Surface organometallic chemistry on metals
Influence of the presence of functional groups grafted at the surface of Rh particles on the competitive hydrogenation of terminal and internal double bonds of unsaturated primary alcohols

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Abstract

Careful hydrogenolysis of organometallic compounds with group VIII metallic surfaces lead to surface organometallic fragments directly grafted on the metallic particles with well-defined structures. The presence of such surface organometallic fragments was demonstrated by various physical and chemical techniques (EXAFS, magnetic measurements, IR spectroscopy, Mössbauer, thermoreduction, etc.). Surface organometallic complexes with an average formula $M_s[M'R_x]_y$ (M: Rh, Pt, Ni; M': Sn, Ge, Si, Se; R: Me, Et, Bu) were proposed. It was recently demonstrated that organometallic fragments with functional groups can also be grafted on a platinum or rhodium surface. In this work, we demonstrate that organo-tin fragments with functional groups, grafted on a silica-supported rhodium surface can strongly modify the regio-selectivity of the hydrogenation of unsaturated primary alcohols. The rate of hydrogenation of *trans*-2-hexenol and 5-hexenol was determined at room temperature under 20 bar of hydrogen in heptane solution for Rh/SiO_2 catalysts which were either used as they were or were modified with $Bu_3Sn(CH_2)_3OH$ or $Bu_2Sn[(CH_2)_2(O(CH_2)_2)_2OMe]_2$. The rate of hydrogenation of the terminal double bond is slightly modified by the presence of functional groups, while that of the internal unsaturation decreases by a factor of 4. These results are explained by the formation of a hydrophilic layer around the metallic particle which inhibits the adsorption of the unsaturated alcohol by its internal double bond. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Surface organometallic chemistry on metals is a new field of chemistry devoted to the study of the reactivity, at a molecular level, of organometallic complexes with metallic surfaces [1]. In some cases, the metallic surface is covered by surface organometallic fragments which can govern the selectivity of this new

kind of material in catalysis. In the previous publications [2–4], we have demonstrated that the selective hydrogenolysis of $Sn(n-C_4H_9)_4$ on rhodium, nickel or platinum catalysts lead to a stable surface organo-tin fragment. The identification of the grafted organo-tin complex have been carried out by various analytical methods (EXAFS, RGN, EM, XPS, magnetism, etc.). All these data are consistent with the formation of a surface complex with the following average formula: $Rh[Sn(n-C_4H_9)_x]_y/SiO_2$ $(1 < x < 3; 0 < y < 0.8)$.
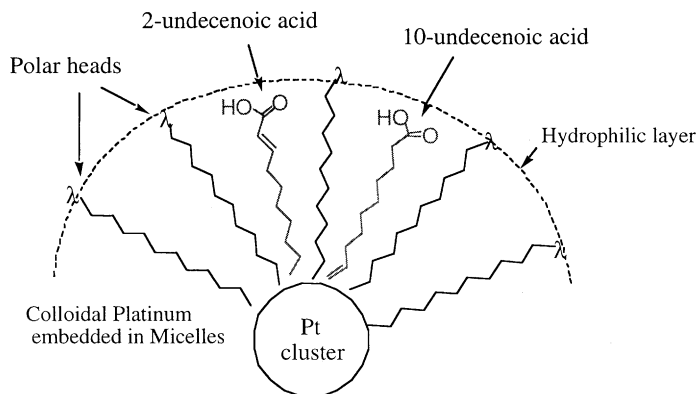
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This solid was very active and selective for the hydrogenation of an α–β unsaturated aldehyde (citral) into the corresponding unsaturated alcohol (geraniol and nerol) [2].

It has been demonstrated [5] that platinum clusters "embedded" in micelles can be regio-selective in the hydrogenation of unsaturated fatty acids. The fatty acid molecule comprises a hydrophobic alkyl chain and a hydrophilic carbonyl group at the end and it is known to form a kind of "Langmuir–Blodget" film. It is thus reasonable to expect that the carboxylic group of the fatty acid solubilized by the micelle is located in the hydrophilic layer of the micelle, far away from the metallic surface, as shown in Scheme 1.

Under these conditions, the C=C double bond of the 10-undecenoic acid is always placed closer to the platinum surface than the C=C bond of the 2-undecenoic acid. On platinum cluster embedded in polyethylene glycol monolaurate, the initial rate of hydrogenation of 10-undecenoic acid is five times that of 2-undecenoic acid. In order to synthesize stable-supported metallic systems surrounded by hydrophobic–hydrophilic layers, we previously demonstrate that organometallic fragments with hydrophilic head can be grafted via a covalent bond on a metallic surface [6]. The presence of a covalent bond is expected to give much stronger stability than a micellar system.

In this work, we demonstrate that surface organometallic fragment with functional groups grafted on a rhodium surface can strongly modify the regioselectivity of the hydrogenation of unsaturated primary alcohols.

2. Experimental

2.1. Catalysts

The monometallic silica-(Aerosil from Degussa, $200 \, m^2/g$) supported rhodium (Rh/SiO$_2$) was prepared by the cationic exchange method, starting from RhCl(NH$_3$)$_4$(OH)$_2$, following the procedure already described [7]. The metal loading is 1.62% (w/w) and the dispersion of the metallic particles, measured by hydrogen chemisorption and electron microscopy, according to [7] is about 0.8 Rh$_s$/Rh.

The bimetallic catalysts was prepared following the procedure already described [6] by interaction between a reduced sample of Rh/SiO$_2$ and Bu$_3$Sn(CH$_2$)$_3$OH or Bu$_2$Sn[(CH$_2$)$_2$(O(CH$_2$)$_2$)$_2$OMe]$_2$ complexes. The desired amount of Rh/SiO$_2$ (generally, 50 mg), reduced under flowing hydrogen at $350 \,^{\circ}C$ during 3 h is introduced, under hydrogen in a Schlenk tube was filled with 5 ml of n-heptane. One equivalent (per surface rhodium) of the organometallic compound is then introduced in the Schlenk tube under atmospheric pressure of hydrogen. After 24 h of reaction, the resulting solid is introduced under argon in the hydrogenation reactor.

2.2. Unsaturated alcohol hydrogenation

The hydrogenation of 2-hexenol and 5-hexenol is performed in a well-stirred stainless steel autoclave filled with 15 ml of n-heptane and 0.4 g of each unsaturated alcohol. The reaction proceeds under 20 bar

Scheme 1. Platinum cluster embedded in micelles, regio-selective in the hydrogenation of unsaturated fatty acid, from Toshima and Takahashi [5].

of hydrogen at room temperature. The kinetics of the reaction is followed by gas-phase chromotography (Chromapack CPWax 57CB, 50 m × 0.32 mm) of samples of the solution taken at regular intervals of time.

The stirring speed is 10 runs/s. It was checked that for reaction rates lower than about 3 mol/l/h, there is no diffusion limitation. The amount of catalyst is then adjusted so as to avoid reaction rates greater than 3 mol/l/h.

The rate of hydrogenation of the two unsaturated alcohols was measured by the slope of the variation of the concentration with time, extrapolated at time zero of the reaction. They are expressed as r_1 for 5-hexenol and r_2 for 2-hexenol ($mmol_{alcohol} \, g_{catal.}^{-1} \, s^{-1}$).

3. Results and discussion

The kinetics of the hydrogenation of *trans*-2-hexenol and 5-hexenol at room temperature, under 20 bar of hydrogen on monometallic Rh/SiO$_2$ catalyst is reported in Fig. 1.

The main product of the reaction is hexanol, but the sum of the concentration of the two alcohols in the solution decreases drastically with time. Various

side products are obtained by either *cis–trans* isomerization (*cis*-2-hexenol) or double bond migration (4-hexenol, 3-hexenol), tautomerization and hydrogenolysis of the C–OH bond (hexane, hexenes). These isomerization processes are well known on noble metals [8,9]. Rhodium is known to be a poor catalyst for hydrogenation of unconjugated C=O bond and in our conditions, the hexanal formed is not hydrogenated, while the other unsaturated alcohols are readily hydrogenated into hexanol.

The kinetics of the hydrogenation of *trans*-2-hexenol and 5-hexenol at room temperature, under 20 bar of hydrogen on Rh/SiO$_2$ catalyst modified by reaction with Bu$_4$Sn, Bu$_2$Sn[(CH$_2$)$_2$(O(CH$_2$)$_2$)$_2$OMe]$_2$ or Bu$_3$Sn(CH$_2$)$_3$OH at room temperature are reported in Figs. 2–4.

In both the cases, the product of the reaction is 1-hexanol. The selectivity of the hydrogenation to the saturated alcohol in the solution does not change with time: the presence of grafted organometallic fragments has almost completely suppressed the isomerization and hydrogenolysis properties of the catalyst surface. The initial reaction rates of hydrogenation of 5-hexenol (r_1) and *trans*-2-hexenol (r_2) and the initial regio-selectivity (r_1/r_2) of the monometallic and bimetallic catalysts are reported in Table 1.
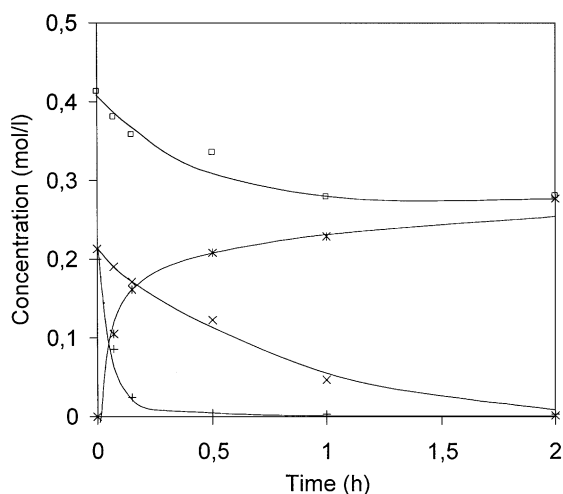

Fig. 1. Kinetics of 2-hexenol and 5-hexenol hydrogenation on rhodium: (+) concentration of 2-hexenol; (×) concentration of 5-hexenol; (∗) concentration of hexanol; (□) total concentration of alcohols (10 mg of catalyst, 20 bar of hydrogen, room temperature, 15 ml *n*-heptane, 0.4 g of substrate).
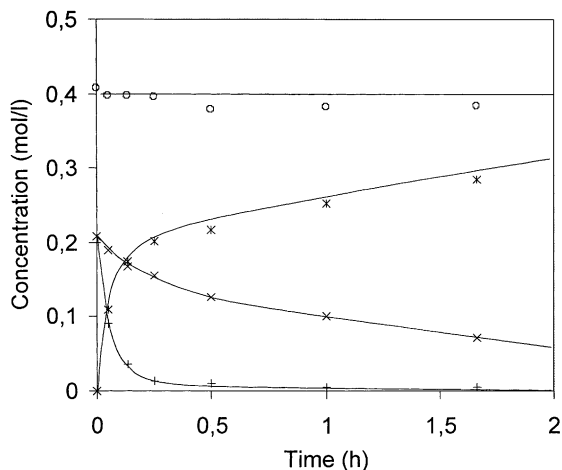

Fig. 2. Kinetics of 2-hexenol and 5-hexenol hydrogenation on rhodium modified by Bu$_4$Sn at room temperature: (+) concentration of 2-hexenol; (×) concentration of 5-hexenol; (∗) concentration of hexanol; (○) total concentration of alcohols (50 mg of catalyst, 20 bar of hydrogen, room temperature, 15 ml *n*-heptane, 0.4 g of substrate).
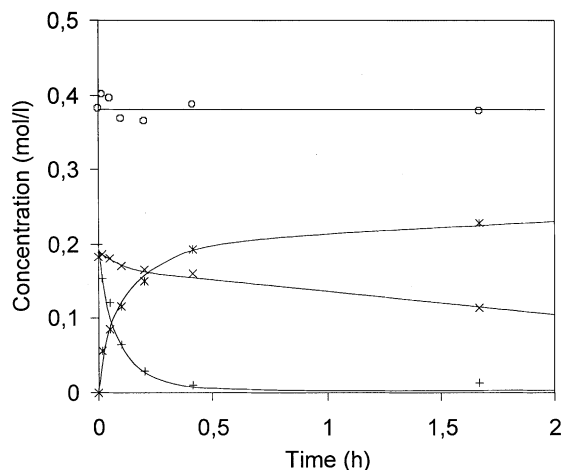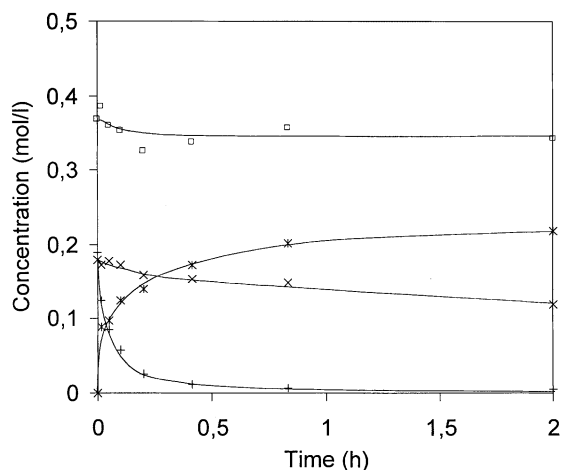
Fig. 3. Kinetics of 2-hexenol and 5-hexenol hydrogenation on rhodium modified by $Bu_2Sn[(CH_2)_2(O(CH_2)_2)_2OMe]_2$ at room temperature: ($+$) concentration of 2-hexenol; ($\times$) concentration of 5-hexenol; ($\ast$) concentration of hexanol; ($\circ$) total concentration of alcohols (50 mg of catalyst, 20 bar of hydrogen, room temperature, 15 ml *n*-heptane, 0.4 g of substrate).

Fig. 4. Kinetics of 2-hexenol and 5-hexenol hydrogenation on rhodium modified by $Bu_3Sn(CH_2)_3OH$ at room temperature: ($+$) concentration of 2-hexenol; ($\times$) concentration of 5-hexenol; ($\ast$) concentration of hexanol; ($\square$) total concentration of alcohols (50 mg of catalyst; 20 bar of hydrogen, room temperature, 15 ml *n*-heptane, 0.4 g of substrate).

The initial rate of hydrogenation of the two unsaturated alcohols decreases drastically when the Rh/SiO_2 catalyst is modified by reaction with the organometallic complexes at room temperature. There is clearly a poisoning effect of the rhodium catalyst by the grafted organometallic fragments, obviously due to the decrease of the number of accessible surface rhodium atoms. The ratio between the initial reaction rate of hydrogenation of the two unsaturated alcohols (a direct measure of the regio-selectivity, r_1/r_2) increases slightly when the Rh/SiO_2 catalyst is modified by the reaction with Bu_4Sn at room temperature. In this case, it is known that about one butyl group remains on the organometallic fragment grafted on the rhodium

surface (formation of a stable Rh_3SnBu fragment [10]). This ratio increases by a factor close to 5 when the organo-tin fragments with functional groups are grafted on the surface of rhodium. In this case, it has been shown that the surface organometallic fragments have the average formula: $Rh_3Sn(CH_2)_3OH$ (60%) and $Rh_3Sn(CH_2)_2(O(CH_2)_2)_2OMe$ (100%) [6]. The nature of the functional group ($-Sn(CH_2)_3OH$ or $Sn(CH_2)_2(O(CH_2)_2)_2OMe$)) has little influence on the reaction rates. It is likely that functional groups grafted on the surface of rhodium particles can form a kind of hydrophilic layer which will be able to orientate the incoming molecules in such a way that the polar groups are situated at the periphery of the particle

Table 1

Initial rates of 5-hexenol (r_1) and 2-hexenol (r_2) hydrogenation on various monometallic and bimetallic catalysts, under 20 bar of hydrogen at room temperature

Catalyst	Modifier	r_1 (mmol$_{alcohol}$ g$_{catal.}^{-1}$ s^{-1})	r_2 (mmol$_{alcohol}$ g$_{catal.}^{-1}$ s^{-1})	r_1/r_2
Rh/SiO_2	No	1.52	0.161	9
Rh/SiO_2	Bu_4Sn	0.29	0.023	13
Rh/SiO_2	$Bu_2Sn[(CH_2)_2(O(CH_2)_2)_2OMe]_2$	0.37	0.0104	36
Rh/SiO_2	$Bu_3Sn(CH_2)_3OH$	0.38	0.0078	49
Rh/SiO_2	$Bu_3Sn(CH_2)_3OH^a$	0.33	0.0072	46

[a] New experiment after filtration of the solid and reuse in identical conditions.
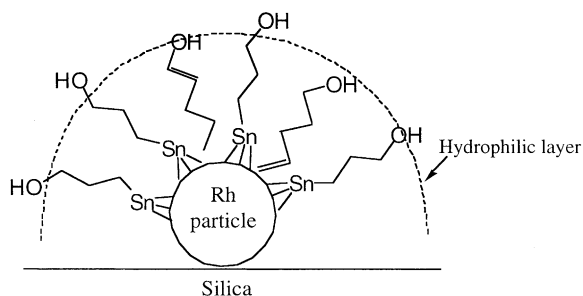
Scheme 2. Rhodium particle covered by grafted functional organo-tin fragments, regio-selective in the hydrogenation of unsaturated alcohol.

(Scheme 2) as proposed by Toshima and Takahashi [5] with platinum particles entrapped in micelles (Scheme 1).

The largest r_1/r_2 ratio is obtained with Rh/SiO$_2$ modified by Bu$_3$Sn(CH$_2$)$_3$OH. In this case, the stability of the catalyst was studied by recycling the experiments. As seen in Table 1, the initial rates of 2-hexenol and 5-hexenol hydrogenation do not vary drastically when the catalyst is recovered by filtration, after complete hydrogenation of 1000 mol of unsaturated alcohol per mole of rhodium and reintroduced into the reaction vessel. It is then expected that organometallic fragments with functional groups grafted on the rhodium surface can be more stable during the hydrogenation reaction, than metallic clusters embedded in micelles, as for these systems, the ratio substrate/metal is no more than 0.05 [5].

4. Conclusion

The competitive hydrogenation of two unsaturated isomers 2-hexenol and 5-hexenol on silica-supported rhodium modified by reaction with organo-tin compounds demonstrates that the presence of grafted organometallic fragment completely suppresses the isomerization and hydrogenolysis properties of the catalyst surface, without variation of the ratio between initial reaction rates of the two isomers. The presence of grafted organometallic fragment with functional groups leads to a clear increase of the ratio between the initial reaction rate of 5-hexenol and 2-hexenol. It seems that functional groups grafted on the surface of rhodium particles can form a hydrophilic layer able to turn the reactant molecules in such a manner that the internal double bond of the 2-hexenol is far from the rhodium surface. Turn over number of at least 2000 was obtained, with recycling possibilities suggesting that these systems can be more stable than metallic clusters embedded in micelles.

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