Catalytic and structural properties of ruthenium bimetallic catalysts: effects of pretreatment on the behaviour of various Ru/Al$_2$O$_3$ catalysts in alkane hydrogenolysis

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Abstract

Very highly dispersed 1% Ru/Al$_2$O$_3$ prepared from Ru(acac)$_3$, after high-temperature reduction, catalyses the hydrogenolysis of n-butane with a high and almost temperature-independent selectivity to ethane. Catalysts having higher Ru contents (2.5 and 4%) are less well dispersed, but show higher turnover frequencies for this reaction, and selectivities which change with temperature, with methane the major product throughout. Oxidation and low-temperature reduction of these catalysts causes loss of metal area, and much enhanced turnover frequencies: product selectivity behaviour is then in each case that characteristic of large metal particles. A final high-temperature reduction leads to lower turnover frequencies, with little change in product selectivity. Results are also reported for catalysts prepared from RuCl$_3$ and from Ru(NO)(NO$_3$)$_3$, and for Ru powder: propane hydrogenolysis has also been examined as an adjunct to this study.

1. Introduction

The reactions of H$_2$ with alkanes, viz. hydrogenolysis, skeletal isomerization, cyclization etc., are members of a class of metal-catalysed reactions that appear to be structure-sensitive, i.e. to respond to variations in particle size and surface morphology in respect of both rates (or turnover frequencies) and product selectivities [1,2]. There is continuing interest in establishing the factors that determine the catalytic behaviour of small metal particles, and in the ways by which their essential character may be changed in a controlled fashion by the addition of a catalytically-inert element or compound [3,4]. By choosing ruthenium as the catalytic metal we are able to

focus on alternative pathways available for hydrogenolysis, since this metal has little activity for other processes under normal conditions. The relative rates of these alternatives, usually expressed as product selectivities, show dramatic differences when an alkane such as 2,2',3,3'-tetramethylbutane is used [5], but corresponding effects are also observed with linear alkanes such as propane, n-butane and n-hexane [5,6]. Interpretation of product selectivity changes in terms of the Kempling–Anderson formalism [7] allows deeper insight into the connections between catalytic behaviour and catalyst structure [6]. For example, with a series of Ru/Al$_2$O$_3$ catalyst prepared from Ru(acac)$_3$, the more highly-dispersed members showed lower turnover frequencies, and with n-butane a greater tendency to central C–C bond fission and to desorption of the intermediate prod-

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uct propane: temperature coefficients of the selectivity parameters were also much smaller on highly-dispersed particles [6].

In an earlier publication [8], the preparation and important physical characteristics of a number of Ru/Al₂O₃ catalysts have been described; this work formed the basis of a Stimulation Action Programme (SC1*-CT91-0681) funded by the European Union, and these catalysts were the basic materials to which it was proposed to add elements of Group 14 (Ge, Sn, Pb) to modify their surface characteristics. The variables included ruthenium concentration and precursor compound. However, before starting to study the effects of modifiers, it was necessary to establish how the variables of the preparation method affected catalytic performance in the case of the pure ruthenium catalysts, and it is the results of this study that are now reported. The alkanes used were ethane, propane, n-and isobutane, the greatest amount of work being done with n-butane. We have used a thermal cycling technique, by which after reduction the temperature of the catalyst is raised in steps of about 10 K over a range of at least 100 K, and then lowered in the same fashion, with samples being taken for analysis from the product stream at each point. This is an economical way of establishing (i) how temperature affects the reaction parameters, (ii) whether, under the condition used, deactivation is occurring, and (iii) if so, how it affects product selectivities. Analogous results for catalysts modified by addition of Group 14 elements will be presented for publication in due course.

Extensive studies of the Ru/TiO₂ system [9–11] had shown the overriding importance to the results obtained with alkane hydrogenolysis of the type of pretreatment afforded to the catalyst, especially when RuCl₃ was used as precursor. Specifically the presence or absence of a calcination step, and the reduction temperature used, were the prime factors, the latter determining whether a 'strong metal–support interaction' (SMSI) would take place or not. Now Al₂O₃ is not expected to show this interaction, and it was therefore surprising to find that Ru/Al₂O₃ catalysts showed similar

behaviour [12], although the effects of the different pretreatments were somewhat less marked. Chloride ion is of course strongly held by Al₂O₃, as it is by TiO₂, but that the results were not wholly due to chloride ion was shown by using Ru(NO)(NO₃)₃ as precursor, when similar effects obtained. In the present work we have continued to apply in sequence to the precursors as received a high-temperature reduction (HTR1), a low-temperature reduction (O/LTR) and a second high-temperature reduction (HTR2), with a cycle of catalytic measurements after each treatment, as described in detail below.

2. Experimental

The preparation and physical characterization of the catalysts prepared specifically for this programme have already been described [8], but for ease of reference their principal features are reproduced in Table 1; all were prepared from the same batch of Rhône Poulenc γ-Al₂O₃, surface area 220 m² g⁻¹. This table also contains information on the additional catalysts SF2 and RuAB37: Degussa Aluminium Oxid C was used in the preparation of the former and Woelhm γ-Al₂O₃ (200 m² g⁻¹) for the latter [5]. Ruthenium powder was used as a physical mixture (10% Ru, 90% Rhône Poulenc γ-Al₂O₃).

Catalyst precursors (ca. 200 mg) were pretreated at atmospheric pressure in a continuous-flow apparatus under microprocessor control. High-temperature reduction HTR1 and HTR2 were performed by heating the sample in

Table 1
Preparation, composition and dispersion of Ru/Al₂O₃ catalysts [8]

Code	Precursor	wt.% Ru	$(H/Ru)_{tot}$
RuEC1	Ru(acac)₃	0.97	0.88
RuEC2	Ru(acac)₃	2.5	0.44
RuEC3	Ru(acac)₃	4.0	0.25
RuNI1	Ru(NO)(NO₃)₃	0.92	0.23
RuCl	RuCl₃	0.78	0.22
SF2	RuCl₃	1.0	–
RuAB37	Ru(acac)₃	0.93	0.91

flowing H_2 (40 cm^3 min^{-1}) at 10 K min^{-1} to 753 K, where it remained for 13 h, before being cooled to reaction temperature. For the intervening O/LTR treatment it was heated in air (623 K, 1 h), and the resulting oxide was then reduced in H_2 (433 K, 1 h). Reactions were performed with a standard gas composition: alkane, 0.071 atm; H_2, 0.714 atm; N_2, 0.215 atm, with total flow-rates of 140 cm^3 min^{-1} for n-butane, and 56 cm^3 min^{-1} for propane. For the thermal cycles the reactor temperature was raised automatically by steps of about 10 K every 20 min, and a sample extracted for analysis 19 min. later (stage 1): the temperature range usually exceeded 100 K, and from the maximum it was returned stepwise to the starting value (stage 2).

Interpretation of the observed product selectivities S_j, defined in terms of the number of moles of each product formed per mole of reactant converted, by means of the Kempling–Anderson formalism [7] has also been described before [10]. Hydrogenolysis of n-butane can be treated as the successive reaction of adsorbed intermediates c_j^* containing j carbon atoms ($j = 1$–4), together with a short-circuit from C_4^* to C_2^* to allow for initial fission of the central C–C bond. The splitting factor F defines the fraction of n-butane reacting in this way. The fraction of any product having j carbon atoms ($j > 1$) that desorbs rather than undergoing further reaction is given by

$$T_j = k_j' / (k_j' + k_j^*)$$

where k_j' and k_j^* are respectively the rate constants for desorption and cracking. Steady-state analysis of the reaction network provides equations with at low conversion take the form

$$(S_2/T_2) + S_3 = 1 + F$$

$$T_3 = S_3 / (1 - F)$$

These cannot be solved for F and T_3 without assuming a value for T_2, which we take to be the same as that of S_2 in the reaction of propane under the same conditions: if this is not available, T_2 is taken to be unity, and the values of F and T_3 are then distinguished by primes or by being printed

in italics in Table 2. Analogous schemes and definitions apply to the reactions of propane and of isobutane [10], save that there being only one type of bond in these molecules, there is no splitting factor to consider.

Results are presented in tables which give rates and selectivity terms at a standard temperature (usually 433 K), and Arrhenius parameters measured over a defined temperature range, in which conversions are large enough to ensure accurate product analysis but not too large for the 'low conversion' assumption to hold (i.e. ca. 10^{-2} to 10%): this range may be less than that actually used. In addition, the dependence of reaction parameters on temperature and on metal dispersion will be illustrated.

Single H_2 chemisorption isotherms were measured at 373 K on samples of EC1 and EC3 after each of the pretreatments described above: outgassing was performed at 623 K, and the H/R$_{tot}$ ratios obtained by extrapolating linear portions of the isotherms to zero pressure. Electron micrographs of selected samples on holey carbon grids were obtained using a JEOL 2000 EX instrument.

3. Results and discussion

3.1. Estimations of ruthenium dispersion and particle size

Performing the O/LTR treatment on EC1 caused (H/Ru)$_{tot}$ to decrease from 0.88 [8] to 0.19, while the HTR2 treatment led to little further change ((H/Ru)$_{tot} = 0.18$). In the case of EC3 the corresponding change was from 0.23 [8] to 0.08, with HTR2 making no further difference. Electron microscopy of EC1 after O/LTR revealed large aggregates of metal that appeared to comprise particles of 5–10 nm in size; their appearance was essentially unchanged by HTR2. In the case of EC3, which after initial reduction was stated [8] to show a wide size distribution [1–10 nm] with agglomerates, TEM after O/LTR failed to reveal any significant change.

One of the objectives of this work was to confirm and extend our understanding of the origin of particle size effects in hydrocarbon transformations on metal catalysts, but with the present system of catalysts there is considerable difficulty in deciding what parameter to use as an indicator of size. In previous publications [6,12] we have used the ratio of chemisorbed H atoms to total Ru atoms, the H atoms being either those irreversibly adsorbed [6], as measured by the isotherm difference method [8], or the total amount as determined from a single isotherm [12]. In this work we propose to use the latter quantity, as it is available for a larger number of catalysts, but it does not actually matter greatly which is used, as there is a good proportionality between the two [8]: this is confirmed by additional information supplied by Dr. B. Coq [13] concerning values of $(H/Ru)_{tot}$ for the first series used [5,6]. For the samples encoded 19B, 38, 45, AB37 and 8, values are respectively 0.07, 0.44, 0.75, 0.91 and 1.42. With these values and those given before [5,8], $(H/Ru)_{irr}$ is $78 \pm 5\%$ of $(H/Ru)_{tot}$ under the conditions of measurement employed.

A further complication in using H_2 chemisorption with Ru catalysts is the commonly-experienced slow rate of uptake, particularly with small particles, even with preparations and pretreatments which should lead to uncontaminated surfaces: that is why in this work we have performed chemisorption at 373 K. Even so, some trouble was experienced in obtaining consistent results with EC1 after the HTR1 pretreatment. The observation [13] that $(H/Ru)_{tot}$ can exceed unity is not surprising in view of literature reports [14], but the conclusion has to be that H_2 chemisorption does not, in the present state of the art, give quantitatively reliable estimates of dispersion or particle size for sizes less than about 2 nm, i.e. dispersions greater than about 50%.

Quite evidently the measured values of (H/Ru) of either sort can at best only provide an estimate of *average* dispersion or size, so that if the particle size distribution is broad, and particularly if it is bimodal, as seems to be the case with catalysts having higher Ru loadings [8] or which have been

treated to increase the particle size (e.g. catalyst 19B [5,13]), it becomes quite meaningless to try to derive even an average particle size from H_2 chemisorption measurements. Fortunately the very highly dispersed samples show a single narrow size distribution [8,13] from which a reasonably accurate mean size can be obtained. Some further discussion of these problems will be given below, when interpretation of the parameters of catalytic behaviour are considered.

3.2. Comparisons of rates and turnover frequencies

Table 2 gives a summary of the results obtained in the hydrogenolysis of n-butane with a number of the Ru/Al_2O_3 catalysts used in this programme, following the standard pretreatments described above. Values for rates and selectivity parameters are those shown at 433 K; rates are expressed per g Ru using the analysed Ru contents where available, and turnover frequencies (TOF) are derived from the value of $(H/Ru)_{tot}$. New results for the catalyst SF2 [15] are included as an indication of the reproducibility attainable over a period of time, with different apparatus and operators. Small amounts of isobutane were detected in some analyses, but they hardly ever exceeded 4% of the products and were often zero: these levels are not considered significant, and isomerization selectivities are therefore not quoted. Corresponding results for propane are shown in Table 3.

We consider first the rates and TOF values, and the following conclusions emerge.
(1) After HTR1, rates for n-butane at 433 K were usually smaller in stage 2 than in stage 1, sometimes, as with RuC1, dramatically so, but with SF2 and Ru powder the difference was minimal.
(2) Extents of deactivation in the n-butane reaction were generally less following pretreatments O/LTR and HTR2 than after HTR1.
(3) Deactivation in the reaction of propane was minimal with each pretreatment.

Table 2
Kinetic and selectivity parameters for n-butane hydrogenolysis over various Ru/Al$_2$O$_3$ catalyst

Catalyst	Temp. range	E (kJ mol^{-1})	lnA	r_h	TOF×10^3 (s^{-1})	S_2	S_3	F	T_3
After HTR1									
RuEC1	358–458	132	42.38	307	9.8	1.387	0.278	0.724	1.008
	457–373	144	45.47	247	7.9	1.356	0.288	0.695	0.943
RuEC2	386–441	120	39.48	420	26.8	1.035	0.332	0.495	0.657
	419–365	149	47.71	474	30.2	0.996	0.344	0.454	0.630
RuEC3	364–420	134	44.01	895	100	0.869	0.354	0.364	0.557
	419–364	139	45.30	788	88.5	0.852	0.361	0.346	0.552
RuNI1	388–430	135	43.37	356	43.4	0.883	0.410	*0.293*	*0.581*
	428–386	144	45.64	300	36.6	0.865	0.389	*0.254*	*0.523*
RuNI2	377–422	118	39.18	628	76.6	0.826	0.381	*0.208*	*0.484*
	429–374	135	46.52	784	95.7	0.825	0.371	*0.196*	*0.465*
RuCl	387–409	116	40.14	500	251	0.992	0.395	*0.527*	*0.835*
	439–386	132	42.10	29.5	1.5	1.075	0.320	*0.514*	*0.658*
Ru powder	419–458	113	31.34	0.95	–	0.781	0.416	0.238	0.546
	447–417	105	29.05	0.98	–	0.823	0.384	0.218	0.464
SF2	374–460	131	41.00	100	–	1.103	0.287	*0.390*	*0.470*
	460–374	125	39.33	101	–	1.098	0.277	*0.375*	*0.443*
SF2 [15]	407–468	133	40.8	43	–	1.03	0.29	*0.32*	*0.43*
RuAB37	393–454	150	47.9	460	14.2	1.010	0.430	*0.440*	*0.768*
After O/LTR									
RuEC1	374–438	122	40.96	1216	180	0.714	0.427	0.206	0.538
	426–373	120	40.61	1350	199	0.707	0.430	0.202	0.539
RuEC2	354–409	126	43.03	2932	823	0.812	0.364	0.296	0.517
	408–354	127	43.27	2600	730	0.795	0.380	0.292	0.536
RuEC3	356–411	132	44.61	2405	844	0.846	0.314	0.297	0.446
	410–358	134	44.92	2285	802	0.833	0.330	0.295	0.468
RuNI1	378–431	118	40.54	2065	–	0.775	0.436	*0.212*	*0.555*
	428–375	116	39.48	1522	–	0.746	0.443	*0.188*	*0.546*
RuNI2	380–411	125	43.02	4426	–	0.875	0.316	*0.189*	*0.391*
	408–375	122	41.98	3291	–	0.835	0.329	*0.164*	*0.395*
RuCl	386–460	150	45.83	64.1	–	0.695	0.180	–	–
	409–377	137	43.13	160	–	0.746	0.220	–	–
Ru powder	420–441	87	27.04	17.6	–	0.825	0.467	0.341	0.709
	438–418	96	28.94	8.6	–	0.807	0.441	0.300	0.630
SF2	373–448	132	41.97	200	–	0.770	0.241	*0.011*	*0.271*
	448–373	129	41.31	239	–	0.789	0.239	*0.028*	*0.245*
SF2 [15]	395–453	132	41.3	97	–	0.76	0.25	*0.01*	*0.25*
RuAB37	383–433	110	38.3	2200	418	0.720	0.440	*0.160*	*0.524*
After HTR2									
RuEC1	374–426	130	41.88	313	48.8	0.812	0.391	0.285	0.547
	436–394	141	45.05	313	48.8	0.813	0.380	0.262	0.515
RuEC2	375–419	140	44.83	352	98.8	0.809	0.400	0.310	0.580
	418–363	142	45.23	328	92.1	0.803	0.403	0.297	0.573
RuEC3	264–419	138	44.45	470	165	0.830	0.358	0.295	0.505
	429–353	141	45.13	402	141	0.835	0.346	0.278	0.479
RuNI1	399–430	141	44.73	286	–	0.764	0.449	*0.212*	*0.572*
	428–386	147	46.55	274	–	0.780	0.418	*0.199*	*0.524*
RuNI2	373–433	127	41.68	596	–	0.770	0.427	*0.197*	*0.532*
	421–378	140	45.27	614	–	0.777	0.409	*0.185*	*0.504*
RuCl	375–473	–	–	359	–	0.780	0.455	*0.235*	*0.595*
	439–386	130	36.84	167	–	0.870	0.340	*0.210*	*0.430*
Ru powder	420–469	95	26.09	0.75	–	0.807	0.435	0.284	0.607
	458–418	93	25.30	0.59	–	1.000	0.407	0.320	0.598
SF2	373–436	158	49.58	296	–	0.982	0.268	*0.268*	*0.366*
	436–373	156	49.39	416	–	0.982	0.281	*0.263*	*0.381*
SF2 [15]	395–453	123	38.5	89	–	0.98	0.21	*0.19*	*0.26*
RuAB37	383–432	125	40.4	318	–	0.770	0.390	*0.160*	*0.464*

For footnotes, see below Table 3.

Table 3
Kinetic parameters and ethane selectivity for propane hydrogenolysis on various Ru/Al_2O_3 catalysts

Catalyst	Pretreatment	Temp. range (K)	E (kJ mol^{-1})	ln$A$	r [a]	TOF$\times 10^3$ (s^{-1})	S_2 [a]
RuEC1	HTR1	395–467	166	49.14	19.6	0.62	0.959
		467–385	166	48.97	22.7	0.72	0.964
RuEC2	HTR1	375–429	156	47.92	102	6.5	0.890
		428–365	155	47.72	96	6.1	0.897
RuEC3	HTR1	365–429	149	46.61	171	19.2	0.860
		429–365	155	48.21	179	20.1	0.865
RuCl	HTR1	420–471	163	46.47	3.3	–	0.876
		460–407	139	40.65	7.7	–	0.900
Ru powder	HTR1	470–511	130	31.71	*0.012*	–	*0.95*
		511–459	128	31.38	*0.015*	–	–
RuEC1	O/LTR	374–435	134	43.35	401	59.3	0.916
RuEC2	O/LTR	353–409	139	46.00	1584	445	0.871
		407–353	141	46.63	1572	441	0.872
RuEC3	O/LTR	354–409	135	44.53	1205	423	0.861
		408–354	138	45.30	1162	408	0.863
Ru powder	O/LTR	458–513	137	39.37	3.7	–	0.944
		478–425	131	37.49	3.0	–	0.940
RuEC1	HTR2	384–436	159	47.61	33	5.1	0.908
		446–384	145	43.95	35	5.5	0.922
RuEC2	HTR2	398–439	144	44.16	64	18.0	0.889
		439–375	147	45.03	68	19.1	0.898
RuEC3	HTR2	364–439	147	44.90	64	22.5	0.886
		428–364	154	47.26	87	30.0	0.896
Ru power	HTR2	451–511	106	25.95	*0.030*	–	*0.95*
		511–469	109	26.81	*0.031*	–	*0.92*

Footnotes to Tables 2 and 3: Rate of reactant removal r_h and selectivity parameters at 433 K. A and r_h in mmol g$_{Ru}^{-1}$. Duplicate entries where given are for stages 1 and 2, respectively. Valid rates may be calculated from E and ln$A$ only in the temperature range cited.
Footnotes specific to Table 2: Italicised values of F and T_3 signify F' and T_3'. TOF for RuCl (HTR1) based on an assumed (H/Ru)$_{tot}$ of 0.56 (see text). For SF2 lit., see [15].
Footnotes specific to Table 3: TOF's for RuEC2 and AB37 (O/LTR) estimated using values of (H/Ru)$_{tot}$ of respectively 0.1 and 0.15.
[a] Italicised values obtained by graphical extrapolation.

(4) Rates were generally greater after O/LTR than after HTR1, the more so with propane than with n-butane; large enhancement factors ($\sim 50\times$) were also observed with ethane and isobutane, using RuEC1. Rates were always much less after HTR2.

It is now necessary to enquire to what extent the differences in rate shown by catalysts having different Ru contents, or made by different routes, or pretreated differently, are explicable in terms of changes in active area. Following the earlier

discussion, we take (H/Ru)$_{tot}$ as the best available indicator of dispersion: Fig. 1 and Fig. 2 show how TOF varies with dispersion for the reactions of n-butane and of propane respectively. It is at once evident that, in confirmation of previous findings (which are included in these figures), rates are not proportional to active areas, and that TOF increases (more steeply than was originally seen [6]) as dispersion decreases. It is also clear that the results for both the HTR1 and the O/LTR pretreatments, although not overlapping, appear
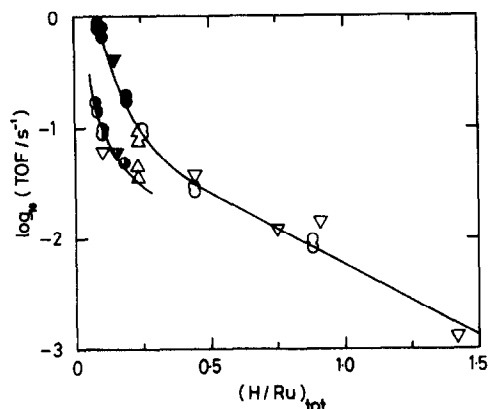
Fig. 1. Variation of TOF for n-butane hydrogenolysis with $(H/Ru)_{tot}$ at 433 K. Circles, RuEC series; triangles, RuNI series; inverted triangles, from [6]. Open points, HTR1; hatched, O/LTR; half-filled, HTR2. Where pairs of linked points are shown, they are the values of stages 1 and 2.
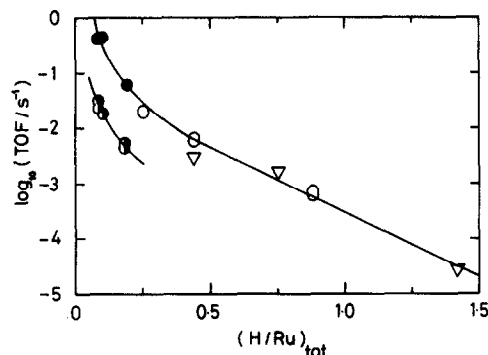

Fig. 2. Variation of TOF for propane hydorgenolysis with $(H/Ru)_{tot}$ at 433 K. Symbols as in Fig. 1.
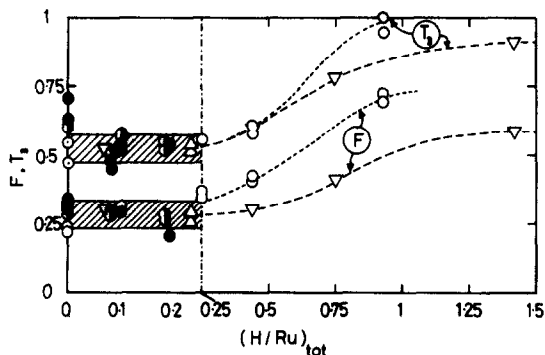

Fig. 3. Dependence of the Kempling–Anderson parameters F and T_3 for n-butane hydrogenolysis in $(H/Ru)_{tot}$. Symbols as in Fig. 1. Results for Ru powder are plotted at zero dispersion.

to lie on the same curves, while TOF's obtained after HTR2 are less than those given following the other pretreatments.

It is important to mention those few materials which do not conform, or cannot be shown to

conform, to the general trends in Figs. 1 and 2. RuCl shows a moderate activity for n-butane hydrogenolysis in stage 1, but in stage 2 its activity is only about 10% of its stage 1 value (Table 2). After another HTR, a thermal cycle was carried out with propane + H_2 (Table 3), and very low rates were found. Unusually, the rate is not increased by the O/LTR treatment, although it is raised by HTR2. We attribute this behaviour to the Cl^- present in this sample [8]; the acidic character thus imparted encourages carbon deposition, which is not entirely removed by the intervening HTR, and perhaps not entirely by O/LTR. Catalyst NI1 shows somewhat lower TOF's for n-butane hydrogenolysis than expected on the basis of its dispersion (Fig. 1), and so a fortiori does Ru19B [6]: there are no obvious explanations for these discrepancies. Catalyst RuNI2 shows exceptional activity after O/LTR, and although its TOF cannot be estimated it is likely to be greater than that of either RuEC2 or 3. Although the Ru powder has been examined by SEM, the range of particle sizes is too large to allow an accurate guess as to its surface area. However it does not seem that, on any reasonable estimate of dispersion, its TOF values would harmonise with the trends shown in Figs. 1 and 2. Rates for both reactions on Ru powder are however much enhanced by the O/LTR treatment. Rates and TOF values shown by catalyst RuAB37 after each pretreatment are intermediate between those of RuEC1 and RuEC2, but in accordance with its initial high dispersion (Table 1) they approximate more closely to the former.

3.3. Comparison of selectivity parameters under standard conditions

Our previous work [6] had shown systematic increases in the parameters F and T_3 with increasing dispersion as measured by $(H/Ru)_{irr}$. Similar, but not identical, trends are shown in the present work (Fig. 3). Those catalysts showing $(H/Ru)_{tot}$ values of less than 0.2, excluding the Ru powder, give very consistent values of F (0.25 ± 0.05) and of T_3 (0.50 ± 0.05), irrespec-

tive of the type of pretreatment to which they have been subjected (Fig. 3). Values of Ru powder obtained after O/LTR and HTR2 are somewhat higher.

In the higher dispersion range, values of these parameters now found agree only qualititatively with these reported earlier [6], and which are incorporated in Fig. 3. We believe that the discrepancies are associated at least in part with the problem of measuring H/Ru ratios at high dispersion, and of using the results in a quantitative manner. What is quite clear is that RuEC1 and Ru8 (from the first series) both show behaviour consonant with very high dispersion ($F \simeq 0.6$–0.7, $T_3 \simeq 0.9$–1.0), and that of the two the former would seem to have the smaller particle size, although this is not what the $(H/Ru)_{tot}$ values indicate. According to the TEM evidence, RuEC1 has a size range of 0.8–1.5 nm [8], and Ru8 has particles mainly between 0.5 and 1.0 nm, with few greater than 2.5 nm [13]. RuAB37, which belongs to the first series [5] but was not studied by us at the time [6], is described [13] as having almost all particles in the range 1 ± 0.25 nm. Nevertheless after HTR1 its product selectivities resemble those of the less well dispersed RuEC2, although after the subsequent treatments they are closely similar to those shown by RuEC1.

The difficulty of precisely correlating catalytic behaviour with particle size is compounded not only by the bimodal character of some of the size distributions, but also by the probable intrinsic variation of activity (i.e. TOF) with size (Figs. 1 and 2). Thus in a mononodal distribution the 'tail' of larger particles will make a disproportionately large contribution to the observed activity, an effect which will be magnified with a bimodal distribution, where the particles of smaller size, although providing the greater part of the surface area, will scarcely supply a significant amount of reaction. It is therefore possible in principle to account for the form of the results in Fig. 3 by postulating just two types of behaviour, viz. one associated with sites of high activity in large particles and another with sites of low activity in very small particles, the results of the intermediate

group being given by the product of number of sites in each group times their activity, integrated over all particles.

It also has to be remembered that the pretreatments applied before H_2 chemisorption or TEM are not always identical to those preceding catalytic tests. While it would be highly desirable to measure an H_2 isotherm on each sample before performing catalysis, this remains a counsel of perfection, and the conjunction of information obtained on different samples, as done here, and as commonly done, has to be accepted.

It is interesting to note that, after HTR1, RuCl shows values of F and T_3 corresponding to an $(H/Ru)_{tot}$ ratio of about 0.6 rather than the measured value of 0.22 (Fig. 3). We note that the reported (CO/Ru) was 0.83 [8], and therefore from the correlation of this ratio with $(H/Ru)_{tot}$ for other catalysts a value of the latter ratio of about 0.56 would have been expected. The most likely explanation is that the low H_2 chemisorption is caused by Cl on the Ru particles, but that this is pushed off by the more strongly adsorbing CO, and that it is also removed to the support by the occurrence of the reaction. Although values of F and T_3 are not reported for RuNI1 and RuNI2 (Table 2), the selectivity values are in line with expectation for particles of 23% dispersion.

In the absence of results for the propane reaction on catalysts RuNI1 and 2, it is only possible to report values of F' and T_3' in Table 2: the values found after HTR1, and the selectivities from which they are derived, are in line with expectation for particles of somewhat low dispersion (both 23% by H_2 chemisorption [8]), although it seems from the results that RuNI1 may be the more highly dispersed of the two. The rates of both increase after O/LTR, the conversion at 433 K in the case of RuNI2 then being over 30%. Changes in selectivities following O/LTR and HTR2 suggest some growth in particle size with RuNI1 only after O/LTR.

Table 2 also contains results obtained with catalyst SF2 following HTR1; they are in satisfactory agreement with those reported earlier [15], also shown in the table. This catalyst was unusual in

showing very little deactivation between stages 1 and 2. Rates are however considerably lower than for other catalysts of the level of dispersion suggested by the product selectivities (<0.3).

Although the principal trends in the values of F and T_3 are qualitatively interpreted in terms of a particle size effect, close inspection of Table 2 suggests that other forces are at work as well. The second HTR produces only negligible changes in dispersion in the case of RuEC1 and 3, and RuEC2 would probably behave in the same way; the very large losses in activity, and decreases in TOF (Fig. 1) are accompanied by small but significant changes in product selectivities and in the Kempling–Anderson parameters (Table 2); they are more sensitively revealed by the former. The surface condition formed by the HTR2 treatment is reversible: in a long series of experiments with RuEC1, it was demonstrated that the more active state could be restored by a further O/LTR following HTR2, and that it could be destroyed and recreated several times. Conversions at 433 K after O/LTR are however often too high (> 10%) to make values of F and T_3 wholly reliable. Similar differences in product distributions after O/LTR and HTR2 treatments are seen with Ru powder, where again no alteration in particle size is expected. Notwithstanding the very considerable differences in behaviour exhibited by the various catalysts after HTR1, and to a lesser extent after O/LTR, the product selectivities show a pleasing uniformity after HTR2 (Table 2, 'After O/LTR' and 'After HTR2').

We should also note that deactivation between stages 1 and 2, where it occurs, is generally accompanied by small decreases in both F and T_3, that is to say, following Fig. 2, changes that correspond to a *decrease* in dispersion. These effects are largest with catalysts having particles in the small-to-medium size range, but are also visible with Ru powder. They may be caused by the blocking of a small fraction of low coordination number atoms such as predominate in very small particles, although the conventional wisdom is that these atoms resist inactivation because of their high activity for hydrogenolysis of C–M or C=M

bonds [16]. An alternative interpretation might be sought in electronic effects upon atoms in the active centre produced by C=M bonds at neighbouring atoms.

3.4. Effects of temperature on rates and product selectivities

As previously demonstrated with catalysts closely related to the RuEC series [6], rates of reactant removal obey the Arrhenius law in both the heating and cooling stages. Some curvature in the Arrhenius plots is commonly detected at high temperatures, and in most cases this is due to the onset of deactivation by carbon deposition. In the reaction of n-butane + H_2 over RuEC1 following HTR1, the effect starts in Stage 1 at about 465 K; the magnitude of the effect increases with the number of carbon atoms in the reactant alkane. Tables 2 and 3 give the values of the Arrhenius parameters in the linear regions; only with the n-butane + H_2 reaction over the Ru powder were any of the Arrhenius plots unsatisfactory.

More interest and importance attaches to the temperature variation of product selectivities and the Kempling–Anderson parameters. Fig. 4 illustrates how for the n-butane + H_2 reaction these vary with temperature for the series RuEC1, 2 and 3 following HTR1; this reveals the effect of dispersion. Fig. 4 also shows the results for RuEC1 following each of the three pretreatments; the effects here are due to a combination of dispersion and surface modification. The behaviour of RuEC1 after HTR1 is quite different from that shown by the other catalyst, or by the other pretreatments of RuEC1: product selectivities scarcely change with temperature, and in particular the methane selectivity S_1 fails to increase with temperature as it does in the other cases. In consequence the parameters F and T_3 remain quite constant. In the other cases S_1 rises steeply, S_2 passes through a maximum and S_3 decreases continuously, this behaviour corresponding to a value of F that is more or less constant in the region of low conversion, and to a value of T_3 that decreases. Some of the variation in F may be due to the
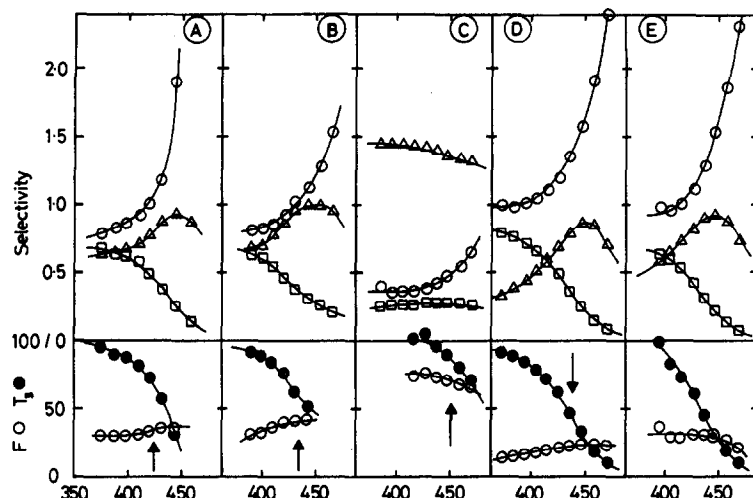
Fig. 4. Temperature-dependence of product selectivities and Kempling–Anderson parameters for n-butane hydrogenolysis: Stage 1 results. A, RuEC3 (HTR1); B, RuEC2 (HTR1); C, RuEC1 (HTR1); D, RuEC1 (O/LTR); E, RuEC1 (HTR2). Circles, S_1; triangles, S_2; squares, S_3. Arrows indicate temperatures at which conversion reaches 10%.

difficulty of accurately interpolating values of S_2 from the propane reaction for the more active catalysts. In the earlier paper [6] we treated values of T_3 to provide an activation energy difference between the processes of reactive desorption of C_3^* and its further bond-breaking, but it now seems that this is merely an empirical device to describe the results, and that the derived numbers lack quantitative significance. What is however clearly evident is that the effect of temperature on the n-butane reaction can be described, in the region where consecutive reactions are unimportant, by a splitting factor F which is almost temperature-independent, and a parameter T_3 which in most cases decreases sharply as the temperature is raised. These observations thus give confidence in the validity of the Kempling–Anderson rake formalism as a means accounting for the results.

We have also followed the variation of product selectives with temperature using RuNI1 and 2 pretreated in each way, the results being of the form expected for moderately poorly dispersed materials: similar behaviour was shown by the Ru powder. RuCl acts somewhat differently in that after HTR1 a high value of S_2 is maintained throughout the temperature range covered, so that (especially in stage 2, where further deactivation has occurred) the F and T_3 parameters are not

markedly temperature-dependent. These observations reinforce the view that RuCl is substantially poisoned by Cl^- after HTR1.

The effects described above are reflected in the different ways in which S_2 in the propane + H_2 reaction changes with temperature, following the standard pretreatments: with RuEC1 after HTR1, its temperature coefficient is markedly less than in the other cases.

4. Concluding remarks

The principal questions with which we are faced in interpreting our findings are as follows. (1) Why do the very highly dispersed Ru/Al_2O_3 catalysts (i.e. RuEC1 after HTR1) show product distributions that change so little with temperature, even although rates show normal Arrhenius behaviour? (2) Why do all less well dispersed catalysts show distribution that change quickly with temperature, in the accustomed sense of obtaining deeper hydrogenolysis as the temperature is raised? (3) Why do values of TOF fall so much when the highly active state formed by the O/LTR treatment is subjected to HTR2, with only small changes to product selectivities? (4) What accounts for the apparent variation of TOF with

dispersion (Figs. 1 and 2), and why does it seem as if the results obtained after HTR1 and O/LTR treatments form a single set, while those that follow HTR2 belong to a different set? We note however (Figs. 1 and 2) that a particle-size dependence is still observed after HTR2.

In previous publications [6,15,17] we have remarked on the correlation between F and T_3 (or F' and T_3'), and have noted that high values of both parameters are associated with Ru surfaces that are probably contaminated, e.g. with Cl^-, or TiO_x or other toxins. This behaviour is observed with a catalyst RuCl after HTR1 in the present work. It is likely that these species, if randomly dispersed over the surface of the Ru particles will eliminate larger active centres, leaving only small isolated groups of atoms, the behaviour of which simulates that of very small particles. It is also possible that the toxins may prefer to occupy comfortable sites on areas of flat surface, so removing sites characteristic of large particles, and leaving only the edge and corner atoms free. Recalling that the small particles originally present in RuEC1 may well be electron-deficient [8], interpretations based on electronic effects cannot be entirely ruled out.

As to the four questions listed above, satisfactory answers require provision of another dimension of information. This is obtained by examining the effect of altering reactant pressures, especially that of H_2, on rates and particularly on product selectivities. Some preliminary account of this work has already been given [18–20], but it is preferable to await a full presentation of the extensive results of this kinetic study before attempting to synthesise a reaction model to account for the effects of both temperature and H_2 pressure. This we hope to do in a forthcoming paper.

Acknowledgements

References

[1] G.C. Bond, Chem. Soc. Rev., 20 (1991) 441; Acc. Chem. Res., 26 (1993) 490.
[2] M. Che and C.O. Bennett, Adv. Catal., 36 (1989) 55.
[3] G.C. Bond and Lou Hui, J. Catal., 142 (1993) 512.
[4] B. Coq, A. Bittar, R. Dutartre and F. Figueras, J. Catal., 128 (1991) 275.
[5] B. Coq, A. Bittar and F. Figueras, Appl. Catal., 59 (1990) 103.
[6] G.C. Bond, R. Yahya and B. Coq, J. Chem. Soc., Faraday Trans., 86 (1990) 2297.
[7] J.C. Kempling and R.B. Anderson, Ind. Eng. Chem. Process Des. Dev., 11, (1972) 146.
[8] B. Coq. E. Crabb, M. Warawdekar, G.C. Bond, J.C. Slaa, S. Galvagno, L. Mercadante, J. Garcia Ruiz and M.C. Sanchez Sierra, J. Mol. Catal., 92 (1994) 107.
[9] G.C. Bond and Xu Yide, J. Chem. Soc. Faraday Trans., 80, (1984) 3103.
[10] G.C. Bond, R.R. Rajaram and R. Burch, J. Phys. Chem., 90 (1986) 4877.
[11] G.C. Bond, R.R. Rajaram and R. Yahya, J. Mol. Catal., 69 (1991) 359.
[12] G.C. Bond, R.R. Rajaram and R. Burch, in M.J. Phillips and M. Ternan (Eds.), Proc. 9th. Int. Congr. Catal., Calgary, Vol. 3, 1988, Chem. Inst. Canada, Ottawa, 1988, p. 1130.
[13] B. Coq, personal communication, April 1994.
[14] B.J. Kip, F.B.M. Duivenvoorden, D.C. Koningsberger and R. Prins, J. Catal., 105 (1987) 243.
[15] G.C. Bond and S.F. Tahir, J. Chem. Soc., Faraday Trans., 87 (1991) 767.
[16] E.H. van Broekhoven, J.W.F.M. Schoonhoven and V. Ponel, Surf. Sci, 156 (1985) 899.
[17] G.C. Bond and R. Yahya, J. Mol. Catal., 69 (1991) 75
[18] G.C. Bond and J.C. Slaa, Catal. Lett., 23 (1994) 293.
[19] G.C. Bond and J.C. Slaa, J. Mol. Cat., 89 (1994) 221.
[20] G.C. Bond, R.H. Cunningham and J.C. Slaa, Topics Catal., 1 (1994) 19.