Surface organometallic chemistry on metals: kinetics of the hydrogenolysis of tetra n-butyl tin on silica and alumina supported rhodium catalysts

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Abstract

The stoichiometry and the kinetics of the hydrogenolysis of tetra n-butyl tin on silica and alumina supported rhodium catalysts has been determined at 298 K in n-heptane. Various Rh/SiO_2 and Rh/Al_2O_3 catalysts have been prepared by exchange from $[RhCl(NH_3)_5](OH)_2$ and by impregnation from $RhCl_3$ respectively. After reduction, metallic dispersions were found to vary from 0.45 to 0.9 as determined by hydrogen chemisorption measurements. Concerning the hydrogenolysis of the organotin complex, the amount of grafted tin was found to depend on the amount of tetra n-butyl tin introduced: since this amount is lower than the value corresponding to a ratio Sn/Rh_s of 0.7, all the tin complex is grafted and the amount of grafted tin is directly proportional to the number of surface rhodium atoms; on average, each surface rhodium atom is able to graft 0.8 $Sn(n-C_4H_9)_x$ fragment. Above this ratio, the amount of grafted tin is almost independent of the amount of complex introduced. These results strongly support the hypothesis that the reaction occurs selectively on the metallic surface. The stoichiometry of the hydrogenolysis, determined by the amount of butane evolved per mole of grafted tin, depends on the coverage of the rhodium surface: for a low coverage, all the butyl groups are hydrogenolyzed, showing the formation of 'naked' tin atoms. For a full coverage, some butyl groups remain fixed on the surface showing the presence of grafted organotin species on the rhodium surface. The stoichiometry of the hydrogenolysis also depends on the reaction time for a given concentration of tetra n-butyl tin: at short reaction times which correspond to low coverages of the metallic particles, all the butyl groups are removed whereas this phenomenon is not observed at longer reaction times for which alkyl groups remain on the metallic surface. Kinetics of the hydrogenolysis indicates that the reaction is first order in 'free surface adsorption site' and zero order in tetra n-butyl tin.

Keywords: Alumina; Hydrogenolysis; Kinetics; Rhodium; Silica; Surface organometallic chemistry; Supported catalysts; Tetra n-butyl tin

1. Introduction

Surface organometallic chemistry on metals (SOMC/M) is devoted to the study of the reactivity of organometallic complexes with the surface of metals [1]. By this method it is possible to prepare relatively well defined catalysts which may be alloys of given composition, adatoms of main group elements on the surface of transition metal particles or 'organometallic fragments' which are likely adsorbed (coordinated) at some particular crystallographic positions of the metallic particles. It has been shown that each of these three different types of materials exhibit interest-

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ing and unusual selectivities in certain catalytic reactions [1].

Partial hydrogenolysis of tetra n-butyl tin [$Sn(n-C_4H_9)_4$] on silica supported rhodium particles leads to bimetallic catalysts which are very active and selective for the hydrogenation of α–β unsaturated aldehydes into the corresponding unsaturated alcohol [2–4], or nitrobenzene into aniline [5]. Total hydrogenolysis of tetra n-butyl tin on silica or alumina supported rhodium, ruthenium or nickel particles leads to bimetallic catalysts which are very active and selective toward ethyl acetate hydrogenolysis into ethanol [6–9], NO–H_2 reaction [10,11], hydrogenolysis and dehydrogenation of alkanes [12,13]. The bimetallic materials have been well characterised by various physical techniques [10–15]. A correlation has been made between the structure of the bimetallic catalyst and its selectivity toward ethanol formation in the hydrogenolysis of ethyl acetate (concept of site isolation) [8]. In this particular case, the preparation of the bimetallic catalyst was achieved by reaction between molecular hydrogen, tetra n-butyl tin and silica or alumina supported rhodium in n-heptane solution.

In order to have a clear understanding of the synthetic route leading to these bimetallic particles (via surface organometallic chemistry), it appeared necessary to study the kinetics of the hydrogenolysis of the organometallic compound. The present work reports the kinetics of this reaction *in solution* and tries to establish the possible relationship between the number of surface rhodium atoms and the amount of grafted organometallic compound. The stoichiometry of the surface reaction is also tentatively determined.

2. Experimental

The monometallic rhodium/silica catalysts are prepared by the conventional ion exchange method previously described [16] using [$RhCl(NH_3)_5$]Cl_2 as precursor. The silica support is an 'Aerosil 200' from Degussa with specific area of 200 m^2/g. The monometallic alumina sup-

ported rhodium is prepared by impregnation of the alumina surface with $RhCl_3$ following the procedure previously described [16].

The dispersion of the monometallic silica and alumina supported catalysts (number of surface rhodium atoms versus the total number of rhodium atoms, Rh_s/Rh_t) is determined by chemisorption of hydrogen at 298 K. According to already published data [16] the stoichiometry of the hydrogen adsorption (number of adsorbed hydrogen atoms per surface rhodium atom, H/Rh_s) is assumed to be equal to 1.2 at 25°C under an equilibrium pressure of 200 mbar of hydrogen. The amount of adsorbed hydrogen is measured by volumetry [16]. Prior to the adsorption measurement of hydrogen, the samples are reduced under flowing hydrogen at 623 K during 3 h and then evacuated at the same temperature for 16 h.

The reaction between the n-heptane solution of tetra n-butyl tin and the monometallic catalysts is performed in a closed glass reactor (Schlenk tube, total volume 80 ml) well stirred, under one atmosphere of hydrogen. The temperature of the reactor is maintained at 298 K by an oil bath. The solvent, n-heptane, is distilled on P_2O_5 and is kept under argon.

Prior to the reaction with tetra n-butyl tin, a known amount of monometallic catalyst (generally 3 g) is reduced in a fixed bed reactor under flowing hydrogen at 653 K during 3 h. After cooling at room temperature under hydrogen, the sample is introduced without any contact with air, into the Schlenk tube. The freshly distilled n-heptane (20 ml) and a known amount of tetradecane (internal standard) are introduced under hydrogen in the Schlenk tube which is then closed under one atmosphere of hydrogen. After 30 min of stirring, the desired amount of tetra n-butyl tin is added via a syringe and the variation of the tetra n-butyl concentration (Q_t) with time is followed by gas chromatographic analysis of the liquid phase, carried out after increasing times, t, of reaction. It has been confirmed in separate experiments that tetradecane used as an internal standard has no effect on the reaction rate.

The amount of tetra n-butyl tin adsorbed on the catalyst (Sn_t) is deduced from the difference between the initial concentration of tetra n-butyl tin (Q_0) and the concentration after the time t of reaction (Q_t). After completion of the reaction, that is when the concentration of tetra n-butyl tin remains constant at Q_f, the total amount of tetra n-butyl tin adsorbed on the surface at full coverage (Sn^f)$_c$ is obtained by the difference between Q_0 and Q_f. One can define the coverage of the metallic surface, θ, at each time t, by Eq. (1):

$$\theta = (Q_0 - Q_t) / (Q_0 - Q_f) \qquad (1)$$

At the end of the reaction, the formation of hydrocarbons is estimated, either in the liquid or in the gas phase. The only hydrocarbon detected is butane. In order to measure the total amount of butane evolved, the reactor is immersed into a cold bath (200 K) in order to completely trap the n-butane, then the analysis of the liquid phase is carried out by GC: the total amount of butane formed during the reaction is thus precisely determined. The catalyst is then filtered and washed with pure n-heptane and the total amount of tin still present on the catalyst (Sn^f)$_a$ is measured by chemical analysis (atomic absorption).

CP-MAS ^{13}C solid state NMR spectra of the samples were taken after various reaction times. For that purpose, the catalyst is first filtered and washed with pure n-heptane under argon, the solvent is then evacuated under vacuum. The solid is transferred to a solid state NMR sample rotor in a glove box under argon. The NMR studies are performed using a Bruker MSL-300.

3. Results

3.1. General features of the reaction: evidence for a selective hydrogenolysis on the rhodium particles

In order to estimate the effect of metal loading, metallic coverage and particle size on the stoichiometry of the surface reaction between the organotin compound and the rhodium surface, various silica and alumina supported rhodium catalysts were prepared and characterized (Table 1).

For silica a fairly wide range of dispersion was achieved (from 45% to 80%) corresponding to a range of metal loading from 0.9% to 1.65%. Such preparations lead to metallic surface areas varying from 39 μmol/g to 128 μmol/g. For alumina as it is frequently observed [16] the degree of dispersion is quite high since a value of 100% is obtained.

Reaction of tetra n-butyl tin with all these catalysts in the presence of one atmosphere of hydrogen has been carried at room temperature. Fig. 1 and Fig. 2 indicate the variation of concentration of tetra n-butyl tin with time for various catalysts and for various initial concentrations (Q_0) of the organotin complex. Blank experiments carried out on silica and alumina support, without metallic rhodium, but pretreated under the same conditions, did not give any detectable adsorption or reaction of the tetra n-butyl tin with the support.

Even given the results of these blank experiments, we can not exclude for the case of alumina or silica supported catalysts, a 'spillover' reaction leading to a migration of the organometallic fragment from the metallic surface to the silica (or alumina) surface or the migration of 'dealkylated' tin atoms inside the metallic particle.

Regarding the reaction with the support, it has been shown [17] that for certain conditions (higher temperatures and/or gas phase reactions), tetra n-butyl tin could react with the silica (or alumina) surface to form a well defined surface complex which can be formulated as $\geq$Si–O–Sn(n-C$_4$H$_9$)$_3$ or $\geq$Al–O–Sn(n-C$_4$H$_9$)$_3$). These surface complexes have been fully characterized by surface microanalysis, infrared and

Table 1
Rhodium loading and dispersion of the samples

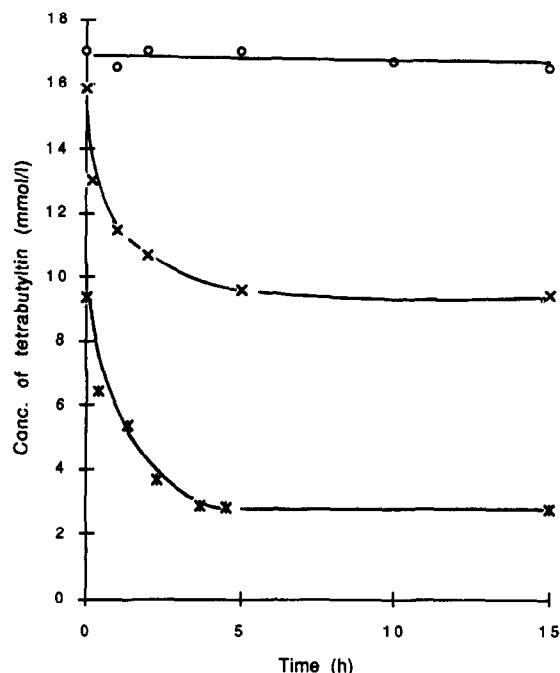| Reference Support	Al(090) Alumina	Si(165) Silica	Si(120) Silica	Si(090) Silica	Si(045) Silica
Rh (wt%)	0.9	1.65	1.2	0.9	0.45
Disp. (D %)	100	80	69	45	60
Rh$_s$ (μmol/g)	87	128	80	39	26

Fig. 1. Variation of the concentration of tetra n-butyl tin during the reaction, using various initial concentrations and 3 g of Al(090) and pure alumina. (×): 3 g Al(090), initial concentration of tetra n-butyl tin: 22.3 mmol/l (*): 3 g Al(090), initial concentration of tetra n-butyl tin: 11.5 mmol/l (○): 3 g of pure alumina, initial concentration of tetra n-butyl tin: 25 mmol/l

Mössbauer spectroscopy and CP-MAS ^{119}Sn and ^{13}C NMR. For $\geq$SiO–Sn(n-C$_4$H$_9$)$_3$ complexes, three ^{13}C NMR signals were observed at 26.3, 15.0 and 10.7 ppm. These peaks were respectively assigned to terminal CH_3, CH_2– (in β and γ position) and Sn–CH_2– carbon atoms. With our silica supported rhodium (Si(165)), the ^{13}C NMR signal obtained after 20 h of reaction at 298 K or 1 and 15 h of reaction at 363 K are reported on Table 2.

Clearly, after reaction between tetra n-butyl tin and silica supported rhodium at 298 K, the formation of a detectable amount of $\geq$SiO–Sn(n-C$_4$H$_9$)$_3$ surface complex is not observed, even after 20 h of reaction. This surface complex is observed only after 15 h of reaction at 363 K and we have to note that in this case, the Sn/Rh$_s$ ratio is greater than unity. This shows that, in the experimental conditions described here, especially in the presence of a liquid non polar solvent (n-heptane), the reaction seems to occur selectively on the metallic phase.

With silica and alumina supported rhodium samples, the concentration of tetra n-butyl tin decreases readily with time to reach a limiting value, Q_f, after ca. 20 h of reaction. As can be seen on Fig. 1 and Fig. 2, the amount of tetra n-butyl tin fixed at 298 K on a given catalyst does not depend on the initial concentration of tetra n-butyl tin (provided that the amount of tetra n-butyl tin introduced is greater than the amount necessary for saturation of the rhodium surface). As expected, but not shown to date, the amount of
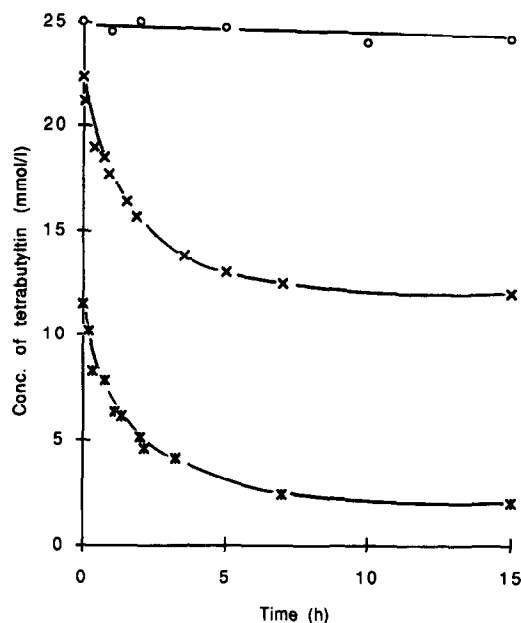

Fig. 2. Variation of the concentration of tetra n-butyl tin with time, using various initial concentrations of tetra n-butyl tin and 3 g of Si(120) and pure silica. (×): 3 g Si(120), initial concentration of tetra n-butyl tin: 15.3 mmol/l (*): 3 g Si(120), initial concentration of tetra n-butyl tin: 9.35 mmol/l (○): 3 g of pure silica, initial concentration of tetra n-butyl tin: 16 mmol/l

Table 2
^{13}C NMR signals obtained after reaction of Sn(n-C$_4$H$_9$)$_4$ with Rh/ Silica Si (165)

T (K)	time (h)	Sn$_d$ (wt%)	Sn/Rh$_s$	^{13}C NMR δ (ppm)
298	20	1.32	0.77	no signal detected
363	1	1.40	0.82	no signal detected
363	15	2.40	1.40	10.7, 15.0, 26.3

Temperature T for one to several hours of reaction. Sn$_d$ (wt%) is the total amount of fixed tin measured by chemical analysis of the sample.

Table 3
Amount of fixed tin after hydrogenolysis

Reference	Rh$_s$ (μmol/ g)	Catal. (g)	Q_0 (μmol/ g)	Q_f (μmol/ g)	$(Sn^f)_c$ (μmol/ g)	$(Sn^f)_a$ (μmol/ g)
Al(090)	87	3	22.3	12.0	69	68
Al(090)	87	3	11.5	2.0	63	nd
Al(090)	87	3	12.7	3.1	64	66
Si(165)	128	2	20.4	10.5	100	nd
Si(120)	80	2	9.3	2.8	66	76
Si(120)	80	2	15.8	9.6	63	74
Si(045)	26	2	5.0	3.3	16	20
Si(090)	39	3	21.7	15.5	41	34
Si(165)	128	3	50.2	33.8	109	110

Conditions: 298 K for 20 h in 20 ml of n-heptane. $(Sn^f)_c$ and $(Sn^f)_a$ are the amounts of fixed tin as determined by two different methods (see the Experimental part).

tetra n-butyl tin fixed seems to be related to the amount of surface rhodium atoms (vide infra).

In order to verify this assumption we have reported on Table 3, the total amount of tetra n-butyl tin fixed on the catalysts surface after 20 h of reaction, measured by two different and independent methods: (i) difference between the initial and the final concentration of tetra n-butyl tin $(Sn^f)_c$ and (ii) chemical analysis of the samples $(Sn^f)_a$.

A fairly good agreement is reached between the values of Sn^f obtained by chemical analysis of the solid $(Sn^f)_a$ and by the variation of concentration of tetra n-butyl tin in solution $(Sn^f)_c$.

Let us consider now the relation between Sn^f and Rh_s represented on Fig. 3 and deduced from the results of Table III. The relationship is linear, indicating that tin, within experimental error, is *grafted on the surface rhodium atoms*. The value of the slope of the straight line corresponding to this linear relationship (0.8) indicates that, on average, each surface rhodium atom is able to graft 0.8 $Sn(n-C_4H_9)_x$ fragment, assuming no surface reconstruction after the grafting.

During the reaction between tetra n-butyl tin and the rhodium surface, butane is the only gas evolved. It has been found that the amount of tin fixed (Sn^f/Rh_s) and the amount of butane evolved (C_4^e/Sn^f) depend on the amount of tetra n-butyl

tin introduced (Sn^i) (Table 4). There is a discontinuity for a tin coverage of 0.3.

1. For a coverage less than 0.3 all the butyl groups are eliminated as butane, and tin is present on the surface as naked tin atoms.
2. For a coverage greater than ca. 0.3 some butyl groups remain on the surface. It is possible to estimate the formula of the corresponding grafted organometallic species $Sn(n-C_4H_9)_x$

Clearly two situations occur: (a) for Sn/Rh_s ratio lower than ca. 0.3, the reaction proceeds with complete hydrogenolysis of the butyl groups. There is no butyl group remaining ($x = 0$) on the catalyst surface, (b) for Sn/Rh_s ration greater than ca. 0.3, some butyl groups remain on the surface ($1 < x < 1.2$). If we assume that for Sn/Rh_s ratio lower than ca. 0.3, tin is completely dealkylated, the number of butyl groups remaining coordinated to tin at high coverage on each organotin fragment is close to two.

3.2. Kinetic study

Tetra n-butyl tin reacts readily with silica or alumina supported rhodium at 298 K in heptane
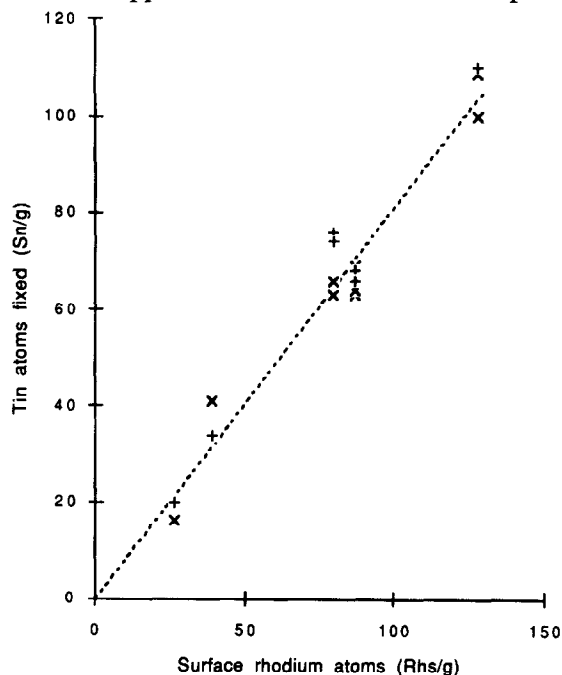

Fig. 3. Amount of tetra n-butyl tin fixed on various silica and alumina supported catalysts against the amount of surface rhodium atoms.

Table 4
Effect of the amount of tetra n-butyl tin introduced (Sn^i) on the amount of tin fixed (Sn^f/Rh_s) and on the amount of butane evolved (C_4^c/Sn^f)

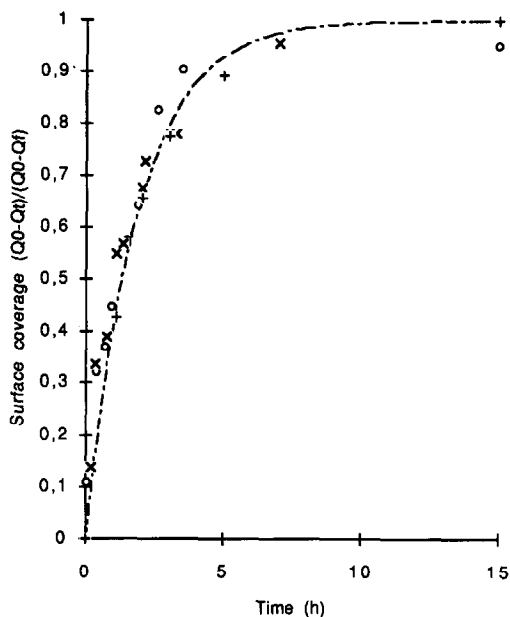| Sample	Al(090)	Si(120)	Si(045)	Al(090)	Si(165)	Si(120)	Si(120)	Si(090)
D (%)	100	69	60	100	80	69	69	45
Sn^f/Rh_s (y)	0.31	0.38	0.65	0.66	0.75	0.77	0.77	0.78
C_4^c/Sn^f	4	3.8	3.0	3.0	3.1	2.8	2.8	2.8
x	0	0.2	1.0	1.0	0.9	1.2	1.2	1.2

After 20 h of reaction at 298 K. The number x represents the average values of the empirical formula $Sn(n\text{-}C_4H_9)_x$.

Fig. 4. Variation with time of the fraction of the metallic surface covered by $Sn(n\text{-}C_4H_9)_x$ fragments (during the reaction between Al(090) and tetra n-butyl tin for various initial concentrations ($\times$) and ($\circ$) 11.5 mmol/l; (+) 22.3 mmol/l. The dotted line is calculated from $\theta = 1 - e^{-kt}$ with $k = 0.6$ h^{-1})

solution under atmospheric pressure of hydrogen. The kinetics of the reaction can be expressed by the variation of coverage θ_t of the surface rhodium atoms by tin organometallic fragments or atoms:

$$\theta_t = (Q_0 - Q_t)/(Q_0 - Q_f) = f(t) \qquad (2)$$

These values are represented in Fig. 4 and Fig. 5, for various silica and alumina supported catalysts and for various initial concentration of tetra n-butyl tin. First of all, as can be observed in Fig. 4 and Fig. 5, the initial reaction rate does not depend significantly on the initial concentration of tetra n-butyl tin; the reaction is zero order in tin complex.

If we assume that the rate of reaction is directly related to the amount of 'free' surface adsorption sites, the coverage of the surface by the organometallic fragments must follow the simple relation (3):

$$\theta = 1 - e^{-kt} \qquad (3)$$

Computational curves obtained following Eq. (3) are drawn in Fig. 4 and Fig. 5 (dotted lines). The value of the rate constant k depends on the nature of the support, the best fit is obtained with $k_a = 0.6$ h^{-1} with alumina and $k_s = 1$ h^{-1} with silica. There is not a very good agreement between the experimental and the computational curves,
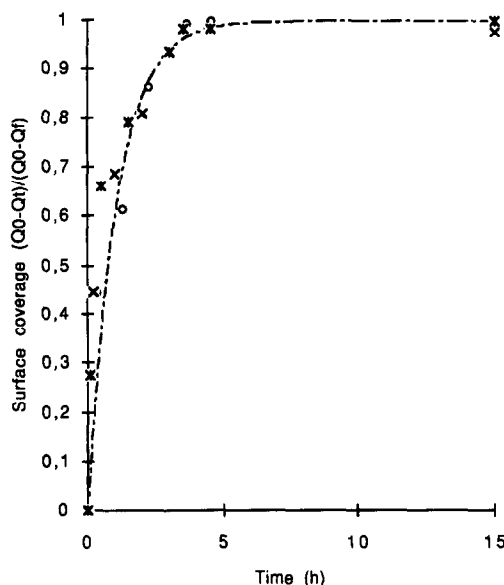

Fig. 5. Variation with time of the fraction of the metallic surface covered by $Sn(n\text{-}C_4H_9)_x$ fragments (during the reaction between silica supported catalysts and tetra n-butyl tin for various initial concentrations ($\circ$) 21.7 mmol/l; (+) 15.8 mmol/l and (+) 9.3 mmol/l. The dotted line is calculated from $\theta = 1 - e^{-kt}$ with $k = 1$ h^{-1})

but as a first approximation we can conclude that the rate of the reaction is greater on silica supported rhodium than on alumina supported rhodium. The reason why there is such difference between the two supports is not clear.

4. Discussion and conclusion

Tetra n-butyl tin reacts readily with silica or alumina supported rhodium, at room temperature, in n-heptane solution, under atmospheric pressure of hydrogen. The total amount of tin fixed after 20 h of reaction is directly correlated to the amount of surface rhodium atoms (Fig. 3). There is no formation of silica (or alumina) grafted $\geq$M–O–Sn(n-C$_4$H$_9$)$_3$ complex (M = Al, Si). These results confirm that the reaction occurs exclusively on the metallic surface (at least at a temperature of 298 K, at short reaction time and for a coverage of the metallic surface lower than unity). The number of tin fixed by surface rhodium atom is close to 0.8: on average, each surface rhodium atom is able to graft 0.8 Sn(n-C$_4$H$_9$)$_x$ fragments.

The reaction proceeds by successive hydrogenolysis of the butyl groups to form butane. The amount of butane evolved depends on the amount of tin fixed. For Sn/Rh$_s$ ratio less than ca. 0.3, there is complete hydrogenolysis of the butyl groups, leading to 'naked' tin atoms. For Sn/Rh$_s$ ratio greater than ca. 0.3, some butyl groups remains on the surface. According to the data of Table 4, it seems that a relatively well defined organometallic fragment Rh$_s$–Sn(n-C$_4$H$_9$)$_2$ could be obtained. This result could be due to the progressive poisoning of a certain type of surface rhodium atoms (kinks, edges, faces) [13] by naked tin atoms and then partial hydrogenolysis of the organotin complex on the other sites of the metallic surface.

The reaction rate is first order in surface rhodium atoms and zero order in tetra n-butyl tin. The rate determining step is independent of the concentration of the alkyl-tin complex.

The first step could be a reversible adsorption of the organometallic on the rhodium surface. This organometallic complex is very bulky and covers several rhodium atoms. The following step, which could be the rate limiting step would be the hydrogenolysis of the first Sn–C bond of the adsorbed complex. The kinetics of the reaction would only be governed by the number of 'free' surface rhodium atoms. Partial hydrogenolysis could be observed at any surface coverage (0 < Sn/Rh$_s$ < 0.8), but full hydrogenolysis could be observed only for low tin coverage (0 < Sn/Rh$_s$ < 0.3).

As seen in Fig. 4 and Fig. 5, the rate constant k_a and k_s which represents the probability of the reaction on surface rhodium atoms depend on the nature of the support. But, the dispersion of the silica and alumina supported catalysts are not in the same range. The alumina supported rhodium is fully dispersed ($D = 1$) and the dispersion of the silica supported catalysts are always lower than 0.8. According to Van Hardevel and Hartog [18], the number of kink and corner atoms compared to the number of faces atoms increases with the dispersion of spherical particles. For atomically dispersed catalyst (Rh/Al$_2$O$_3$), there is no atom on faces, we could propose than the fast reaction occurs on faces atoms and the slower one only on defects. This would be unexpected as it is generally assumed that defects sites have greater catalytic activity than faces [12].

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