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Particle Size, Precursor, and Support Effects in the Hydrogenolysis of Alkanes over Supported Rhodium Catalysts

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A series of Rh catalysts of widely varying dispersion has been prepared using γ-alumina as support and Rh acetylacetonate ($Rh(acac)_3$) as precursor. The hydrogenolyses of *n*-hexane (*n*H), methylcyclopentane (MCP), and 2,2,3,3-tetramethylbutane (TeMB) were investigated as model reactions. Clear dependence of turnover frequency on Rh particle size is observed for *n*H and MCP hydrogenolysis, but only slight changes of selectivities occur with these alkanes. By contrast, large modifications of both specific activity and selectivity appear when TeMB is reacted. TeMB hydrogenolysis is thus a reliable tool for studying modifications of the surface structure of rhodium particles. This probe was used to investigate the effects of precursor and support on rhodium catalysts. The effect of chlorine is appreciable and shifts the selectivity of TeMB hydrogenolysis toward that of large particles. This is attributed to a different morphology of the rhodium particles. When the effect of dispersion of the metal is taken into account, no support effect is observed when SiO_2 or ZrO_2 is used as support. The different properties of rhodium on MgO can also be attributed to a different morphology of the particles. For Rh/TiO_2 prepared from $RhCl_3 \cdot 3H_2O$, the catalytic properties are similar to those of Rh/Al_2O_3 of moderate dispersion whatever temperature is used for reduction. Rh/TiO_2 prepared from $Rh(acac)_3$ and reduced at 573 and 773 K simulates the catalytic properties of particles smaller than indeed observed. This effect can be interpreted by a partial coverage of the Rh surface by TiO_x species (SMSI). This SMSI effect disappears upon reduction at 873 K.

INTRODUCTION

It is still difficult to predict the effect on the catalytic properties of the precursors and carriers used to prepare supported metallic catalysts. A detailed study on the influence of precursors on synthesis gas conversion was reported recently by Kip *et al.* (*1*). For Rh/SiO_2 obtained from $RhCl_3$, the turnover frequency (TOF) increased when the percentage of exposed Rh atoms decreased, whereas a constant TOF was observed for the samples prepared from $Rh(NO_3)_3$. In both cases, the selectivity to methane decreased. Using the urea technique ($RhCl_3$ in buffered urea at pH 2.5), well-dispersed samples could be obtained, and these showed the catalytic behaviour of large particles prepared by the incipient wetness technique with $RhCl_3$. Such a behaviour suggested that different morphologies of the metallic particles are obtained when either the nature of the precursor or the method of preparation is changed.

Other examples can be found concerning the conversion of hydrocarbons. Nunez *et al.* (*2*) compared the catalytic properties for ethane hydrogenolysis of Rh particles supported by silica or alumina and obtained either from $RhCl_3$ or $Rh(NO_3)_3$. The influence of precursor was very small when the same carrier was used, but Rh/SiO_2 was more active than Rh/Al_2O_3 whatever the precursor. A recent paper from our group (*3*) reported a strong influence of the size of Rh particles on both activity and selectivity for alkane hydrogenolysis. Selectivity changes are particularly interesting since they should reflect different types of adsorbed species. A good example is the conversion of

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2,2,3,3-tetramethylbutane which gives, as main product, either iC_7 on small particles, or iC_4 on large particles. This change of selectivity can be attributed to different types of adsorbed species, as proposed by Brown *et al.* (*4*) from D_2 exchange, which would be $\alpha\gamma$ on sites of low coordination and $\alpha\delta$ on sites of high coordination. The decomposition of metallacyclopentanes, reported by Grubbs *et al.* (*5*) gives experimental demonstration that splitting of C–C bonds in metallacyclopentanes ($\alpha\delta$-like organometallic complexes) requires a high coordination of the metal atom. McKinney *et al.* (*6*) proposed an interpretation of this phenomenon in terms of orbital symmetry: C–C bond splitting is symmetry allowed only for a high coordination of the metal atom.

Alkane hydrogenolysis is therefore a very sensitive probe for the investigation of structure effects. In a preliminary study (*7*), Rh/Al_2O_3 catalysts prepared from different precursors were compared. It was reported that well-dispersed catalysts (Rh particle size <1 nm) prepared from $RhCl_3$ exhibited the same selectivity patterns as larger particles prepared from Cl^--free precursors. This effect was attributed to a different morphology of the Rh particles. In a former study on the hydrogenolysis of cyclopentane over Rh/Al_2O_3 catalysts (*8*) it was reported that faceted particles, which exhibit dense planes, were more active than small particles. Recent work on the effect of redox cycling on the rate of ethane hydrogenolysis over Rh/SiO_2 catalysts has also illustrated the great importance of particle morphology (*9*, *10*).

The relative importance of particle size, morphology of the particles, and coverage of the surface by TiO_x species on the properties of Rh/TiO_2 is still obscure. Most of the work concerning strong metal–support interaction (SMSI) has been performed on CO hydrogenation. On Rh/TiO_2 obtained from $RhCl_3$, van 't Blik *et al.* (*11*) reported that, when measured at similar dispersions, the activities of Rh/Al_2O_3 and non-SMSI Rh/TiO_2 catalysts hardly differed. Reduction of the Rh/TiO_2 catalysts at 773 K decreased their initial activities substantially compared to reduction at 523 K, but the steady-state activities were very near. It was thereby concluded that the SMSI state no longer remains, to a great extent, as the reaction proceeds.

For the conversion of hydrocarbons on Rh/TiO_2, rather conflicting results have been reported. Resasco and Haller (*12*) compared the hydrogenolysis of ethane, butane, and cyclohexane and the dehydrogenation of cyclohexane on Rh/TiO_2 catalysts prepared in a basic medium (Cl^--free). When the size of Rh particles decreased, the TOF for alkane hydrogenolysis slightly increased for catalysts reduced at 473 K, but decreased sharply for catalysts reduced at 773 K. High-temperature reduction suppressed selectively hydrogenolysis of cyclohexane, whereas dehydrogenation was retained. An effect of the support was thus evidenced, which was the highest when the Rh particles were the smallest. Schepers *et al.* (*13*) compared the hydrogenolysis of *n*-hexane, 2,2-dimethylbutane, and methylcyclopentane on Rh/TiO_2 prepared from $RhCl_3$. The effect of the reduction temperature on the catalytic properties was small: a decrease in activity by a factor lower than 10 was observed after reduction at 1138 K, and the selectivity was hardly affected for *n*-hexane and methylcyclopentane. With neohexane, at a reaction temperature of 564 K, the selectivity for neopentane changed from 77.2% (conversion = 5%) after reduction at 573 K, to 79.8% (conversion = 9.5%) or 72% (conversion = 1.0%) after reduction at 1138 K. It can thus be concluded that neither the activity nor the selectivity was significantly altered. For Rh/TiO_2 catalysts obtained by impregnation with $RhCl_3$, Anderson *et al.* (*14*) reported for *n*-hexane hydrogenolysis an increase in turnover frequency in the SMSI state, but the selectivity was unaffected.

These differences in catalytic behaviour for alkane hydrogenolysis can be ascribed, in part, to the nature of the reactant. The structure sensitivity of different alkanes has been reported previously (*3*) to be rather sensitive to the structure of the hydrocarbon: the influence of particle size on TOF was small for *n*-hexane, medium for 2,2-dimethylbutane, and large for 2,2,3,3-tetramethylbutane hydrogenolysis. The variations of the initial selectivity (conversion <5%) with the particle size were inappreciable for 2,2-dimethylbutane, relatively small for *n*-hexane, but noteworthy for 2,2,3,3-tetramethylbutane.

The comparison of *n*-hexane, 2,2,3,3-tetramethylbutane, and methylcyclopentane conversions can therefore give a clearer description of Rh/TiO_2 catalysts. The present article summarizes some of the results obtained for supported Rh catalysts when changing the precursor and/or the carrier.

EXPERIMENTAL

Catalysts. Rh/Al_2O_3 catalysts were prepared, either by ligand exchange between protons of the carrier with rhodium acetylacetonate ($Rh(acac)_3$) dissolved in toluene (*15*), or by ion exchange between $RhCl_3 \cdot 3H_2O$ and γ-Al_2O_3 in acidic medium (pH 2) or $(Rh(NH_3)_5Cl)Cl_2$ and γ-Al_2O_3 in basic medium (pH 9). The support was γ-Al_2O_3 from Rhône-Poulenc (200 m^2/g), and the precursors were $Rh(acac)_3$ (Aldrich, purity >97%), $RhCl_3 \cdot 3H_2O$ (Merck), and $(Rh(NH_3)_5Cl)Cl_2$ (Ventron).

Rh/SiO_2 catalysts were prepared by ion exchange at pH 9 between $(Rh(NH_3)_5Cl)Cl_2$ and SiO_2 from Davison (350 m^2/g).

Rh/MgO and Rh/ZrO_2 catalysts were prepared by deposition on the carrier of $Rh_4(CO)_{12}$ dissolved in *n*-pentane. Magnesia was obtained by pyrolysis of $Mg(OC_2H_5)_2$ at 573 K and Rh/ZrO_2 catalysts were supplied by the Politecnico di Milano (Dr. C. Mazzochia).

Rh/TiO_2 catalysts were prepared either by deposition of $Rh(acac)_3$ in toluene on TiO_2 or by ion exchange between $RhCl_3$ at pH 2 and TiO_2. Titania was Degussa P25 (120 m^2/g).

Characterization. The chemisorption of hydrogen was carried out in a conventional volumetric apparatus at 298 K in the 0- to 20-kPa pressure range. The sample was first reactivated *in situ* under flowing hydrogen at 673 K overnight, then evacuated to 1.2×10^{-4} Pa, at the same temperature, for 3 h. High-purity hydrogen (99.9995%) was then adsorbed. The linear part of the isotherm was extrapolated to zero pressure to determine the hydrogen uptake. On very well-dispersed samples with particle sizes below 1 nm, the stoichiometry of hydrogen adsorption reached values higher than 1. Kip *et al.* (*16*) have reported that the stoichiometry of hydrogen adsorption changes with particle size and surpasses unity on small particles. This introduces an uncertainty about the number of surface Rh atoms, which can reach 30% on well-dispersed catalysts. It must then be realized that small changes in catalytic activities have little significance; changes in selectivity thus appear to have a higher reliability for characterizing a catalyst. The size of the metallic particles was checked by transmission electron microscopy (TEM). Table 1 summarizes the main characteristics of the catalysts. The distributions of particle sizes reported in Fig. 1 attest to the homogeneity of particle sizes. The good agreement between chemisorption and TEM for Rh/Al_2O_3 attests to the reliability of the value of the average size.

Catalytic tests. The reactions, in high-purity hydrogen (99.99%), of *n*-hexane (*n*H, Fluka, purity >99.5%), methylcyclopentane (MCP, Carlo Erba, purity >99.63%), and 2,2,3,3-tetramethylbutane (TeMB, Aldrich, purity >99.99%) were carried out under atmospheric pressure in a microflow reactor. The effluents were analyzed by sampling on-line with a gas chromatograph equipped with a capillary column J and W (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 ranged from 463 to 508 K, and

TABLE 1

Preparation and Characteristics of Rhodium Catalysts

Sample	Precursor	wt% Rh	Calcination temperature (K)	Reduction temperature (K)	H/Rh	Particle size by TEM (nm)
Support: alumina						
RAl2C	$Rh(acac)_3$	0.4	673	673	1.5	<1
RAl2D	$Rh(acac)_3$	0.45	673	673	1.7	—
RAl2E	$Rh(acac)_3$	0.74	773	773	1.5	—
RAl6	$Rh(acac)_3$	1.16	No	773	0.9	—
RAl8	$Rh(acac)_3$	1.32	No	773	0.74	—
RAl4	$Rh(acac)_3$	1.4	No	773	0.75	—
RAl3	$Rh(acac)_3$	2.6	No	973[a]	0.35	—
RAl5	$Rh(acac)_3$	2	No	1173[a]	0.08	—
RAl7	$RhCl_3,3H_2O$	0.4	673	773	1.1	—
CGF22	$RhCl_3,3H_2O$	0.25	673	773	1	1
CGAF	$RhCl_3,3H_2O$	1.80	No	773	0.27	4.8
Support: TiO_2						
RTi1	$Rh(acac)_3$	0.4	—	573	0.84	1.5–1.6
RTi2S	$Rh(acac)_3$	0.4	—	773	0.23	1.5–1.6
RTi3S	$Rh(acac)_3$	0.4	573	873	0.23	2.2
RTi4	$RhCl_3,3H_2O$	0.4	—	573	0.50	—
RTi5	$RhCl_3,3H_2O$	0.4	—	773	0.15	—
RTi6	$RhCl_3,3H_2O$	0.4	—	873	0.20	—
Support: ZrO_2						
$RhZrO_2$	$Rh_4(CO)_{12}$	1	—	573	1	—
Support: MgO						
RhMgO	$Rh_4(CO)_{12}$	0.9	—	573	1	—
Support: SiO_2						
CGF17	$Rh((NH_3)_5Cl)Cl$	0.25	700	773	1	1

[a] Reduction with hydrogen saturated by water (2.6 kPa).

the molar ratios of reactants were $H_2/n\mathrm{H} = 14.0$, $H_2/\mathrm{MCP} = 15.5$, $H_2/\mathrm{TeMB} = 44$. Under these conditions of reaction the catalytic activity was stable as a function of time on stream.

Activities are expressed as turnover frequencies (TOF) or number of molecules of reactant converted per surface metal atom and per hour. Selectivities are defined as $Si = 100\ C_i/\Sigma_1^n\ C_i$, where C_i is the molar concentration of product i. Selectivities were measured at low conversions, usually less than 5%, in order to avoid secondary reactions. They therefore represent initial selectivities. Hydrogenolysis of alkanes on rhodium under these conditions is a simple reaction, with a single C–C bond splitting. The fragmentation factors ($\xi = C_i/(\Sigma_1^{n-1}\ i/n\ C_i)$ defined following Paál and Tétényi (*17*) are close to 2, except for large particles on which multiple fragmentations ($\xi > 2$) can occur.

RESULTS

Catalytic properties of Rh/Al_2O_3 obtained from $Rh(acac)_3$. The results obtained on this series of catalysts are reported in Tables 2–4 for *n*H, TeMB, and MCP, respectively. These catalysts contain no chlorine, and the dispersion could be changed in a wide range. It appears clearly that the sensitivity of the reaction to the size of Rh particles varies with the nature of the hydrocarbon: hydrogenolysis of *n*-hexane shows a weak sensitivity, like that of

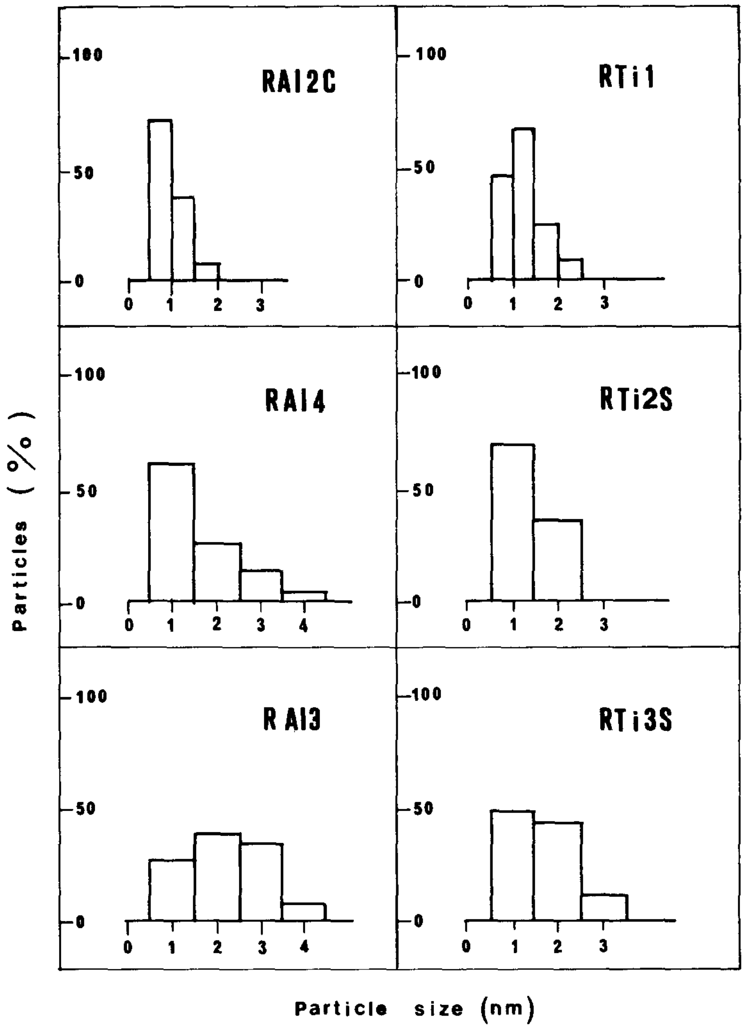

FIG. 1. Particle size distribution of some supported rhodium catalysts.

TABLE 2

Catalytic Properties of Catalysts Prepared from Rh(acac)$_3$ for the Conversion of *n*-Hexane at 493 K

Sample	H/Rh	Conv. (%)	TOF (h^{-1})	Product distribution (%)					
				C_1	C_2	C_3	nC_4	nC_5	iC_6
RAl2C	1.5	2.8	185	21.8	24.8	20.6	21.8	10.8	—
RAl2D	1.7	4.3	240	21.6	24.7	20.8	21.5	10.3	1.16
RAl2E	1.5	3.4	153	17.1	25.8	23.9	23.4	9.0	0.6
RAl6	0.9	3	98	16.0	25.8	25.6	23.4	9.0	0.2
RAl8	0.74	4.8	116	23	21	21	19.6	13.4	0.2
RAl4	0.75	3.5	73	16.6	22.7	25.7	21.5	12.6	—
RAl3	0.35	3.2	67	21	19.1	23.3	18.3	18.3	—
RAl5	0.08	0.3	65	43.6	11.9	14.9	13.2	16.4	—

TABLE 3

Catalytic Properties of Catalysts Prepared from $Rh(acac)_3$ for the Conversion of 2,2,3,3-Tetramethylbutane at 493 K

Sample	H/Rh	Conv. (%)	TOF (h^{-1})	Product distribution (%)		
				C_1	iC_4	223TrMB[a]
RAl2C	1.5	1	6.5	49.6	4.4	45.9
RAl2D	1.7	3.3	12	52.8	4.7	42.5
RAl2E	1.5	2.3	7.2	45.0	13.7	41.2
RAl6	0.9	4.2	7.6	16.6	68	15.4
RAl8	0.74	5	24	11.6	78.7	9.7
RAl4	0.75	2.3	11.3	6.6	86.1	7.3
RAl3	0.35	4.5	20	4.7	91.4	3.9
RAl5	0.08	2.6	33	5.9	91.5	2.6

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

methylcyclopentane. By contrast, two different reactions are observed for TeMB: there is practically pure splitting of the central bond on particles larger than 3 nm, and pure demethylation on particles smaller than 1 nm. Some changes in the turnover frequency are also noted, which confirm the sensitivity of the reaction to the surface structure.

Influence of Cl^- ions on the properties of Rh/Al_2O_3. The catalytic properties, for the conversion of TeMB, of a series of catalysts containing Cl^- ions are reported in Table 5. Chlorine can be introduced either in the first step of ion exchange or later by treatment of a metallic catalyst prepared from $Rh(acac)_3$ by a HCl solution. On the catalysts prepared from $RhCl_3$, the amount of chlorine on the final catalyst can also be changed by the chemical treatments: the varying residual Cl^- content of RAl7 and CGF22 may then be a result of a different partial pressure of water in the course of reduction.

At low dispersion, the comparison of CGAF and RAl3 samples shows that the effect of the precursor is small. At high dispersion, however, two effects appear: there is a clear decrease in activity, which reaches a factor between 10 and 100, and an increase in the selectivity for iC_4, which is very clear at the highest Cl^- content (CGF22), with 26.5% iC_4 selectivity compared to 4–14% for well-dispersed RAl2C and RAl2E.

For a Cl^--free sample, the adsorption of Cl^- ions from HCl solution also induces an effect on activity and selectivity. Starting from RAl2C, as parent catalyst, different amounts of Cl^- were introduced from HCl solutions. The dried solids were then reduced at 673 K directly (RAl2Cl1, RAl2Cl3), or suffered an intermediate calcination step at 623 K (RAl2Cl2). Chemical analysis provides evidence that, upon such an acid treatment by HCl, 90% of the chlorine introduced is removable; the residual

TABLE 4

Catalytic Properties of Catalysts Prepared from $Rh(acac)_3$ for the Conversion of Methylcyclopentane at 493 K

Sample	H/Rh	Conv. (%)	TOF (h^{-1})	Product distribution (%)						
				C_1	iC_4	iC_5	C_5	2MP	3MP	nH
RAl2C	1.5	1.2	43	11.5	1.7	4.9	0.8	42.5	27	11
RAl2D	1.7	2.6	74	10	1.1	4.7	1.1	45.7	25.8	11.9
RAl2E	1.5	2.5	68	5.4	0.6	2.6	0.5	52.9	25.4	12
RAl6	0.9	6	192	2.1	0.2	0.2	0.3	67.6	24.3	3.8
RAl8	0.74	3.4	306	3.7	0.4	2.1	—	65.1	24.1	3.6
RAl4	0.75	5.7	480	1.6	—	0.7	—	70	23.5	3
RAl3	0.35	4.7	509	—	—	—	—	72.5	23.5	2.16
RAl5	0.08	2.3	360	8.4	0.9	4.1	0.8	61.3	21.7	2.4

TABLE 5

Catalytic Properties of a Series of Chlorine-Containing Catalysts for the Hydrogenolysis of 2,2,3,3-Tetramethylbutane at 493 K

Sample	Chlorine Cl/Rh (at/at)	H/Rh	Conv. (%)	TOF (h^{-1})	Product distribution (%)		
					C_1	iC_4	223TrMB
RAl7	6.6	1.1	0.7	0.9	42.1	11.6	46.2
CGF22	11.2	1	—	0.07	43.0	26.5	30.0
RAl7A[a]	1.5	1.1	0.6	0.22	45.8	13.1	41.1
RAl2Cl1[b]	11	0.93	0.4	1.1	45.6	17.1	37.2
RAl2Cl2[c]	—	0.90	1.7	5.3	45.8	13.7	41
RAl2Cl3[d]	—	0.90	0.25	1.1	48.8	8.1	43.2
RAl2N[e]	—	1	2.1	11.2	45.2	10	44.8
CGAF	—	0.27	6.4	39	11.2	75.1	10.8
RAl1	—	1	3.5	14	37	18	45

[a] RAl7 washed with water at 353 K, then reduced at 673 K.

[b] RAl2C treated with HCl solution (Cl^-/Rh = 100), dried, reduced at 673 K.

[c] RAl2C treated with HCl solution (Cl^-/Rh = 100), dried, calcined at 673 K, reduced at 673 K.

[d] RAl2C treated with HCl solution (Cl^-/Rh = 10), dried, reduced at 673 K.

[e] RAl2C treated with NH_4OH (NH_4^+/Rh = 100), dried, reduced at 673 K.

content on RAl2Cl1 compares well with that of GGF22 and RAl7 catalysts.

It appears that the addition of Cl^- by impregnation reduces the turnover frequency by a factor of 6 and shifts the selectivity for isobutane from 4.4 to 8–17%. The calcination step removes the contamination of the surface by Cl^-, since the turnover frequency is restored, but the selectivity to iC_4 remains high (13.7%). The impregnation of RAl2C by a NH_4OH solution (NH_4^+/Rh = 100) results in much smaller modifications of the catalytic properties.

Effect of the support. Table 6 presents the catalytic properties, for the conversion of TeMB, of a series of catalysts prepared using SiO_2, MgO, ZrO_2, or TiO_2 as carriers. Chlorine-free precursors were used for MgO-, ZrO_2-, and TiO_2-based catalysts, and under the preparation conditions used

TABLE 6

Influence of the Support on the Catalytic Properties of Rhodium for the Hydrogenolysis of 2,2,3,3-Tetramethylbutane at 493 K

Sample	H/Rh	Conv. (%)	TOF (h^{-1})	Product distribution (%)			E_a (kJ mol^{-1})
				C_1	iC_4	223TrMB	
RTi1	0.84	1	8	39.4	26.3	34.3	235
RAl2E	1.5	2.3	7.2	45.0	13.8	41.2	—
RhMgO	1	0.9	0.2	17.5	69.7	12.8	230
$RhZrO_2$	1	3	15.3	52.6	12.4	35.1	242
CGF17	1	2	23	49.6	13.8	36.6	167
RTi4	0.5	3.4	13.9	10.1	83.3	6.6	—

TABLE 7

Influence of the Temperature of Reduction of Rh/TiO$_2$ Catalysts on Their Catalytic Properties for the Hydrogenolysis of 2,2,3,3-Tetramethylbutane at 493 K

Sample	Reduction temp. (K)	H/Rh	Conv. (%)	TOF (h^{-1})	Product distribution (%)		
					C$_1$	iC$_4$	iC$_7$
Precursor Rh(acac)$_3$							
RTi1	573	0.84	1	8	39.4	26.3	34.3
RTi2S	773	0.23	2	12	36	28	35
RTi3S	873	0.23	4.2	18	8.2	84.2	7.7
Precursor RhCl$_3$ · 3H$_2$O							
RTi4	573	0.5	3.4	14	10.1	83.3	6.6
RTi5	773	0.15	6.5	69	1.1	88	5.8
RTi6	873	0.20	4.2	54.5	7.9	89.5	7.5

Rh/SiO$_2$ did not retain chlorine (*18*). Rh/TiO$_2$ was reduced at 573 K in order to avoid the SMSI state. These well-dispersed catalysts must be compared to RAl2 samples reported in Table 3. It appears then that the catalytic properties of Rh/SiO$_2$ and Rh/ZrO$_2$ are comparable to those of RAl2E. Therefore no large effect of the support is observed. Rh/MgO, however, which presents a high dispersion of Rh, shows the selectivity of medium-size Rh particles and a very low activity. The nH and MCP conversions give normal behaviours, as expected for reactions much less sensitive to the particle size.

TABLE 8

Turnover Frequencies and Distribution of Products for the Conversion of n-Hexane on Rh/TiO$_2$ Catalysts Reduced at Different Temperatures

Sample	TOF (h^{-1})	Product distribution (%)					
		C$_1$	C$_2$	C$_3$	nC$_4$	nC$_5$	iC$_6$
RTi1	147	16	27	24	24	9	—
RTi2S	93	17.2	25	23	23	11	—
RTi3S	118	17.7	23.9	22	23	13	0.2
RTi4	57	23	22	19	21	15	—
RTi5	243	23	22	18	21	16	—
RTi6	26	15	24	24	24	12	0.25

Note. Samples are described in Table 7.

The catalytic activities of Rh/TiO$_2$ catalysts reduced at 573 K are close to those of Rh/Al$_2$O$_3$ of similar dispersion and are prepared by the same procedures. Nevertheless, both RTi1 and RTi4, prepared from different precursors but reduced at 573 K, exhibit selectivity patterns for TeMB hydrogenolysis typical of Rh/Al$_2$O$_3$ of smaller particle sizes, RAl2E and RAl4, respectively (Table 7). Reduction of Rh/TiO$_2$ at 773 or 873 K decreases the H$_2$ uptake, which does not correspond to a sintering of the Rh particles (Fig. 1). TOF increases slightly, but the selectivity is not affected, with the exception of RTi3S which behaves like medium-size Rh particles. After treatment at 873 K the effect of the precursor disappears. The catalytic properties for the hydrogenolysis of n-hexane are reported in Table 8 and show a moderate increase, or stability, for turnover frequencies and little variation in the distribution of products.

DISCUSSION

The first point which appears clearly is the different structure sensitivity of nH, MCP, and TeMB hydrogenolysis. The two former reactions show appreciable changes in TOF, but not in selectivities. By contrast, clear changes in both activity and selectivity occur with TeMB hydrogenolysis which reveals itself as very sensitive to the surface structure and as able to detect more subtle changes on the Rh particles. The conclusions reached previously concerning the effect of particle size on the selectivity of TeMB hydrogenolysis (*3*) remain valid and are even amplified when using $Rh(acac)_3$, since the smallest particles catalyze practically pure demethylation. The proposal that the surface intermediate is an $\alpha\gamma$-adsorbed species on small particles and an $\alpha\delta$-adsorbed species on large particles finds a strong experimental support. As discussed earlier, the hydrogenolysis of *n*H can proceed by several routes and is then much less structure sensitive (*3*). A consistent description of these results can be given assuming that the coordination number of the surface rhodium atoms controls the catalytic properties. With this reasonable hypothesis the results reported here for TeMB hydrogenolysis are the catalytic counterpart of the stoichiometric reaction of metallacyclopentanes (*5*) and TeMB hydrogenolysis can be used as a catalytic probe of the surface.

The effect of the precursor on the catalytic properties of Rh depends on the size of the particles: at low dispersion the precursor has no clear effect. At high dispersion, the catalysts obtained from $RhCl_3$ show a lower activity and a higher selectivity for iC_4. The decrease in activity can be reproduced in part by adsorbing Cl^- ions on RAl2C, but a calcination at 623 K followed by reduction at 673 K restores the initial activity. It can then be postulated reasonably that redox cycling, performed during the preparation of CGF22 and RAl7 samples, scavenged Cl^- ions from the Rh surface, as reported by Kip *et al.* (*1*). The changes in selectivity would not then be a result of chlorine adsorption, but of a reconstruction on the surface of the Rh particles induced by chlorine. Chlorine on the support, in the vicinity of the Rh particles, could also have a strong influence by changing the contact angle with the Rh particles, for instance. The higher selectivity for *i*-butane of these catalysts prepared from $RhCl_3$ can be reconciled with the observed dispersion assuming that these small particles are epitaxially located on the support and thus exhibit dense planes, as is known for Pd/Al_2O_3 (*19*).

From the comparison of the catalysts prepared using several supports and chlorine-free precursors, it can be concluded that no support effect exists on SiO_2, ZrO_2, or Al_2O_3. Two supports have a particular behaviour: MgO and TiO_2. Well-dispersed Rh/MgO exhibits the selectivity of larger Rh particles on alumina. In that case also, a modification of the morphology of the Rh particles can be an acceptable interpretation, but the low turnover frequency is not understood.

As stated previously, the two Rh/TiO_2 catalysts reduced at 573 K (RTi1, RTi4) show catalytic properties similar to those of smaller Rh particles when supported by Al_2O_3. Moreover, the selectivity is little modified when the samples are reduced at 773 K (RTi2S, RTi5) and are then pushed into the SMSI state. It then seems likely that some kind of SMSI is initiated even at 573 K, as reported by Anderson *et al.* (*14*). For instance, from its H_2 uptake ($H/Rh = 0.84$), RTi1 should exhibit an iC_4 selectivity for TeMB hydrogenolysis of 70% at least, so the experimental value of 26% indicates a lower coordination of the Rh surface atom. This behaviour can be rationalized assuming a dilution of the Rh surface by migrating TiO_x species.

By reduction of Rh/TiO_2 at high temperature TOF tends to increase. This behaviour is not correlated with a great change of the particle size as evidenced by TEM examination (Fig. 1), and also reported by others for Rh/TiO_2 (*13, 14*). This increase in TOF may reflect either a lower coverage by TiO_x species, which could agglomerate into islands, or a modification of the strength of H_2 adsorption as proposed for Ru/TiO_2 model catalysts (*21*).

The comparison of the present results obtained for Rh/TiO_2 catalysts prepared from $Rh(acac)_3$ with those in the literature implies that the salt used to introduce rhodium has a large influence on the catalytic properties of the final catalyst. Mériaudeau *et al.* (*20*) and Schepers *et al.* (*13*) reported a decrease in activity for hydrogenolysis of *n*-butane, *n*-hexane, 2,2-dimethylbutane, and methylcyclopentane on Rh/TiO_2 in the SMSI state; in those investigations the catalysts were prepared by impregnation with $RhCl_3$ and the Rh particle size ranged from 2 to 2.5 nm. Anderson *et al.* (*14*) prepared Rh/TiO_2 by impregnation with $RhCl_3$ at pH 8 and obtained samples of similar dispersion (H/Rh = 0.59). They report an increase by a factor of 2–3 in the turnover frequency for *n*-butane hydrogenolysis after reduction at 773 K, which is in agreement with the results reported here for RTi4 and RTi5 samples. In the present work, for both TeMB and *n*-hexane conversions the turnover frequency is either constant or higher after reduction at 773 K, and therefore the conditions of preparation of the catalyst have a notable influence on the catalytic properties, most probably by changing the reducibility of the metal or the surface properties of the support.

In conclusion, the catalytic properties of rhodium for the hydrogenolysis of alkanes are very sensitive to the size of the Rh particles, and thereby to the coordination of Rh surface atoms. Their properties can be changed over a wide range depending on the precursor, or the support, used in the preparation. Most of the changes can be accounted for by a modification in the morphology of the rhodium particles. In the case of TiO_2, a partial coverage of the dense planes of the smaller Rh particles by TiO_x species agrees with the results of TeMB conversion. However, those particles of rhodium larger than 2 nm show the same catalytic properties whether they are supported by titania or by alumina.

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