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Catalytic and structural properties of ruthenium bimetallic catalysts: hydrogenolysis of propane and n-butane on Ru/Al_2O_3 catalysts modified by a Group 14 element

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Abstract

The addition of Ge as Ge^nBu_4 to H-covered Ru/Al_2O_3 (RuEC1) leads after in situ reduction at high temperature (HTR1; 758 K) to decreases in H_2 chemisorption capacity and even more marked falls in activity for hydrogenolysis of propane and of n-butane. Changes in product selectivities are slight, and all Ge-containing samples exhibit similar characteristics to the parent RuEC1, which is very highly dispersed. Although loss of activity is chiefly due to encapsulation of the Ru^0 particles by amorphous GeO_x species, these affect neighbouring active sites by decreasing the equilibrium constant for alkane dehydrogenation to the reactive species. This conclusion follows from determinations of the rate-dependence on H_2 pressure and mathematical modelling of the results.

Similar behaviour is shown by the less well-dispersed RuEC3, where activity loss and selectivity changes are partly due to encapsulation by GeO_x of smaller particles: some evidence for selective blocking of Ru atoms in low coordination number sites by Sn species formed analogously is however obtained. H_2 pressure-dependence of the rate of n-butane hydrogenolysis was determined at four different temperatures with a GeO_x-modified RuEC3, whence a true activation energy (50 kJ mol^{-1}) and an enthalpy change for the alkane dehydrogenation step were obtained.

Oxidation and low-temperature reduction (O/LTR) of catalysts previously subjected to HTR1 led to very large increases in rate, and to changes in product selectivites, that suggested the creation of large, essentially pure, Ru particles; the modifier could not be wholly re-united with them by a second HTR.

Ru/Al_2O_3 catalysts of the NI series, prepared from inorganic precursors, showed greater dispersion in the presence of the modifier, the catalytic behaviour being in harmony with this observation.

Keywords: Bimetallic catalysts; Hydrogenolysis; Propane; Butane; Ruthenium; Alumina; Modified catalysts

1. Introduction

The first paper in this series has described the preparation and characterization of a number of supported Ru catalysts, to some of which an element of Group 14 (Ge, Sn or Pb) had been either added subsequently or had been incorporated as a compound in the preparation [1]. We have already reported the effects on rates of alkane hydrogenolysis of various pretreatments to the pure Ru catalysts [2] and on the kinetics of hydrogenolysis of the lower alkanes on some

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of these catalysts [3]; other colleagues have described the hydrogenolysis of 2,2,3,3-tetramethylbutane on pure Ru catalysts and some of their bimetallic counterparts [4]. This paper concerns the hydrogenolysis of propane and of n-butane on bimetallic Ru catalysts; with these simpler alkanes it may be possible to understand more fully how the modifying element changes the structure of the active centre. We also now have the benefit of further EXAFS measurements [5] to aid the interpretation of our results.

The theoretical basis of these studies has been developed in earlier publications [1,6]. Briefly it is believed, from the products of hydrogenolysing 2,2,3,3-tetramethylbutane, which are either isobutane or methane + 2,2,3-trimethylbutane, that on Ru particles of a sufficient size Ge atoms formed from a tetra-alkylgermane are randomly distributed over the metal surface, showing no preference for any particular class of surface site: the average size of Ru atom ensembles therefore becomes *smaller*. The larger atoms of Sn and Pb, formed analogously, seem however to show a preference for blocking sites containing Ru atoms of *low* coordination number, such as may be found at edges and corners, as the resulting catalytic behaviour simulates that of *large* particles [6] on which larger active centres comprising *high* coordination number atoms may be found. The validity of these models has been confirmed by quantum chemical calculations [7]. The purpose of the present work was to see whether the hydrogenolysis of linear alkanes responded similarly to the presumed differences in surface structure produced by the modifying atoms.

2. Experimental

2.1. Catalysts

The chemical and physical properties of the catalysts principally used in this work have been described in detail in an earlier publication [1]: the quantities that are needful to know in order to understand the results reported here are reproduced for convenience in Table 1. Briefly, the RuEC series was prepared using $Ru(acac)_3$, and the Group 14 element was added by reaction of a tetra-alkyl compound with the reduced Ru/Al_2O_3. RuNI1 was made with $Ru(NO)(NO_3)_3$, and the modified versions by co-impregnation with a solution containing this salt and a salt of the Group 14 element. The RuAB37 series had been prepared at Montpellier some time ago, by essentially the same method as that used for the RuEC series; their characteristics and behaviour in catalysed reactions of alkanes have been described before [6,8]. The $(H/Ru)_{tot}$ value for RuAB37 is 0.91 [2] and, on the basis that $(H/Ru)_{tot}$ is 1.28 ± 0.09 times $(H/Ru)_{irr}$ [2], the corresponding values for the modified catalysts are as shown in Table 1.

Table 1
Composition and H_2 chemisorption capacity of Ru-containing bimetallic catalysts

Catalyst	[Ru] (wt.%)	[M] (wt.%) [a]	$(H/Ru)_{tot}$	Catalyst	[Ru] (wt.%)	[M] (wt.%) [a]	$(H/Ru)_{tot}$
RuEC1	0.97	–	0.88	RuEC3	4.0	–	0.25
RuEC1Ge1	0.97	0.15	0.59	RuEC3Ge1	4.0	0.41	0.12
RuEC1Ge2	0.97	0.30	0.54	RuEC3Sn1	4.0	0.51	0.19
RuEC1Ge3	0.97	0.70	0.41	RuNI1	0.92	–	0.23
RuEC1Sn1	0.97	0.26	0.51	RuNI1Ge3	1.37	0.84	0.42
RuEC1Sn2	0.97	0.54	0.32	RuNI1Sn1	1.43	0.26	0.38
RuEC1Pb1	0.97	0.51	0.66	RuAB37	0.9	–	0.91
				RuAB37Ge	0.9	0.12	0.50
				RuAB37Sn	0.9	0.27	0.52

[a] M = modifying element.

2.2. Pretreatment and reaction conditions

Each sample of catalyst was first reduced in flowing H_2 (40 cm^3 min^{-1}) for 13 h at 753 K (HTR1). In certain cases the stability of the modified catalysts under the oxidising conditions used previously [2] was examined by applying (to the same sample as that used to test activity after HTR1) an oxidation (air, 623 K, 1 h) followed by reduction overnight at 433 K (O/LTR). Further, after activity testing, the same sample was again reduced overnight at 753 K (HTR2), and its behaviour studied. Further details of the procedure used were provided earlier [2]. Reactions were conducted in a continuous-flow reactor at atmospheric pressure. Two types of experiment are reported. (1) In thermal cycling the temperature was raised in steps of about 10 K over at least 100 K, a sample being removed for analysis towards the end of each 20 min isothermal period (stage 1), the temperature then being lowered back to the starting temperature in similar steps (stage 2) [2]. (2) For determination of the isothermal H_2 kinetics, the reaction pulse method [3] was used, in which known flows of H_2, alkane and N_2 were passed over the catalyst for only 1 min, towards the end of which time a sample was taken for analysis: the alkane flow was then stopped, and the H_2–N_2 mixture then passed for 19 min in order to restore the surface. Various H_2 concentrations ($\sim$ 0.02–0.8 atm) were obtained by altering the H_2 flow-rate, and the N_2 flow-rate sympathetically in order to keep the total flow constant; they were changed randomly, and standard values (usually H_2: alkane = 10:1) were interposed frequently to check for deactivation. Corrected rates were obtained by interpolation as described before [3]; they are expressed as mmol alkane reacted per g Ru per h.

2.3. Treatment of results

Product selectivities are given as the number of molecules of product formed for each alkane molecule reacted: thus for propane

$$S_1 + 2S_2 = 3$$

and for n-butane

$$S_1 + 2S_2 + 3S_3 = 4$$

It is unnecessary to cite values of S_1. Application of the Kempling–Anderson formalism [2,3] converts these molar selectivities into selectivity parameters, which for n-butane comprise F (defining the probability of central bond fission), and T_2 and T_3 which give the chances that adsorbed C_2 and C_3 species respectively will be converted into gaseous ethane or propane, rather than suffer further cracking. The equations that relate selectivities to these parameters are

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

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

cannot be solved, so it is necessary to assume that T_2 is the value of S_2 found in the reaction of propane under the corresponding conditions. Alternatively, where the propane reaction has not been performed, we assume T_2 to be unity (an approximate but not precise assumption): values of F and T_3 so derived are denoted by primes, and are italicised in the table of results.

H_2 chemisorption...	$H_2 + 2^* \rightleftharpoons 2H^*$	...K_H
Alkane dehydrogenation...	$C_nH_{2n+2} + (2n+3-x)^* \rightleftharpoons C_nH_x^* + (2n+2-x)H^*$	...K_A
Rate determining step...	$C_nH_x^* + H^* \rightarrow C_mH_y^* + C_{n-m}H_{x-y+1}^*$	...k_1
Fast final step...	$C_mH_y^* + (2m+2-y)H^* \rightarrow C_mH_{2m+2} + (2m+3-y)^*$	

$$\text{Rate} = k_1 K_A P_A (K_H P_H)^{(n-x)/2} / [K_A P_A + (K_H P_H)^{(n-x)/2} + (K_H P_H)^{(n+1-x)/2}]^2$$

Scheme 1. Reaction scheme and derived rate equation ES5B. *Note*: in the text and tables, extent of dehydrogenation of the alkane is defined by the number a of H_2 molecules evolved, so that $a = n + 1 - x/2$.

2.4. Mathematical modelling

A full description of the modelling procedure and its underlying philosophy has been given previously [3]; the reaction scheme and the derived rate expression ES5B are shown in Scheme 1.

3. Results

3.1. Effects of the modifying element on H_2 chemisorption

H_2 chemisorption isotherms have been measured for all catalysts used in this work, and the results published [1]; we have also explained [2] our reasons for preferring to use the *total* amount adsorbed, viz. $(H/Ru)_{tot}$, rather than the amount *irreversibly* adsorbed, as a means of estimating the free Ru surface. Semi-quantitative comments on particle size distributions as observed by TEM have also been made [1]. The chief purpose of these measurements is to count the number of uncovered Ru atoms and hence to estimate turnover frequencies (TOFs) for the catalysed reactions *per surface Ru atom* Ru_s. We do not know *a priori* the efficiency with which the modifiers mask the surface of the Ru particles [9], and so the values of $(H/Ru)_{tot}$ must be used to give this information. There are however a number of possible complications that need to be noted; these include (i) the slow attainment of equilibrium [1], (ii) possible interference by impurities (e.g. Cl [10], C), (iii) the compound nature of the chemisorbed state of H [11], (iv) the lack of certain knowledge of the H: Ru_s stoichiometry, especially at high dispersion, and (v) the unknown influence of the modifier, including the possibility of spillover onto it. Even in the absence of a modifier, it is meaningless to use the results of H_2 chemisorption to estimate a mean particle size when there is evidence (as there is from TEM in a number of cases [1]) of bimodal particle size distributions. Equally one cannot use $(H/Ru)_{tot}$ values in the presence of a modifier to estimate mean size, even if there is no suggestion from TEM of bimodality. Notwithstanding all these uncertainties, we propose to use $(H/Ru)_{tot}$ measurements to give the number of free Ru_s atoms, and to interpret derived conclusions with appropriate caution.

With the RuEC1 series, $(H/Ru)_{tot}$ falls as the Ge concentration is increased, but less than proportionately (Table 1 and Fig. 1), while at approximately equal surface concentrations of modifier Sn is more, and Pb is less, effective than Ge in lowering $(H/Ru)_{tot}$ (Fig. 1). Each Ge atom therefore initially prevents the chemisorption of about 1.5H atoms, although subsequent additions are less effective. Each Sn atom blocks about two H atoms, and each Pb atom about one.

The less well dispersed RuEC3 [1] behaves differently (Table 1), each Ge atom blocking only about one H atom, while each Sn atom is somewhat less effective. The same trend is also seen with the apparently well dispersed RuAB37 [6] (Table 1 and Fig. 1), where each Ge atom initially stops the chemisorption of about two H atoms.

3.2. Effects of modifiers on hydrogenolysis rates and selectivity parameters at constant temperature

Hydrogenolysis rates for both n-butane at 433 K (Table 2) and for propane at 473 K (Table 3) are suppressed as the Ge concentration in the RuEC1 series is increased, much more quickly than the $(H/Ru)_{tot}$ decreases. Thus the TOFs also decrease, in the manner shown in Fig. 2, where the values relative to that for the unmodified RuEC1 are used. The selectivity parameters F and T_3 both decrease with increasing Ge concentration (Table 2) and thus also with $(H/Ru)_{tot}$ (Fig. 3): the effect is however only marked with RuEC1Ge3. There are only very slight changes in S_2 for the propane reaction (Table 3).

The situation with RuEC1 modified by Sn

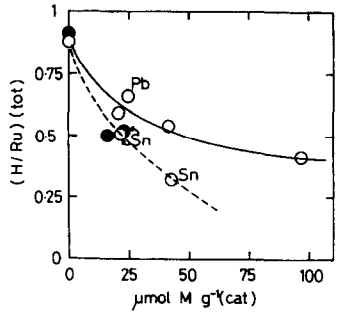


Fig. 1. Dependence of $(H/Ru)_{tot}$ on concentration of modifier. Open points, RuEC1 series; hatched points, RuAB37 series. Points for catalysts containing Sn or Pb are labelled accordingly: unlabelled points are for Ge-containing catalysts.

and Pb is different. In the latter case, the slight reduction in $(H/Ru)_{tot}$ (Table 1) scarcely affects hydrogenolysis rates (Table 2 and 3): if anything they are slightly faster, and TOFs higher than for RuEC1 itself (Fig. 2). Product selectivities are also virtually unchanged. With Sn the rates have been lowered by about one-third, although the TOFs are not much changed; a slight decrease in the values of F (Table 2) is however noted.

With the RuEC3 series, the inclusion of Sn lowers the rates of hydrogenolysis by a factor of about 35, and the TOFs by a slightly smaller factor (Tables 2 and 3). Ge is somewhat less effective in lowering rates and TOFs, and in both systems the selectivity parameters F and T_3 are reduced: their values are all much smaller than for any of the RuEC1 series (Fig. 3). Catalysts of the RuEC3 series suffer much less from deactivation between stages 1 and 2 than

Table 2
Kinetic parameters [a] for n-butane hydrogenolysis over various Ru-containing bimetallic catalysts after pretreatment HTR1

Catalyst	Temp. range (K)	E (kJ mol^{-1})	ln A	r_h	TOF × 10^3 (s^{-1})	S_2	S_3	F or F'	T_3 or T_3'
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
RuEC1Ge1	406–480	123	38.06	42.3	2.0	1.300	0.316	0.714	1.104
	480–406	145	43.27	17.5	0.83	1.230	0.349	0.670	1.058
RuEC1Ge2	427–501	123	36.45	8.6	0.44	1.170	0.363	0.620	0.955
	501–416	144	41.40	4.1	0.21	1.116	0.395	0.596	0.978
RuEC1Ge3	427–507	122	33.56	0.8	0.055	1.050	0.369	0.502	0.740
	507–437	130	35.91	0.6	0.041	0.936	0.414	0.417	0.716
RuEC1Sn1	386–449	123	39.63	2.1	11.0	1.271	0.329	0.671	1.000
	471–396	143	44.25	88.0	4.8	1.190	0.364	0.617	0.949
RuEC1Pb1	387–450	128	41.23	277	11.7	1.360	0.290	0.719	1.030
	449–375	144	42.19	185	7.8	1.310	0.390	0.681	0.968
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*
RuNI1Ge3	400–452	142	43.62	57.0	3.8	0.908	0.423	*0.331*	*0.633*
	450–398	146	44.53	50.7	3.4	0.911	0.410	*0.321*	*0.604*
RuNI1Sn1	389–452	123	39.61	227	16.7	1.056	0.419	*0.477*	*0.800*
	450–398	150	46.72	137	10.1	1.020	0.430	*0.451*	*0.784*
RuEC3	364–420	134	44.01	895	100	0.869	0.854	0.364	0.557
	419–398	139	45.30	788	88.5	0.852	0.361	0.346	0.552
RuEC3Ge1	400–441	145	44.50	70.5	16.4	0.765	0.388	0.262	0.526
	440–398	143	43.94	68.2	15.9	0.768	0.379	0.258	0.511
RuEC3Sn1	400–441	131	39.75	24.6	3.6	0.819	0.347	0.299	0.495
	440–398	131	39.43	23.0	3.4	0.827	0.328	0.290	0.462
RuAB37	393–454	150	47.9	460	14.2	1.010	0.430	*0.440*	*0.768*
RuAB37Ge	413–471	141	42.5	30	1.6	0.846	0.527	*0.373*	*0.840*
RuAB37Sn	394–452	139	42.6	53	3.0	0.735	0.460	*0.195*	*0.571*

[a] Rate r_h, TOF and selectivity parameters at 433 K; r_h and A in mmol g_{Ru}^{-1} h^{-1}.

Table 3
Kinetic parameters [a] for propane hydrogenolysis over various Ru-containing bimetallic catalysts after pretreatment HTR1

Catalysts	Temp. range (K)	E (kJ mol^{-1})	ln A	T (K)	r_h	TOF × 10^3 (s^{-1})	S_2
RuEC1	395–467	166	49.14	433	19.6	0.62	0.959
	467–383	166	48.97	433	22.7	0.72	0.964
RuEC1Ge1	418–491	127	37.99	473	257	12.7	0.940
	490–427	149	43.21	473	205	9.7	0.939
RuEC1Ge2	429–501	120	34.33	473	41.2	2.1	0.938
	501–417	146	40.63	473	31.0	1.6	0.936
RuEC1Ge3	440–513	105	28.64	473	7.4	0.51	0.948
	523–439	120	32.04	473	4.5	0.31	0.948
RuEC1Sn1	408–468	171	50.13	433	12.1	0.66	0.947
	468–399	176	51.33	433	12.2	0.67	0.950
RuEC1Pb1	388–470	162	47.94	433	20.6	0.87	0.952
	470–396	158	47.16	433	24.2	1.03	0.953
RuEC3	365–429	149	46.61	433	171	19.2	0.860
	429–365	155	48.21	433	179	20.1	0.865
RuEC3Ge1	400–441	146	43.10	433	12.1	2.82	0.875
	440–398	149	43.85	433	12.5	2.92	0.874
RuEC3Sn1	400–440	134	39.87	433	5.2	0.77	0.860
	460–398	136	39.43	433	4.7	0.69	0.860

[a] At the temperature given in column 5.

do those of the RuEC1 series, and there is correspondingly little change between the selectivities in the two stages.

The results available for the RuAB37 series are less complete (Table 2), because the propane reaction was not performed in this case: however the reductions in rate are much as for the RuEC3 series, the addition of Sn again causing the selectivity parameters F' and T_3' to decrease. Inclusion of Ge more effectively suppresses both rate and TOF, F' being decreased slightly but T_3' raised. In the RuNI series, Sn is markedly less effective in lowering the rate than is Ge; however, inclusion of any of the modifiers in any concentration in the preparation (made by co-impregnation) appears to result in *smaller* Ru particles, since the $(H/Ru)_{tot}$ ratio is raised. This conclusion was confirmed in the case of RuNIGe1 by TEM observations [1]. It is therefore impossible to separate quantitatively the effects of particle size and of surface modi-

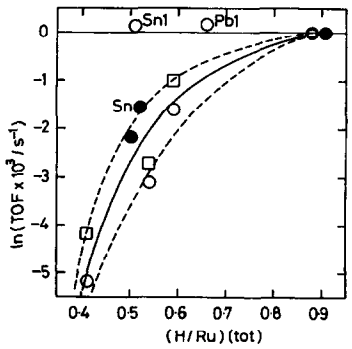


Fig. 2. Decrease in the TOF for alkane hydrogenolysis relative to that for the unmodified Ru/Al_2O_3's as a function of $(H/Ru)_{tot}$. Circles, n-butane (433 K); squares, propane (473 K). Other symbols as in Fig. 1.

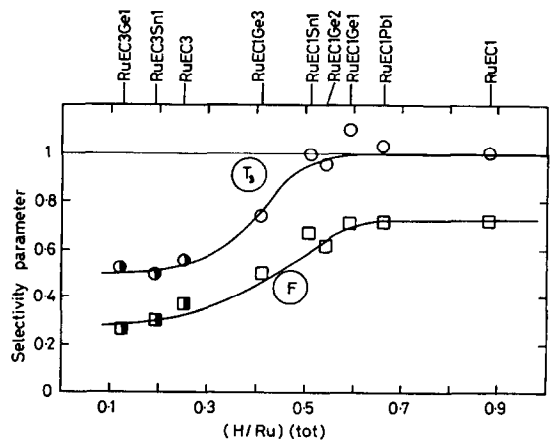


Fig. 3. Dependence of selectivity parameters F and T_3 on $(H/Ru)_{tot}$ for RuEC1 and RuEC3 series (stage 1 results, 433 K).

fication in this series. The effect of Sn is to *raise* both F' and T_3' quite considerably, to about the values shown by RuAB37: this supports the view than Ru NI1Sn1 shows the behaviour of quite small Ru^0 particles (H/Ru ≃ 0.8), only slightly modified if at all by Sn. With RuNI1Ge3 the selectivity parameters are moved to a much smaller extent in the same direction, and the rate is lowered about six-fold.

3.3. Effect of temperature on rates and product selectivities

As has been shown in our earlier publication [2], the state of the surface is even more fully revealed by examining the temperature coefficients of the selectivities parameters. For example, with RuEC1 after HTR1, selectivities were almost temperature-independent, and in a second paper [3] this behaviour was shown to correlate with a lack of dependence on H_2 pressures, except at the lowest values. These effects were ascribed to a high enthalpy of adsorption. With the less well-dispersed RuEC3, selectivities were both temperature- and H_2 pressure-dependent, because on the larger particles present in these catalysts the H_2 adsorption enthalpy was lower [2,3].

All the bimetallic catalysts of the RuEC1 series show the same small variation of selectivities with temperature as RuEC1 itself; indeed with RuEC1Ge3 (Fig. 4) the temperature coefficients are even smaller. There is no indication with either the RuEC3 or the RuAB37 series that the modifier produces much change in the temperature dependence of the selectivities: however in the RuNI1 series it tends to decrease in the sequence (Fig. 5).

RUNI1 > RuNI1GE1 > RuNI1Sn1

The effect of thermal cycling on the selectivity parameters F and T_3 in to decrease their values slightly in the case of the RuEC1 series, but the effects are much smaller or non-existent in the case of the less well dispersed RuEC3 and RuNI1 series (Table 2).

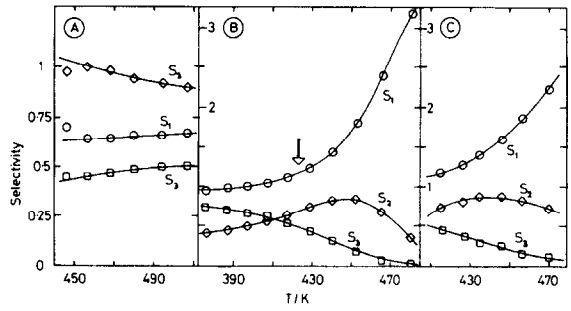


Fig. 4. Variation of product selectivities with temperature for RuEC1Ge3 following pretreatments (A) HTR1; (B) O/LTR; (C) HTR2 (stage 1 results). The arrow in (B) indicates the temperature at which conversion reaches 10%.

Stage 1 activation energies for the n-butane reaction (Table 2) are slightly lowered by inclusion of Ge, and markedly so for the propane reaction (Table 3): values for both reactions are usually 120–127 kJ mol^{-1}. For all catalysts in the n-butane reaction the stage 2 activation energies are raised, to about 145 kJ mol^{-1}, similar increases being noted in the propane reaction, but only with the Ge-containing samples. Effects of this kind are also seen with the RuNI1 series (Table 2), but not for either reaction with the RuEC3 series, for which, as we have already seen, there is comparatively little deactivation between stages 1 and 2.

3.4. Effect of Ge as modifier on the kinetics of alkane hydrogenolysis

We have previously [3] investigated how variation of H_2 pressure affects hydrogenolysis

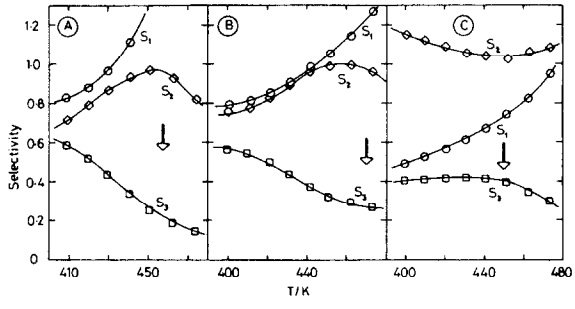


Fig. 5. Variation of product selectivities with temperature for (A) RuNI1, (B) RuNI1Ge3, and (C) RuNI1Sn1, following HTR1 pretreatment (stage 1 results). The arrows indicate the temperatures at which conversion reaches 10%.

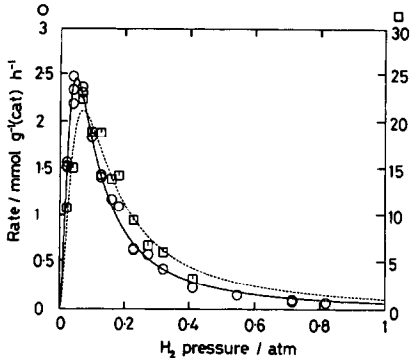


Fig. 6. Rate as a function of H_2 pressure for RuEC1 (□) and RuEC1Ge1 (○) at 428 K. The curves in this figure and in Fig. 7 are constructed using equation ES5B and the constants shown in Table 6.

rates, and have modelled the results by means of the equation termed ES5B [12] which is based on a plausible mechanism which invokes a partially dehydrogenated form of the alkane as the reactive intermediate (see Scheme 1). We have carried out such measurements with propane and with n-butane on RuEC1Ge1 at 427 K (see Fig. 6 for the n-butane results; corresponding results for RuEC1 [3] are shown for comparison), and with n-butane on RuEC3Ge at four temperatures between 379 and 410 K (see Fig. 7 for the results at 379 and 410 K, and the corresponding results for RuEC3 at 379 K). All measurements were preceded by the HTR1 treatment. The constants for the equation ES5B derived from these results by the optimisation

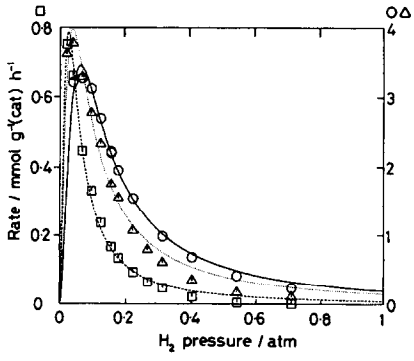


Fig. 7. Rate as a function of H_2 pressure for RuEC3 at 379 K (△), and for RuEC3Ge at 379 K (□) and 410 K (○).

routine [3] are shown in Table 6, where they are compared with those for the unmodified catalysts obtained under the closest possible conditions [3]. The curves drawn in Figs. 6 and 7 are obtained by use of these constants, and give a visual impression of the goodness of fit.

While a meaningful assessment of the effect of the modifier cannot be made in the case of propane, because results at the same temperature are not available, some discussion of the results obtained with n-butane is in order. Comparison of the values of the constants obtained with RuEC1 and RuEC1Ge1 at ~ 427 K, and with RuEC3 and RuEC3Ge at 379 K, both suggest that the observed decreases in rate under the standard conditions (Table 2) are due not only to a lowering of k_1 by a factor of 4–6 (which is not unexpected) but also to an 8-fold depression of K_A, and a halving of K_H: values of x or a are comparatively unaffected. We may also compare the computed constants for the reactions of propane and of n-butane on RuEC1Ge1 at 427 K (Table 6). The value of k_1 is somewhat larger for n-butane, and K_A is about 12 times greater: this suggests that a smaller fraction of the adsorbed propane is dehydrogenated to the reactive form than is the case with n-butane, and this is in line with the larger number of H atoms that have to be removed to achieve it (viz. ~ 4.7 compared to ~ 2.7).

It is not easy to decide exactly what significance to attach to the constants shown in Table 6. Of course the computation procedure yields very *precise* values, since it takes no account of experimental error in the measured points, and this in itself is a limiting factor. Standard deviations are also readily computed, but are not of great use for purposes of comparison, since their values depend on the range of values of the rates. The apparent close similarity between the shapes of the kinetic curves for RuEC1 and RuEC1Ge1 (Fig. 6) is misleading, because the analysis shows (Table 6) an eight-fold difference in K_A and a more than two-fold difference in K_H. Experience based on the consequences

to the values of the equilibrium constants of making small arbitrary changes to the coordinates of the experimental points teaches that they have a disproportionate effect, and that therefore differences in K_A and K_H of less than a factor of two should not be heeded. Note however that k_1 is simply a scaling factor, and its value is quite reliable. The reliability of the computed constants is much greater if the position of the maximum is clearly defined by the experimental points, but unfortunately this is not so here because the maxima lie at very low H_2 pressures (Figs. 6 and 7). It should also be greater where as with RuEC3Ge1 the extent of deactivation during the measurements is minimal.

Analysis of the results obtained by measuring the rate dependence on H_2 pressure at various temperatures with RuEC3Ge1 (see also Table 6) provides a further insight. The Arrhenius plot of k_1 (see Fig. 8) yields a true activation energy of 50.3 kJ mol^{-1}, while the Van't Hoff isochore plot of K_A (see also Fig. 8) gives a $-\Delta H_A$ of -93.5 kJ mol^{-1}, only a little higher than that [3] for RuEC3 itself (-84.3 kJ mol^{-1} [3]). The observed lowering of K_A is therefore chiefly to be associated with the entropy changes accompanying the dehydrogenation process. The Van't Hoff plot for K_H passes through a gentle maximum, as was observed before with unmodified Ru catalysts after HTR1 [3]: $-\Delta H_H$ must therefore be close to zero when the surface is substantially covered by H atoms.

The changes in the form of the H_2 order curves with temperature (Fig. 7) indicates that

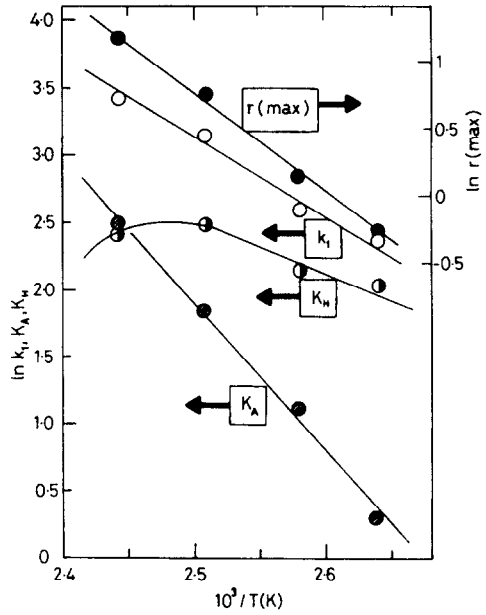


Fig. 8. Arrhenius plots for the rate constant k_1 and for the maximum observed rates r_{max}, and Van't Hoff plots for the equilibrium constants K_A and K_H obtained with RuEC3Ge after HTR1.

the *apparent* activation energy has to be a function of the H_2 pressure at which the rate is measured. This has been shown previously in the case of RuEC1 [3] and of Pt/Al_2O_3 [13], and is also true for RuEC3Ge in the present work (see Fig. 9A). In order to negate the effects of changing relative concentrations of reactive species with temperature, an Arrhenius plot may be constructed using the rate at the maximum for each temperature, where θ_H equals θ_A, A being the dehydrogenated alkane. For the present results such a plot gives a true

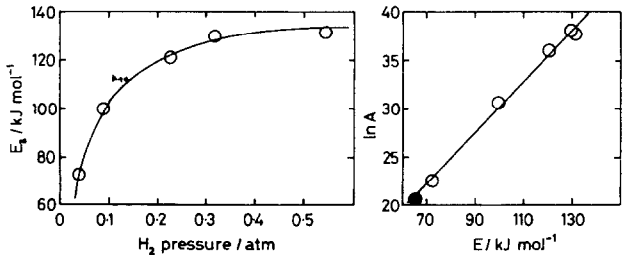


Fig. 9. (a) Apparent activation energy as function of H_2 pressure from rates for RuEC3Ge after HTR1. (b) Compensation effect shown by activation energies plotted in (a), with the true Arrhenius parameters derived from r_{max} (Fig. 8) (filled point).

activation energy of about 62 kJ mol^{-1} (Fig. 8), but it is probably less reliable than that derived from k_1 because the fastest rates observed (which are those used for this plot) are less than the maximum rates. This is because the H_2 pressure could not be lowered sufficiently to cover the rate maximum at the lower temperatures. These Arrhenius parameters display a convincing compensation effect (see Fig. 9B), which encourages speculation [3,13,14] that such effects may often arise from comparing rates on different catalysts at various rather than constant concentrations of reactant species.

Effects of H_2 pressure on selectivities are much as expected. With RuEC1Ge1 they hardly alter, the same behaviour having been shown by the parent RuEC1 [3]; with RuEC3Ge1 they respond sensitively to changing H_2 pressure, as was the case also with RuEC3 [3]. Values of F' are not markedly temperature-dependent.

3.5. The effect of oxidation and re-reduction

In our earlier work [2] we have noted that conversion of the metal in a pre-reduced Ru/Al_2O_3 catalyst to the oxide, followed by its reduction under mild conditions (viz. the O/LTR treatment), led to much increased rates and turnover frequencies. The effect appeared to be partially explicable not only by the substantial increase in particle size accompanying this treatment, but also perhaps by the formation of a rougher (i.e. more defective) surface and/or the presence of unreduced Ru^{x+} ions [2]; such ions are known to be present in the highly dispersed RuEC1 even after HTR [5]. We shall be reporting the results of EXAFS and further catalytic studies on catalysts subjected to O/LTR in due course. The role of these latter factors is shown by the fact after HTR2 the rates for this catalyst are lowered to about the values found after HTR1, although the TOFs are higher, because HTR2 does not cause any further major increase in particle size [2]. It therefore seemed desirable to explore the effect of these further treatments on the bimetallic catalysts; this is shown by the results for the catalysts RuEC1Ge3, RuNI1Sn, RuAB37Ge and RuAB37Sn in Table 4: corresponding results for the unmodified catalysts are reproduced for ease of reference.

The results show that the O/LTR treatment leads to some very marked, indeed startling, increases in activity (compare Tables 2 and 4). For the pure Ru/Al_2O_3 catalysts the factors, based on rates at 433 K, are about five; this effect has been ascribed [2] to an increase in TOF in consequence of the growth in particle

Table 4
Kinetic parameters [a] for n-butane hydrogenolysis over various Ru-containing bimetallic catalysts after pretreatment O/LTR

Catalyst	Temp. range (K)	E (kJ mol^{-1})	ln A	r_h	S_2	S_3	F'	T'_3
RuEC1	374–438	122	40.96	1216	0.714	0.427	*0.142*	*0.499*
	373–426	120	40.61	1350	0.707	0.430	*0.137*	*0.500*
RuEC1Ge3	376–417	124	42.64	3454	0.711	0.382	*0.153*	*0.454*
	417–376	129	43.73	2783	0.736	0.404	*0.140*	*0.471*
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*
RuNI1Sn1	378–410	139	46.80	3620	0.765	0.382	*0.148*	*0.450*
	408–376	123	42.12	2570	0.742	0.395	*0.138*	*0.460*
RuAB37	383–433	110	38.3	2205	0.720	0.440	*0.160*	*0.524*
RuAB37Ge	373–435	114	39.3	2150	0.720	0.465	*0.185*	*0.571*
RuAB37Sn	373–434	111	38.7	2661	0.735	0.433	*0.168*	*0.520*

[a] Rate r_h, TOF and selectivity at 433 K; r_h and A in mmol g_{Ru}^{-1} h^{-1}.

size that this treatment causes. However for the modified RuNI1 the factor is about 15, for the modified RuAB37 about 50–70, but for RuEC1Ge3 it is of the order of 5000! It is quite evident that the oxidative treatment has removed the inhibiting species (GeO_x, Sn^{x+}) from the surface of the Ru particles, and that the ensuing mild reduction has not restored them. The resulting Ru^0 particles are therefore more or less clean, and show the same kind of high activities as the pure Ru catalysts after the same treatment. However, while in the RuAB37 series the rates after O/LTR are all very similar (Table 3), for the RuEC1 and RuNI series the rates shown by the bimetallic catalysts are some two-and-a-half times *greater* than those of the corresponding pure Ru/Al_2O_3's. The effect is especially marked between RuEC1 and RuEC1Ge3 (Table 4). Unfortunately we were unable to determine the H/Ru ratios after the O/LTR treatment, so we cannot calculate TOFs. Stage 1 activation energies are about the same as those found after HTR1 (they are somewhat lower in the RuAB37 series), but do not show the consistent elevation in the less active stage 2 that characterises the HTR1 treatment (Table 2).

Further confirmation that activity following O/LTR is essentially due to unmodified (or only slightly modified) Ru particles comes from the selectivity parameters (Table 4). Differences from the values given by the pure Ru/Al_2O_3's are comparatively minor, although where the activity of the 'modified' catalyst is greater there is a lowering of the values of T_3', and, in the case of RuNI1Sn1, of F' as well: these changes are in the sense expected for an *increase* in particle size [8].

It is then of interest to see whether, or to what extent, modification may be re-instituted on the Ru surface by a further high-temperature reduction (HTR2: see Table 5). Rates for the modified catalysts are lower than those found after O/LTR, consistent with the behaviour of pure Ru/Al_2O_3's [2], but generally higher than after HTR1. Detailed inspection of the rates leads us to conclude that in the RuNI series there is no restoration of the modifying species (although the value of T_3' is lower for the Sn-containing sample), some limited restoration in the RuAB37 series, and perhaps somewhat more in the case of RuEC1Ge3. On the whole, however, the modifications observed after HTR1, whatever their cause, are far from fully replaced by HTR2, and any oxidative treatment above room temperature is therefore best avoided.

Table 5
Kinetic parameters [a] for n-butane hydrogenolysis over various Ru-containing bimetallic catalysts after pretreatment HTR2

Catalyst	Temp. range (K)	E (kJ mol^{-1})	ln A	r_h	S_2	S_3	F'	T_3'
RuEC1	374–426	130	41.88	313	0.812	0.391	*0.203*	*0.492*
	436–394	141	45.05	313	0.813	0.380	*0.194*	*0.473*
RuEC1Ge3	405–456	130	39.61	28.1	0.851	0.312	*0.163*	*0.373*
	457–407	138	41.45	24.6	0.841	0.325	*0.165*	*0.390*
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*
RuNI1Sn1	377–430	138	43.62	188	0.848	0.366	*0.214*	*0.467*
	419–387	151	47.16	201	0.848	0.358	*0.205*	*0.452*
RuAB37	383–432	125	40.4	318	0.770	0.390	*0.160*	*0.464*
RuAB37Ge	384–434	133	42.0	165	0.810	0.345	*0.155*	*0.408*
RuAB37Sn	402–433	130	41.4	190	0.810	0.370	*0.180*	*0.450*

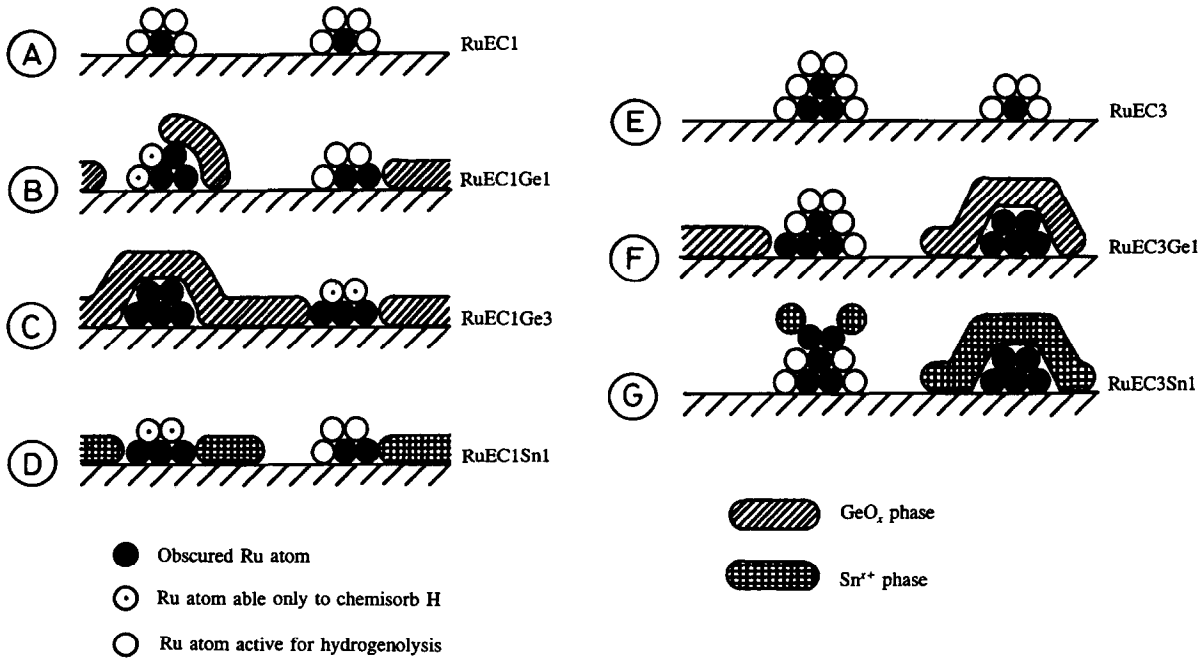
[a] Rate r_h, TOF and selectivity at 433 K; r_h and A in mmol g_{Ru}^{-1} h^{-1}.

4. Discussion

4.1. Structure and activity of RuEC1 series bimetallic catalysts

We consider first the structure and properties of *Ge-containing catalysts* of the RuEC1 series following HTR1 (Scheme 2). We recall that RuEC1 itself is shown by a number of tests (H_2 chemisorption (Table 1), TEM, EXAFS [1,5]) to have extremely small metallic particles, probably containing only a dozen or so atoms, its catalytic properties being characterised by high values of both T_3 (~ 1.0) and F (~ 0.75), and a lack of marked dependence of product selectivities on both temperature [2] and H_2 pressure [3]. This behaviour was attributed to strong chemisorption of H atoms, and may be denoted by the term *small particle behaviour* (**SPB**). It is inevitable that Ru particles as small as those present in RuEC1 after HTR1 cannot display the variety of types of site available in larger particles, and that the discrimination that the Group 14 elements may then show between different classes of site on larger particles will not be possible with those having only a few atoms. Materials containing such particles are however catalytically active, although TOFs for hydrogenolysis of propane and of n-butane (Tables 2 and 3) are 10–30 times lower for RuEC1 than for RuEC3. However the larger particles in RuEC3 show quite different product selectivities ($T_3 \simeq 0.5$, $F \simeq 0.3$) and much more marked variation with temperature and H_2 pressure [2,3], probably because the H atoms are more weakly chemisorbed. This may be called *large particle behaviour* (**LPB**). We conclude that *most if not all of the small particles in RuEC1 are catalytically active*, and that activity is not simply due to a few large and very active particles.

Although the addition of Ge or other modifiers to RuEC1 is unlikely to confirm the hypotheses described in the Introduction based on earlier work with larger particles [6], the EXAFS studies on the Ge-containing catalyst of the RuEC1 series [5,15] reveal useful information.



Scheme 2. Representations of surface structures present in variously modified RuEC1 and RuEC3 after HTR1.

They provide no evidence for Ru–Ge bonding in the samples investigated, with the possible exception of RuEC1Ge3. Nevertheless it is quite certain that the capability of the small particles in RuEC1 to chemisorb H_2 and especially to hydrogenolyse alkanes is lowered progressively as the Ge content is raised (Tables 1 and 2, Fig. 1). The EXAFS evidence suggests [15] that the Ge is present as an amorphous oxide, not as crystalline GeO_2, and that therefore the Ge atoms formed in the initial reaction of the Ge alkyl with the reduced Ru surface were oxidised on exposure to the air, and that even the stringent HTR1 conditions failed to reduce them back to Ge^0. The Ru particles are therefore probably either partially or completely covered by oxo-germanium species (GeO_x) in which Ru–O–Ge but not Ru–Ge bonds are present (Scheme 2, A–C). Each very small Ru particle may comprise only a single active centre, or two or three at the very most, so that *partial* obscuration by GeO_x may inactivate it completely for hydrogenolysis, although H_2 chemisorption might still be possible. This would explain the apparent trend of decreasing TOF with increasing Ge concentration (Fig. 2).

This model also interprets other features of the reactions catalysed by the RuEC1 series. (i) There is no progressive decrease in F and T_3 with the Ge-containing RuEC1 series (Table 2, Fig. 3), most of which show essentially **SPB**. (ii) Only in the case of RuEC1Ge3 is there some suggestion of a decrease in the selectivity parameters, and of some formation of Ru–Ge bonds: the residual low activity might however be partly due to a few uncoated larger particles. (iii) There is no progressive change in activation energy with Ge content, except in the propane reaction where (Table 3) it is lowered by the first Ge addition. (iv) The quite marked deactivation between stages 1 and 2, which is a feature of the partially-coated catalysts, and which is more noticeable with n-butane than with propane (Tables 2 and 3), implies that a very slight 'carbon deposition' may complete the deactivation of particles already partly covered: the increase in activation energy in stage 2 could reflect an alteration in the H chemisorption strength induced by multiply-bonded carbon species on particles retaining their activity.

The dangers of relying simply on results obtained at a fixed H_2: alkane ratio are however well illustrated by the results in Table 6, which show that the inclusion of Ge in RuEC1 causes a substantial decrease in K_A and a smaller one in K_H, as well as the decrease in k_1 which would be expected on the above model. This result suggests that GeO_x species on or adjacent to Ru particles exert some influence particularly on the alkane dehydrogenation equilibria and to a lesser extent on K_H. Values of k_1 are depressed (by factors of 4–6) more than propor-

Table 6
Optimum values of the constants of the rate expression ES5B obtained through the effect of H_2 pressure variation on rates of hydrogenolysis

Catalyst	Alkane	T (K)	k_1	K_A	K_H	x	a
RuEC1	C_3H_8	418	80.0	17.1	24.8	3.32	2.34
RuEC1Ge1	C_3H_8	427	11.7	0.49	7.1	3.26	2.37
RuEC1	n-C_4H_{10}	428	153.6	47.3	23.2	7.32	1.34
RuEC1Ge1	n-C_4H_{10}	427	24.5	6.2	10.1	7.08	1.46
RuEC3	n-C_4H_{10}	379	37.2	9.9	16.2	7.62	1.19
RuEC3Ge1	n-C_4H_{10}	379	10.7	1.2	7.7	7.04	1.48
RuEC3Ge1	n-C_4H_{10}	388	13.3	3.0	8.6	6.91	1.55
RuEC3Ge1	n-C_4H_{10}	399	23.3	6.3	12.0	7.74	1.13
RuEC3Ge1	n-C_4H_{10}	410	31.0	11.9	11.3	7.40	1.30

tionately to the decrease in $(H/Ru)_{tot}$, as is usually the case when the active centre is larger than that required for H_2 chemisorption (see Fig. 2). Note that the difference in temperature between the two data-sets for propane is not large enough to account for the changes in the equilibrium constants. Concerning the K_A values, we conclude that a smaller fraction of the chemisorbed alkane is able to undergo dehydrogenation to the reactive species, but that the same species are reactive both on RuEC1 and on RuEC1Ge1, as witnessed by the constant values of F and T_3 (Table 2 and Fig. 3). We should also note that RuEC1Ge1 suffered a 60% loss in activity during measurement of the H_2 kinetics, which took place over three days, and required frequent use of standard conditions (10:1 H_2: alkane) in order to correct for this. The detailed method, with typical results, has already been described for RuEC1 [2]. This deactivation, at fixed temperature, has an imperceptible effect on selectivity parameters (Figs. 3 and 6B), perhaps because the catalysts is partially carbided throughout. Thus the inclusion of Ge, and the variation of H_2 concentration, both affect the number of reactive centres, but not their composition as indicated by the values of F and T_3. The form of the dependence of rate on H_2 pressure as interpreted by the reaction network in Scheme 1 and the derived equation ES5B means that below the maximum the rate is governed by $[H^*]$ and above the maximum by $[C_nH_x^*]$, which is turn is limited by the availability of vacant sites needed to receive the H atoms sloughed off the alkane.

The lack of change of selectivities with H_2 pressure in the case of RuEC1Ge1, observed with both propane and butane, is characteristic of **SPB**, while the variations observed with RuEC3Ge1, which closely resemble those shown by the parent, epitomise **LPB** [3].

There is little to add concerning the Sn and Pb additions, which have little effect either on rates or selectivities (Tables 1 and 2, Figs. 1–3). Sn has a minor effect on rates, and increases the deactivation between stages 1 and 2, so there may be some partial interaction in this case. The essential features of **SPB** are however retained.

4.2. *Structure and activity of the RuEC3, RuAB37 and RuNI series*

Our interpretation of the effect of adding Ge and Sn to RuEC3 (Table 2 and Fig. 3) is based on the observations that the unmodified catalyst has a bimodal particle size distribution [1] and that EXAFS results [5] show no evidence of Ru–Ge bonding, although as with RuEC1 some Ru–O–Ge bonding is not excluded. Although we cannot quantify the relative amounts of large and small particles from the TEM results [1], we may suppose that the large ones are responsible for the greater part of the activity since their intrinsic activity is greater. The observed reductions in rate and decreases in F and T_3 (Table 2) may therefore be due to two factors: (i) complete encapsulation of the small particle fraction, plus in the case of Sn (ii) the possible extra effect of decorating low coordination number Ru^0 atoms, as the prior literature [6] suggests. We note that Sn depresses the rate more than Ge in this case (Scheme 2, E–G).

Concerning the RuAB37 series (Table 2), discussion is more difficult because propane hydrogenolysis has not been carried out, and we have only F' and T_3' values. These do not change greatly on Ge addition, although the rate is much decreased. The Ru^0 particles in the parent catalyst are quite small (Table 1), and so it seems likely that the Ge (probably as amorphous GeO_x) coats them completely or at least partially, so that residual activity is due to some 5% which remain active but little altered. Behaviour is thus similar to that of the RuEC1 series, and once again there is a very marked activity loss ($\sim$95%) while the H/Ru ratio falls by less than 50%. Addition of Sn has however a much greater effect on F' and T_3' in the direction of **LPB**. This is probably not due to selective site blocking because the particles are too small; remaining possibilities include (i) activity due to a few large uncovered (or selec-

tively covered) particles, and (ii) a restructuring of the Ru + Sn to give some large ensembles of Ru atoms.

Finally we consider the NI series, in which we have observed [1] the unusual effect of the modifiers causing the Ru^0 dispersions to be greater than for the parent RuNI1 (Table 1); the mechanism of this effect is not yet clear, but the values of F' and T_3' confirm the trend towards **SPB**, shown more markedly in the case of Sn than with Ge. The modifiers do however cause the rates to decrease (Table 2), so the faster rates that might have been expected are not observed in consequence of the encapsulation of some Ru^0 particles. The O/LTR treatment leads to much increased rates in each case (Table 4) and to alterations in selectivity parameters that are consistent with a change to **LPB**. Rates are substantially decreased by HTR2, but F' and T_3' still point to **LPB** (Table 5).[9]

Acknowledgements

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