived from sets 1 B and 1 C where F' changes in an artificially rapid manner because of the inadequacy of taking  $T_2$  as unity. When the temperature dependence of F' is small, the principal effect of temperature on selectivities is through  $T'_{3}$ ; otherwise both factors contribute to comparable extents.

Grouping the sets of results according to  $\Delta E_F$ , however, is misleading, since low values tend to be found at low temperatures (*i.e.* with the most active catalysts), medium values (ca. 12-18 kJ mol⁻¹) in the 423-473 K range and the highest value  $(37 \text{ kJ mol}^{-1})$  with the only catalyst (set 1 I) sufficiently inactive to require the use of temperatures > 473 K. Indeed, with the 758 and 893 K reduction temperatures, some of the values of F' for both catalysts, when overlaid, lie on the same or similar curves, providing striking evidence that in this respect at least the same heat treatments with different metal concentrations sometimes produce equivalent structures. An example of this is shown in fig. 4, from which it follows that the different values of  $\Delta E_F$  obtained in different temperature ranges may only represent segments of a continuous curve not properly represented by the Arrhenius function.

The temperature dependence of  $T'_3$  may be treated similarly to give an activationenergy difference  $\Delta E_3 (= E_3^* - E_3')$ . Once again discounting sets 1 B and 1 C, thirteen of the remaining sixteen sets give an average  $\Delta E_3$  of 37 kJ mol⁻¹ (20–77 kJ mol⁻¹), only sets 1G, 1H and 1I giving much higher values (166, 66 and 121 kJ mol⁻¹, respectively). With this exception there are no systematic variations of  $\Delta E_3$  with metal content or treatment.

# CHEMICAL AND STRUCTURAL CHANGES AND THEIR EFFECTS ON RATES AND SELECTIVITIES

We have succeeded in showing that ruthenium/titania catalysts can be converted into the SMSI state, although this is not achieved simply by reduction of the chloride precursor at ca. 773 K: other conditions have to be fulfilled, the necessary effects being obtained either by using a very high reduction temperature (ca. 900 K) or by an

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Fig. 5. Symbolic representation of the chemical and structural changes accompanying reduction and oxidation. The dots in the first row symbolise chloride ions: metal shown in black is catalytically active, the other being inactive.

intermediate oxidation. The contradictory results mentioned in the Introduction thus become easier to understand. The SMSI state in this system is not so easily attained as with other noble metals supported on titania.

While describing our results we have outlined certain hypotheses to account for them: it now remains to try to draw these together to provide a coherent model for the effects of the pretreatments on the catalysts' structures and compositions and hence on their catalytic behaviour. We have identified two principal effects: (i) the chloride concentration and (ii) the spreading of an oxide phase during the oxidation treatment over the titania surface. We now summarise our perception of what takes place: a symbolic representation is shown in fig. 5.

We believe that there are three types of ruthenium metal which can be formed: (i) small particles of average size 0.7-1.2 nm (see table 1), (ii) a very highly dispersed form, possibly a monatomic raft and (iii) metal having succumbed to an SMSI. This last form is essentially inactive as a catalyst. Some of these forms can coexist; the chloride content affects the transitions between them, as well as acting as a catalyst poison. According to our method of interpreting product yields, the particulate form affords values of F' > ca. 0.30, while the dispersed form gives values < 0.16.

The first reductions at 623 K produce small particles and, to a limited extent with the 5% loading, rafts formed by partial oxidation in the drying stage (fig. 5); these

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account for its relatively high activity, the product distributions betraying its origin. Heavy chloride contamination limits the activity, especially for the 1% catalyst: this inhibits the spreading of the oxide phase in the subsequent oxidation, the rates not being so high after oxidation following reductions at higher temperatures (table 2), but product selectivities (table 3) clearly show that most of the activity is attributable to metal which has passed through the dispersed oxide form (predominantly the  $\delta$ -phase, fig. 1). We think that the  $\alpha$ - and  $\beta$ -phases formed by calcination of the ruthenium chloride at 473 K are particulate and not much affected by the support, whereas the less reducible  $\gamma$ - and  $\delta$ -phases formed by oxidation of the metal are very much affected by the support and are stabilised by being in intimate contact with it: hence we believe it to be spread over the support as an extremely thin layer. An approximate calculation based on the normal density of ruthenium(IV) oxide shows that 5% ruthenium evenly spread over 50 m² g⁻¹ titania would form a layer 0.17 nm thick, i.e. approximately one monolayer. The motivation for the spreading may lie in the structural compatibility of the two oxides. This process goes almost but not quite to completion after reductions at the higher temperatures, which is why we think residual chloride inhibits the spreading. Even metal in the particulate SMSI state can be dispersed by oxidation. Reduction of the oxide layer by the reactants at 388–443 K therefore produces highly dispersed metal which is not subject to SMSI (fig. 5). However, it is not clear why the 5% loading produces higher specific activities, but as noted above the great range of rates observed renders differences of less than a factor of three almost insignificant.

Raising the temperature of the first reduction to 758 K gives higher rates, especially in the case of the 1% catalyst: the chief effect here is probably the removal of chloride, and it is accompanied by an increase in the values of F' and  $T'_3$  [compare sets 1 A and 1 D and 5 A and 5 D (table 1)]. Reduction at 893 K gives particulate metal subjected to SMSI: with the 1% metal most of it is in this form (fig. 5), but with the 5% loading a considerable part is not affected and the resulting parameters (set 5G) are similar to those for set 5D.

The decrease in the activity following a second reduction at 623 K is due chiefly to the onset of SMSI, the residual activity showing similar parameters to those after oxidation (especially, for low values of F', compare sets 1 B and 1 C and 5 B and 5 C): it is therefore attributed to parts of the highly dispersed phase which have not suffered SMSI. Second reductions at 758 K inactivate all the dispersed phase because of the intimacy of contact between the metal and its support, the remaining activity being due to a few particles which were not spread in the oxidation ( $F' \approx 0.3$ ). The same is true after a second reduction at 893 K, except now almost all the particles in the 1% catalyst (which are smaller than those in the 5% catalyst, see table 1), have suffered SMSI. Its low activity necessitates the use of a high-temperature range for its study and comparison of the parameters with those of other sets is therefore difficult.

Comparison with the behaviour of 1% ruthenium/silica is instructive. After a first reduction at 623 K, F' is higher than for any ruthenium/titania catalyst (0.48, see table 3), but decreases markedly on oxidation without there being a significant change in activity. In fact the absolute value of F decreases from 0.54 to 0.19 and  $T_2$  and  $T_3$  also decrease;¹³ we have previously ascribed these changes to the removal of chloride. We have to recall that the function  $T_i^{-1}-1$  measures the rate of further bond breaking relative to that of desorption: a decrease in  $T_2$  or  $T_3$  therefore betokens an increase in activity for processes occurring within the adsorbed phase. The second reduction of ruthenium/silica is without major effect (tables 2 and 3). There is no evidence that ruthenium oxide spreads on silica as it seems to on titania, although peculiar phenomena, perhaps related to those observed by us, have been reported²¹ with

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ruthenium/alumina, as well as with other noble metals on this support. Higher activities for several reactions including water-gas shift and methanation of carbon monoxide were induced by air treatment at 773 K, although in this case the effect could not be related to reversible changes in dispersion. However, no other convincing explanation was offered.

The conclusion that oxidation followed by low-temperature reduction of ruthenium/titania produces a new kind of active site characterised by high activity (table 2), low activation energy (table 3), high methane yield and low values of F' and  $T'_3$  (table 4) is inescapable. Since the rate-determining step probably lies in the chemisorption of the n-butane molecule,³ it seems likely that the structure of the adsorbed C4 molecule differs from that found on particulate metal. The concept of the existence of both particulate and dispersed forms of supported metal is not new.¹ They have been detected¹² on both rhodium and platinum on alumina, and each is responsible for a distinctly different product set in the reaction of n-pentane with hydrogen. Our results may therefore constitute a further and striking example of how in a structure-sensitive reaction the architecture of the active site can affect both rate and product selectivity. We would therefore tentatively ascribe the two principal lines in the compensation-effect plot (fig. 2) to the existence of two distinctly different kinds of active site. We cannot safely speculate on the origin of the changes to ruthenium which produce this different pattern of behaviour. It may be either electronic or geometric: interaction involving electron transfer from ruthenium atoms to Ti⁴⁺ ions is a possibility. The dramatic changes associated with heat treatments in reducing and oxidising atmospheres in the ruthenium/titania system are in marked contrast to the absence of such changes in the platinum/silica system in the same range of temperature.6

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