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Catalytic Properties of Well Dispersed Supported Ruthenium Alloys

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Small particles of Ru alloyed with Sn, Pb, Sb, Ge, or Si were prepared by reacting a well dispersed Ru/Al_2O_3 parent sample with an organometallic compound of the desired modifier, by the so-called controlled surface reaction method. Two series of RuSn samples were thus obtained from parent Ru catalysts of 75% and 35% dispersion. The adsorption of hydrogen as a function of the amount of Sn shows a large initial decrease on the smaller particles, and a linear variation on the less dispersed catalyst. These catalysts were compared to Ru/Al_2O_3 catalysts of widely varying dispersion in the hydrogenolysis of *n*-hexane (*n*H) and 2-methylpentane (2MP) at 458 K, and of 2,2,3,3-tetramethylbutane (TeMB) at 473 K. On pure Ru/Al_2O_3 catalysts a strong effect of particle size is observed, both on turnover frequencies and on selectivities. When the dispersion is increased, turnover frequencies and deep hydrogenolysis decrease; the selectivity for TeMB hydrogenolysis is shifted from splitting of the central bond (2 iC_4) to demethylation (C_1 + iC_7), and that of *n*H from the cleavage of external to internal bonds. The addition of about 0.3 wt% of Sn or Pb to the well dispersed Ru sample shifts the catalytic properties towards those of large particles, while a similar amount of Ge stimulates an opposite behaviour and shifts the catalytic properties toward those of smaller particles. These effects can be attributed to the preferential occupancy of edge and corner sites by Sn or Pb in bimetallic catalysts, as predicted by the theory of topological segregation. Ge could either be localised at the dense planes or be randomly distributed. On larger Ru particles, the addition of Sn has only little effect on selectivity. In that case no topological segregation was expected and the catalytic results suggest the formation of Sn islands.

INTRODUCTION

The extent to which the catalytic properties of metals can be affected by alloying has been extensively reviewed (*1–6*). The inclusion of an inactive component in the surface of an active metal usually lowers the catalytic activity for hydrogenolysis of C–C bonds, but changes little the activity for hydrogenation. Moreover, this effect can occur at low concentration of the additive, if the latter segregates at the surface. This concept of surface segregation is now well established (*3*). The additive can alter the properties by several different mechanisms, which can be summarized in terms of electronic or geometric factors, the respective importance of which is still discussed. Many results have favoured the ensemble theory, which supposes that a given reaction requires as the active site an ensemble of *n* free and neighbouring metallic atoms (*1, 6*). In this model the addition of an inactive metal such as Cu or Au always decreases catalytic activity. The changes of selectivity can then be attributed to a different size of the ensemble required for the given reaction.

The catalytic properties of very small particles of alloys are not well documented. They could be interesting because topological segregation should occur when the size of the particles reaches 1–2 nm. Previous theoretical calculations suggested that the distribution of the two components should not be random (*7, 8*), and that for the same reasons which produce an enrichment of the surface in one component, a segregation of

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this component to sites of lower coordination should also occur. Recently these proposals received additional support in a study by Strolh and King (*9*). These authors modelled perfect cubooctahedral bimetallic particles with a Monte Carlo simulation technique that uses a coordination-dependent potential model. They reached the conclusion that in the Pt–*Ib* system (*Ib* = Cu, Ag, Au) an enrichment of the surface layer with the *Ib* metal does occur. Moreover, on this surface layer Cu, Ag, and Au segregate to the low coordination sites, edges and corners. The extent of this segregation depends on both the cluster size and the *Ib* element.

These low coordination sites, such as edges and corners, represent a notable part of the surface of small particles. Such bimetallic catalysts can be obtained by controlled surface reaction of an organometallic compound with a supported metallic catalyst (*10–12*). They are model systems, which allow one to control more easily the dispersion of the alloy since the particle size is determined, to a first approximation, by that of the parent monometallic catalyst. They offer an opportunity of checking the possibility of topological segregation which could exist on small particles.

In a previous work concerning RhCu/SiO_2 (*13*) we proposed a topological segregation of Cu at the surface of Rh particles with a size of 2–3 nm. This proposal was based on the changes of activity and selectivity for the conversion of several hydrocarbons, including *n*-hexane, 2-methylpentane, 2,2-dimethylbutane, 2,2,3,3-tetramethylbutane, and methylcyclopentane. On pure rhodium catalysts, these reactions show different sensitivities to the surface structure (*14*). 2,2,3,3-Tetramethylbutane, for instance, is split into CH_4 and isoheptane on small particles (size <1 nm), whereas a selective central cleavage into isobutane occurs on particles larger than 5 nm. This behaviour reflects the formation of different surface intermediates, $\alpha\gamma$ and $\alpha\delta$, which have been postulated also for 2,2,3,3-tetramethylbutane/D_2 exchange (*15*). For the reactions of 2,2,3,3-tetramethylbutane on Rh, the activation energy for exchange is 84 kJ mol^{-1} (*15*), whereas it is 210–250 kJ mol^{-1} for hydrogenolysis (*14*). It can then be supposed that the slow step of the reaction is the decomposition of the surface complex. In organometallic chemistry the stoichiometric reaction of metallacyclopentanes has been shown by Grubbs *et al.* (*16*) to depend on the coordination of the metallic complex: thus C–C bond splitting was observed for high coordinations only. The preferred formation of isobutane on large particles appears as the catalytic counterpart of this finding, and the conversion of 2,2,3,3-tetramethylbutane is then a sensitive probe for the coordination of the surface atoms.

This study on rhodium has been extended to ruthenium and some of its alloys in a recent short publication (*17*). Ruthenium is very active for the hydrogenolysis of C–C bonds (*18–21*). The addition of Cu or Au decreases both the activity and the selectivity for deep hydrogenolysis (*22–25*). We report here the catalytic properties of Ru catalysts modified by the addition of Sn, Pb, Sb, Ge, or Si to Ru catalysts of different dispersions by the reaction of organometallic compounds. Hydrogenation of benzene and hydrogenolysis of various alkanes, were taken as test reactions.

In the ensemble theory, the decrease of particle size is formally equivalent to a dilution of the active surface by alloying, since both effects tend to reduce the size of the ensembles available at the active metal surface. It is then interesting to compare these two effects. The decrease of the size of the ruthenium particles affects the catalytic properties for alkane hydrogenolysis (*26*), and the tendencies are the same as for rhodium. For the sake of clarity we will briefly recall them in the present work, including results for a few Ru/Al_2O_3 catalyst of different dispersions (*26*).

EXPERIMENTAL

Reactants

Hydrogen of high purity grade (99.99%) was used for the catalytic experiments, and hydrogen of ultra-high purity (99.995%) for adsorption measurements. The hydrocarbons used were *n*-hexane, *n*H (Fluka, purity >99.6%), 2-methylpentane, 2MP (Aldrich, purity >99.4%), 2,2,3,3-tetramethylbutane, TeMB (Aldrich, purity >99.99%), and benzene (Fluka, purity >99.9%). Ruthenium acetylacetonate from Aldrich (purity >97%) was used as precursor for the catalysts. This precursor was chosen in order to avoid the effect of chlorine upon the chemisorption or catalytic properties (*20, 27–29*). The precursor was dissolved either in dehydrated benzene or in trichloroethylene (purity >99.5%).

The second metal was introduced as tetra-*n*-butyl tin (Merck, purity >95%), tetra-*n*-butyl lead (Alfa Products, purity >98%), tetra-*n*-butyl germanium (Alfa Products), tetra-*n*-butyl silicon (Petrach System), or tri-*n*-butyl antimony (Alfa Products). These organometallic compounds were dissolved in *n*-heptane (Fluka, purity >99%). The carrier was γ-alumina from Woelm (surface area 200 $m^2\ g^{-1}$).

Catalyst Preparation

The Ru/Al_2O_3 samples were prepared by ligand exchange from the acetylacetonate precursor according to procedures described by Boitiaux *et al.* (*30*), and reported in detail elsewhere (*26*). A benzene solution of the precursor was contacted with the carrier for several hours. After ligand exchange had proceeded, the solution was either filtered to obtain a well dispersed catalyst or evaporated to reach medium dispersion. The resulting solid was reduced under flowing hydrogen (1 $cm^3/g/s$) at 673 K overnight.

The bimetallic $RuMe/Al_2O_3$ samples (*Me* = Sn, Pb, Ge, Si, or Sb) were prepared by contacting *in situ* a prereduced Ru/Al_2O_3 parent catalyst with the desired amount of $(C_4H_9)_4Sn$, for instance, in *n*-heptane solution. The controlled surface reaction was carried out under hydrogen atmosphere at room temperature with a solid/liquid ratio of 1 g/10 cm^3. The solid was then dried and reduced directly under hydrogen at 673 K, to obtain true bimetallic particles.

Catalyst Characterisation

The dispersion of ruthenium was determined by hydrogen chemisorption following the method proposed by Yang and Goodwin (*31*). The hydrogen adsorption measurements were made at room temperature in a conventional volumetric apparatus. The sample was reactivated *in situ* overnight at 673 K. It was then outgassed to 5×10^{-3} Pa for 3 h at the same temperature. Isotherms of total H_2 adsorption (H_{total}) on the fresh catalyst were determined from 6.6 to 33 kPa. The time for equilibration at each pressure ranged between 3 and 4 h. The catalysts were then evacuated for 10 min at 293 K and a second adsorption was carried out in the same manner. The difference between the two isotherms gave the irreversibly adsorbed hydrogen, for which the stoichiometry $H_{irr}/Ru_s = 1$ has been reported (*32*). The results of chemisorption were checked by transmission electron microscopy using a JEOL 100CX microscope. The agreement was generally good for Ru/Al_2O_3.

Catalytic Experiments

The reaction of benzene, *n*-hexane, 2-methylpentane, and 2,2,3,3-tetramethylbutane with hydrogen were carried out at atmospheric pressure in a microflow reactor operated at low conversion in order to avoid heat and mass transfer limitations. The effluents were analyzed by sampling on line to a gas chromatograph equipped with a J & W capillary column (30 m × 0.5 mm i.d., DB1 apolar bonded phase). An aliquot (50 to 100 mg) of the sample used for chemisorption measurements was reactivated *in situ* under flowing hydrogen at 673 K overnight. The reaction temperatures were from 423 K to 493 K for alkane conversions, and 292 K for benzene conversion. The molar ratios of reactants were $H_2/nH = 14.0$, $H_2/2MP = 9.4$, $H_2/TeMB = 44$, $H_2/\text{benzene} = 10.7$. With these conditions of reaction the catalytic activity was stable as a function of time on stream for the conversion of alkanes.

TABLE 1

Chemical Compositions and Adsorption Properties of Supported Ru Catalysts

Sample	wt% Ru	Adsorption capacities		
		H_{total}/Ru	H_{rev}/Ru	H_{irr}/Ru
Ru19B[a]	0.86	0.07	—	0.07
Ru38[a]	1.0	0.44	0.09	0.35
Ru11[a]	0.61	0.69	0.31	0.38
Ru45[b]	1.0	0.75	0.10	0.65
Ru37[b]	0.93	0.92	0.17	0.75
Ru7[b]	0.31	1.4	0.30	1.1

Note. All catalysts were reduced at 673 K, except Ru19B obtained by the cycle reduction 673 K, oxidation in air 723 K, reduction 673 K (from Ref. (*26*)).

[a] Prepared by evaporation of the solution.

[b] Prepared by ligand exchange, then filtration of the solid.

RESULTS

Characterisation of the Catalysts

The chemical compositions of the samples and the Ru dispersion are reported in Table 1 for the Ru/Al_2O_3 samples, and in Table 2 for the supported alloys. At high dispersion, the stoichiometry H_{irr}/Ru is larger than unity, in agreement with the proposal made by Vis *et al.* (*33*) that the stoichiometry of H_2 adsorption surpasses 1 on small particles.

It is interesting to note that the addition of tin also puts forward some differences in the adsorption of hydrogen as a function of Ru particle size. If we plot (Fig. 1) the H_{irr}/Ru ratio as a function of the amount of tin, it appears that a linear plot is obtained on the large particles of Ru38: this is the behaviour expected if one atom of Sn covers one atom of Ru and there is a hydrogen chemisorption stoichiometry of 1. However, on the smaller Ru particles of Ru37 the toxicity of tin for hydrogen adsorption is initially much higher when compared to that observed on Ru38. This change might suggest a particular localisation of those Sn atoms which are introduced first.

The size of the bimetallic clusters (series RuSn/Al_2O_3 issuing from Ru37) is not significantly different from that of pure ruthenium particles of the parent catalyst (Figs. 2–4 and Table 1). This behaviour was expected from the small amounts of the second metal introduced.

Benzene Hydrogenation

The activities for the hydrogenation of benzene at 292 K are reported in Table 3. They are expressed as turnover frequencies or numbers of molecules converted per surface metal atom and per hour. For pure Ru catalysts, the turnover frequency does not change much with dispersion, since a variation of 4 at most is observed. A significant decrease of activity is observed mainly for RuSn alloys with a high Sn amount where the specific activity then falls by a factor of 30 (Ru37SnC).

Hydrogenolysis of Alkanes

The conversion of alkanes around 460 K on Ru catalysts gives essentially hydrogenolysis. After a small decrease of the initial rate, typically 30%, a steady state activity

TABLE 2

Chemical Compositions and Adsorption Properties of the Ru*Me*/Al_2O_3 (*Me* = Sn, Pb, Sb, Ge, Si) Bimetallic Catalysts

Sample	*Me*/Ru (at/at)	Adsorption capacities		Size by TEM (nm)
		H_{irr}/Ru	H_{rev}/Ru	
Ru37	0	0.75	0.16	1.05
Ru37SnA	0.26	0.39	0.11	0.9
Ru37SnB	0.63	0.31	0.11	1
Ru37SnC	0.84	0.27	0.11	1.1
Ru37Ge	0.18	0.41	0.12	—
Ru37Si	0.20	0.37	0.11	—
Ru38	0	0.35	0.09	2.2
Ru38SnA	0.27	0.22	0.06	—
Ru38SnB	0.45	0.17	0.06	2.3
Ru38SnC	0.62	0.11	0.07	—
Ru45	0	0.65	0.08	—
Ru45Pb	0.23	0.26	0.09	—
Ru45Sb	0.13	0.33	0.09	—

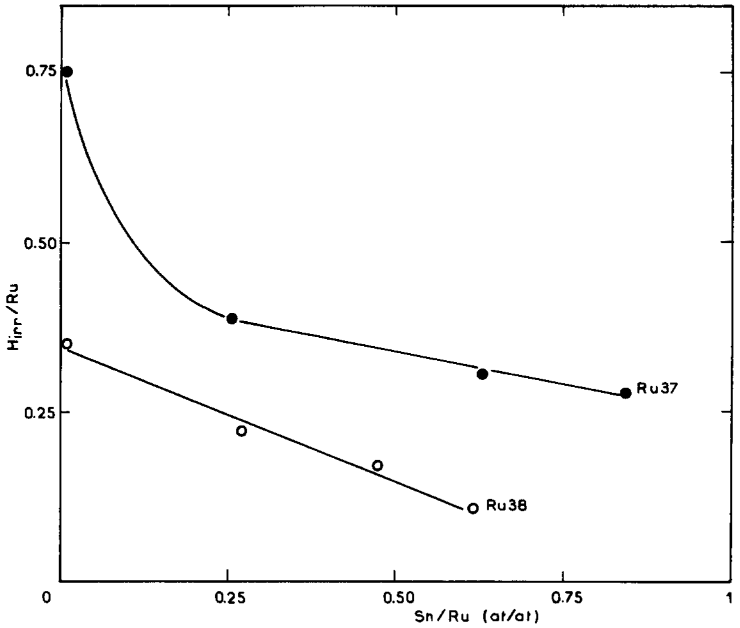

FIG. 1. Hydrogen chemisorption (H_{irr}/Ru) on alumina-supported ruthenium catalysts as a function of tin content.

was reached in the conditions of the reaction. No noticeable change of selectivity was observed during this period. Since the conversion level was kept low (<2%), the readsorption of products was minimised and the selectivities thus referred to primary products. The following parameters were evaluated:

TABLE 3

Turnover Frequencies (TOF) for the Hydrogenation of Benzene over Ru/Al_2O_3 and $RuMe/Al_2O_3$ Catalysts at 292 K

Sample	*Me*/Ru (at/at)	H_{irr}/Ru	TOF (h^{-1})
Ru19B	0	0.07	4030
Ru11	0	0.38	2360
Ru37	0	0.75	1000
Ru7	0	1.1	1310
Ru37SnA	0.26	0.39	1050
Ru37SnB	0.63	0.31	330
Ru37SnC	0.84	0.27	35
Ru37Ge	0.18	0.41	1900
Ru37Si	0.2	0.37	730
Ru45Sb	0.13	0.38	3860
Ru45Pb	0.23	0.26	2430

conversion:

$$= \left(\sum_{1}^{n} i/n\, C_i\right) \Bigg/ \left(C_n + \sum_{1}^{n} i/n\, C_i\right) \times 100$$

selectivity for compound C_i:

$$S_i = C_i \Big/ \left(\sum_{1}^{n} C_j\right) \times 100.$$

In these expressions, C_i = mole percent in the effluent of products with i carbon atoms; C_n = mole percent in the effluent of reactant with n carbon atoms.

As for benzene hydrogenation, the specific activity, or turnover frequency (TOF), is defined as the number of molecules of reactant transformed per unit time for one surface metal atom. The depth of hydrogenolysis, or number of fragments obtained from one molecule of reactant, was characterised by the fragmentation factor ξ defined, following Paál and Tétényi (*34*) as

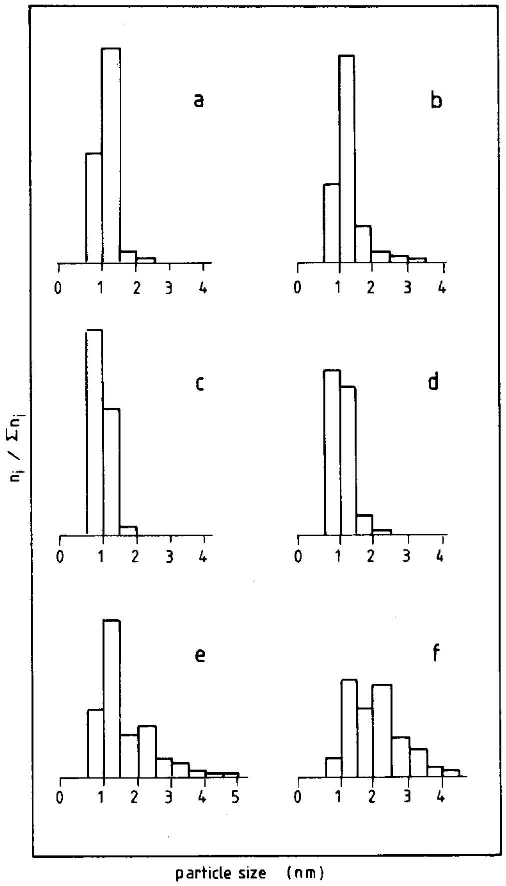

FIG. 2. Particle size distribution of alumina-supported ruthenium catalysts: (a) Ru37; (b) Ru37SnA; (c) Ru37SnB; (d) Ru37SnC; (e) Ru38; (f) Ru38SnB.

$$\xi = \sum_{1}^{n} C_i \Big/ \sum_{1}^{n-1} i/n\, C_i$$

A value of 2 represents the splitting of one single bond, whereas $\xi > 2$ shows the occurrence of multiple fragmentations, in one sojourn at the surface.

Tables 4–7 report the catalytic properties of the Ru*Me*/Al_2O_3 and of the parent Ru/Al_2O_3 samples. As with supported rhodium catalysts (*14*), the variations of turnover frequencies with particle size depend on the hydrocarbon which is converted and higher specific rates are obtained at low dispersion.

TABLE 4

Turnover Frequencies for the Conversion of *n*-Hexane and 2-Methylpentane at 458 K and 2,2,3,3-Tetramethylbutane at 473 K on Ru/Al_2O_3 and Ru*Me*/Al_2O_3 Catalysts

Sample	*Me*/Ru (at/at)	H_{irr}/Ru	Turnover frequencies (h^{-1})		
			*n*H	2MP	TeMB
Ru37	—	0.75	42	30	1.2
Ru37SnA	0.26	0.39	21	13	0.9
Ru37SnB	0.63	0.31	0.45	0.38	0.04
Ru37SnC	0.84	0.27	0.1	0.09	0.01
Ru37Ge	0.18	0.41	5.2	4.6	0.02
Ru37Si	0.2	0.37	34	—	2.5
Ru45	—	0.65	50	40	1.5
Ru45Pb	0.23	0.26	9	5.9	1
Ru45Sb	0.13	0.38	7	18.7	0.23
Ru38	—	0.35	83	100	4.2
Ru38SnA	0.27	0.22	22.7	20	0.2
Ru38SnB	0.45	0.17	0.6	1	0.02
Ru38SnC	0.62	0.11	0.16	0.6	0.01

As a general rule, deep hydrogenolysis is important at low dispersion, and decreases when the dispersion increases. In the conversion of TeMB, demethylation to 2,2,3-trimethylbutane (2,2,3TrMB) reaches the

TABLE 5

Distribution of the Products for the Conversion of *n*-Hexane at 458 K on Ru/Al_2O_3 and Ru*Me*/Al_2O_3 Catalysts

Sample	Product selectivities (%)						ξ
	C_1	C_2	C_3	C_4	C_5	iC_6	
Ru37	25.8	22.1	20.3	17.2	12.1	2.4	2.25
Ru37SnA	53.5	20.3	10.9	8.0	6.2	1.0	3.15
Ru37SnB	31.4	21.1	20.6	16.4	9.1	1.6	2.50
Ru37SnC	35.4	19.6	18.1	17.4	9.6	—	2.45
Ru37Ge	21.6	21.1	23.3	18.3	9.6	6.6	2.20
Ru37Si	21.8	19.9	19.7	17.6	16.2	4.9	2.10
Ru45	28.7	21.4	19.1	15.9	12.3	2.6	2.30
Ru45Pb	30.0	20.4	16.4	14.1	11.2	8.2	2.40
Ru45Sb	27.2	21.1	18.8	15.9	11.9	5.3	2.30
Ru38	48.5	20.8	12.2	8.7	8.3	1.1	2.95
Ru38SnA	41.1	19.3	15.3	11.7	10.6	1.9	2.60
Ru38SnB	29.5	21.1	19.9	16.3	10.2	3.1	2.35
Ru38SnC	41.7	19.9	14.5	12.4	9.2	2.0	2.70

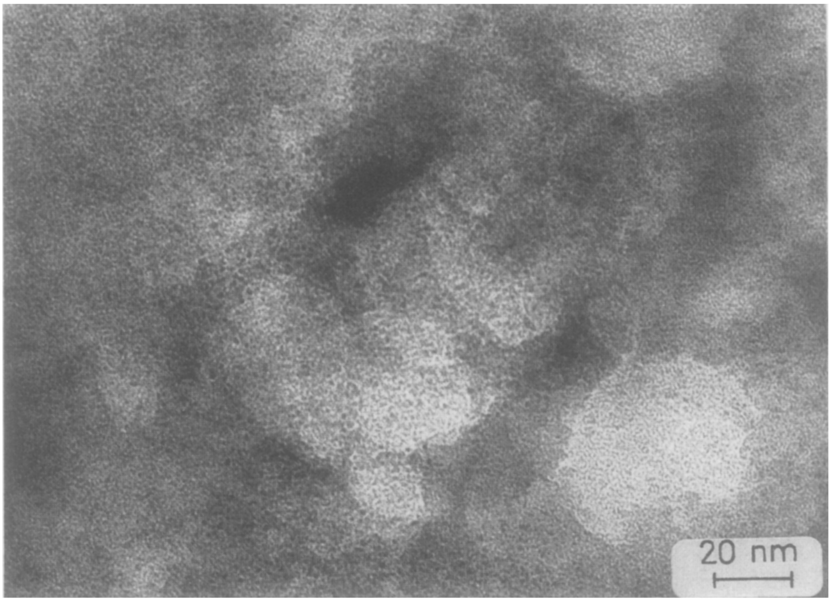

FIG. 3. Electron micrograph of Ru/Al_2O_3 (Ru37).

highest selectivity on the well dispersed Ru catalysts. In the conversion of *n*-hexane, internal splitting to propane is favoured at high dispersion, whereas demethylation predominates at low dispersion.

The apparent activation energies determined for these reactions are reported in Table 8. Upon alloying no great change was observed, except for TeMB, for which the activation energy decreased at high Sn loading.

DISCUSSION

As mentioned above, Ru catalysts are highly sensitive to chlorine, which could obscure, even at trace level, the occurrence of a size or alloying effect. The activity in a "facile" reaction, in the Boudart terminology, can then constitute a test for a Ru clean surface. Thus the near constancy of the activity for the hydrogenation of benzene on Ru/Al_2O_3 (Table 3) rules out the possible effect of contaminants contained in the support. The catalytic properties for alkane conversion may then be attributed to the modification of the structure induced by the dispersion or the alloying of the metal.

The occurrence of deep hydrogenolysis ($\xi > 2$) at very low conversion shows that alkane adsorption on Ru is strong; therefore the reaction rate for the splitting of fragments formed by the first C–C cleavage is higher than their rate of desorption. The decrease of deep hydrogenolysis when the dispersion increases reflects then a lower heat of adsorption on the smaller particles.

The large variations of activity and selectivity as a function of particle size have been attributed to the existence of different surface intermediates which depend on both the structure of the hydrocarbon and the coordination of the surface sites (*26*). A consistent description can be given assuming the formation of these complexes, evidenced by D_2/TeMB exchange on rhodium (*15*), such as metallacyclopentanes for the $\alpha\delta$ species, formed on the dense planes, and metallacyclobutanes for the $\alpha\gamma$ species, formed on edge and corner sites. These surface complexes could then react as pre-

TABLE 6

Distribution of the Products for the Conversion of 2,2,3,3-Tetramethylbutane at 473 K over Ru*Me*/Al_2O_3 and Ru/Al_2O_3 Catalysts

Sample	Product selectivities (%)					ξ	Selectivity factor (SFT)
	C_1	C_2	C_3	iC_4	223TrMB[a]		
Ru37	28.1			45.5	26.3	2.02	1.73
Ru37SnA	42.3	8.3	3.0	42.3	4.1	2.95	10.3
Ru37SnB	43.8	10.2	7.8	24.5	13.5	2.60	1.81
Ru37SnC	37.7			32.9	28.9	2.15	1.13
Ru37Ge	39.1			28.3	32.6	2.10	0.86
Ru37Si	22.5			51.2	26.3	<2	1.94
Ru45	23.1			61.3	12.5	2.17	4.9
Ru45Pb	26.2			66.4	7.5	2.30	8.85
Ru45Sb	22.7			65.3	12	2.20	5.4
Ru38	27.4	4.0	2.0	63.4	3.4	2.45	18.6
Ru38SnA	29.9	5.8	3.8	60.5		2.60	
Ru38SnB	25.7	3.2	13.4	48.9	8.8	2.30	5.6
Ru38SnC	46.2			50.3	3.5	2.95	14.4

[a] 223TrMB: 2,2,3-trimethylbutane.

dicted for isolated organometallic compounds (*16*), the decomposition of which depends on the coordination number of the metal atom. It can be pointed out that, as for rhodium (*14*), the activation energy for hydrogenolysis on ruthenium (125–167 kJ/mole) is higher than that of deuterium exchange, which supports our proposal that decomposition of the surface complex would be the rate-determining step. The selectivity factor SFT = iC_4/2,2,3-trimethylbutane in the conversion of TeMB can then

TABLE 7

Distribution of the Products for the Conversion of 2-Methylpentane at 458 K over Ru/Al_2O_3 and Ru*Me*/Al_2O_3 Catalysts

Sample	Product selectivities (%)							ξ
	C_1	C_2	C_3	iC_4	iC_5	nC_5	iC_6	
Ru37	26.5	15.1	4.5	18.0	20.5	4.7	11.0	2.02
Ru37SnA	44.3	10.7	3.8	19.4	14.7	1.8	15.5	2.40
Ru37SnB	33.6	17.2	4.0	20.5	15.5	3.6	3.7	2.20
Ru37SnC	36.3	17.9	5.4	19.7	17.0	—	—	2.25
Ru37Ge	26.8	20.9	3.9	22.8	14.7	5.3	5.9	2.10
Ru45	31.3	15.5	5.3	17.4	18.8	4.3	7.5	2.15
Ru45Pb	34.0	14.8	4.7	17.8	20.7	1.0	2.2	2.30
Ru45Sb	30.8	15.3	4.7	17.2	18.9	2.7	10.4	2.30
Ru38	43.4	10.6	5.5	14.4	17.5	3.6	4.0	2.30
Ru38SnA	39.7	9.9	4.7	14.9	17.3	3.1	9.4	2.25
Ru38SnB	32.6	15.3	4.9	17.4	17.3	4.2	7.0	2.15
Ru38SnC	36.1	15.4	7.4	18.0	13.0	4.8	3.5	2.25

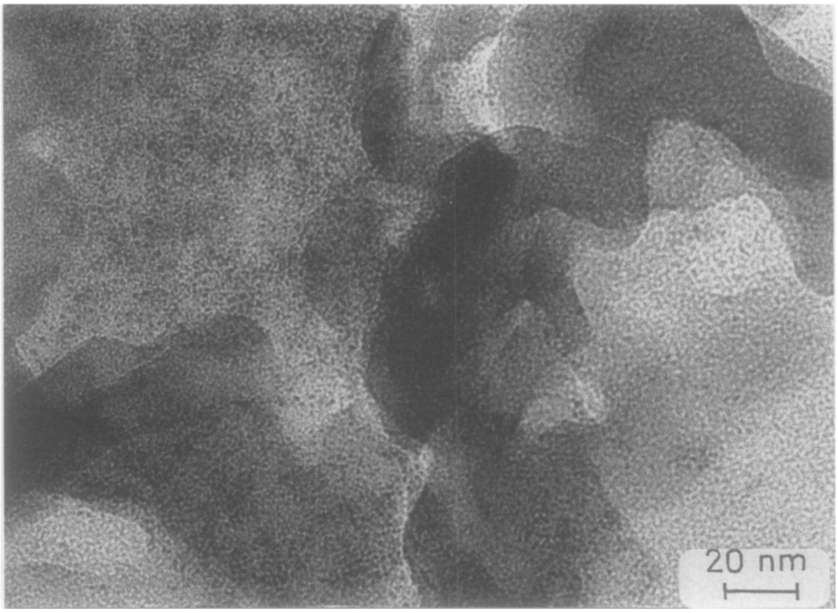

FIG. 4. Electron micrograph of RuSn/Al_2O_3 (Ru37SnC).

represent a characteristic of the average coordination of the Ru surface atoms. Indeed the SFT value decreases when the size of the Ru particles decreases. However, this change of SFT with Ru dispersion is somewhat obscured by the occurrence of multiple fragmentations of iC_4 and 223TrMB adsorbed moieties. Actually, at higher hydrogen pressure (≃350 kPa) deep hydrogenolysis is suppressed and the SFT value decreased from 15 on large particles to 0.9 on small ones (*26*).

TABLE 8

Activation Energies for the Conversion of Alkanes over Ru/Al_2O_3 and Ru*Me*/Al_2O_3 Catalysts

Sample	Activation energy (kJ mol^{-1})		
	*n*H	2MP	TeMB
Ru37	112	99.0	153
Ru37SnA	112	100	160
Ru37SnB	117	118	153
Ru37SnC	113		100
Ru37Ge	130	117	156
Ru37Si	123		125
Ru45	116	94.5	172
Ru45Pb	117		158
Ru45Sb	92.5	110	

It is interesting to compare the effects of particle size and of alloying on the catalytic properties for alkane conversion. The addition of a small amount of Sn (0.26 wt%) to Ru37 (size of the particles in the range 1–1.5 nm) has only a small effect on activity, but shifts the selectivity patterns towards those of larger Ru particles: deep hydrogenolysis increases, internal splitting of *n*-hexane and demethylation of TeMB decrease. This behaviour, reproduced to a smaller extent when Pb is added to Ru, cannot be explained by the ensemble theory of alloys. Indeed, this model predicts a shift of the properties in the direction of smaller particles upon the addition of an inactive component to the metallic surface, as found elsewhere for NiCu alloys (*35*). By contrast, the assumption of a topological segregation of Pb, and especially of Sn, at the surface of Ru*Me* bimetallic particles can give a rational interpretation for that phenomenon. In this model, Sn or Pb would preferentially occupy low coordination sites, edges and corners, thereby leaving Ru on the facets of the particles. The average coordination of the Ru atoms left free then increases, and the catalytic properties of larger Ru particles are reproduced for the conversion of alkanes.

This site segregation at the surface of Ru*Me* bimetallic particles is sustained by several theoretical predictions (*7–9*). In these mathematical derivations it is reported that the same physical reasons which produce an enrichment of the surface in one component should initiate a segregation of the same component to sites of lower coordination number (edges and corners). Two different models have been proposed to account for phase separation: the component which segregates at the surface can be the more volatile metal, or the metal with the lower surface energy (*36*), or the metal with the larger atomic volume (*37*). In the case of Sn, Pb, or Sb, both models predict a surface segregation of these components in bulk Ru alloys. It is then consistent with thermodynamics to propose in that case a preferential localisation of Sn or Pb at edge and corner sites on the small Ru bimetallic particles. In the case of Ge and Si the situation is more complex, since the two models result in opposite predictions. It is then difficult, on a thermodynamic basis, to be definite about the situation. However, for the conversion of alkanes, RuGe,RuSi/Al_2O_3 catalysts show different behaviour as compared with RuSn, RuPb/Al_2O_3 at low content of the second metal. In particular, the addition of germanium shifts the properties of ruthenium towards those of smaller particles: an increase of both internal cleavage of *n*H and demethylation of TeMB occurs. With respect to the behaviour of RuSn,RuPb/Al_2O_3, we can conclude that germanium in bimetallic RuGe particles does not segregate at corners and edges. Unfortunately catalysis alone cannot discriminate between a random distribution and a preferential localisation at the facets, since both would imply the formation of ensembles of small size. RuSi/Al_2O_3 and RuSb/Al_2O_3 show an intermediate behaviour since the selectivity of the parent catalyst is less modified. A possible interpretation may be a nucleation of Si or Sb islands at the surface.

Let us now reconsider with this hypothesis the hydrogen adsorption on RuSn samples reported in Fig. 1. Vis *et al.* (*33*) showed that the stoichiometry of hydrogen adsorption is higher than 1 on very small particles, and hence on atoms of low coordination. The preferential coverage of these atoms by Sn in the case of Ru37 can account for the observed variations. The different behaviour of Ru38 can be simply accounted for by the small number of these atoms of low coordination on the large particles of this sample. It must be kept in mind that the fraction of edge and corner atoms decreases rapidly when the particles grow. Therefore hydrogen adsorption also supports the proposal of topological segregation of Sn atoms at the surface of the smaller particles.

If additional amounts of Sn are introduced on the same Ru base catalyst, Sn atoms have no choice and must cover the dense planes of the particle: the classical phenomenon of dilution of the surface is then observed with a shift of the catalytic properties towards those of small particles (Ru37SnC), as is well known for RuCu or RuAu (*22–24*).

When Sn is added to larger Ru particles, as in the case of Ru38, it shows an inhibitor effect on activities, but little effect on selectivities. However, the decrease of hydrogen adsorption reflects the partial coverage of the surface with Sn. On Ru38, with 35% dispersion, the number of sites of low coordination is small and topological segregation cannot be detected. The fact that selectivities are practically independent of the amount of Sn on Ru38 series would suggest that tin grows as islands at the surface of the larger Ru particles.

For benzene hydrogenation, a constant turnover frequency is observed when the particle size is changed, but a clear decrease is noted at high Sn loadings on bimetallic RuSn/Al_2O_3 catalysts. This reproduces the results previously reported for this reaction catalyzed by PdRh (*38*) and RhCu (*13*) catalysts. This common behaviour on these different systems confirms the idea that benzene hydrogenation, unlike hydrogenation of olefins, requires an ensemble of several metal atoms.

CONCLUSIONS

Catalytic reactions constitute a powerful probe for the characterisation of the surface properties of highly dispersed bimetallic clusters. In this work they have provided evidence for $\mathrm{Ru}Me/\mathrm{Al_2O_3}$ (Me = Sn, Pb, Sb, Ge, Si) bimetallic catalysts that:

(1) a topological segregation of Sn, and to a lesser extent Pb, takes place at the bimetallic surface, with the second metal occupying sites of lower coordination, i.e., corners and edges, displacing Ru onto the facets.

(2) Ge seems more randomly distributed at the surface, and may be localized preferentially on dense planes.

It is thus interesting to find that these additives are specific and that dilution is not the general rule.

From the practical point of view, the preparation of supported alloys by controlled surface reaction with organometallic compounds is a powerful method to reduce hydrogenolysis. The different behaviour of Sn and Ge additives could provide a new interpretation of the properties of PtSn and PtGe reforming catalysts.

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