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Surface organometallic chemistry on metals: influence of organometallic fragments grafted to the surface of Rh particles on the competitive hydrogenation of terminal and internal double bonds of unsaturated primary alcohols

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Abstract

Hydrophobic organotin fragments, grafted to the surface of a rhodium particle can strongly modify the rate of the hydrogenation of internal or terminal carbon–carbon (C–C) double bonds of unsaturated primary alcohols. In this work, the rate of hydrogenation of *trans*-2-hexenol and 5-hexenol was determined at room temperature under 20 bar of hydrogen in butanol + water (30 + 10) solution for Rh/SiO_2 catalysts which were either used unmodified or modified with $Sn(n\text{-}C_4H_9)_4$. It was found that the presence of alkyl groups decreases the ratio between the rate of hydrogenation of the terminal and internal double bond by a factor of 4. These results are explained by the formation of a hydrophobic layer around the modified particle which inhibits the adsorption of the unsaturated alcohol by its internal double bond.

Keywords: Surface organometallic chemistry on metals; Selective hydrogenation of unsaturated alcohols; Rhodium–tin catalysts

1. Introduction

The selective hydrogenation of internal or terminal carbon–carbon (C–C) double bonds in unsaturated molecules functionalized with polar groups is difficult to achieve using heterogeneous catalysts. It was first observed over supported palladium or platinum in water that a C–C double bond of an unsaturated carboxylic acid was more quickly hydrogenated when the double bond was far from the hydrophilic head rather than when it was far from the hydrophobic tail [1]. It was then demonstrated that platinum particles supported on alumina, modified by the adsorption of carboxylic acids, can be used as catalysts with monomolecular polar layer systems [2]. Application of these systems to the selective hydrogenation of unsaturated alcohols was performed in nonpolar media [3]. It was assumed that, via the hydroxyl group as a hydrophilic label, the unsaturated alcohol is adsorbed by its polar head, in the hydrophilic phase, to the surface of alumina and thus the double bond near the hydrophilic group can more easily approach the platinum surface. Consequently, the C–C double bond which was close to the hydroxyl group was easily hydrogenated. Since these systems are not stable in polar solvents, their application to the regioselective hydrogenation of unsaturated carboxylic acids is difficult. In order to overcome the destruction of the carboxylic layer on Pt/Al_2O_3, Kuno et al. [4] prepared alkylsilyl-modified platinum supported on silica. It was assumed that the alkylsilyl reagent

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was bonded to the silica surface by a covalent bond. Competitive hydrogenation of 9-decenoic acid and 2-decenoic acid was carried out over unmodified and alkylsilyl-modified catalysts in ethanol. It was observed that the alkylsilyl-modified catalyst exhibits a higher chemoselectivity than the unmodified catalyst. It was proposed that the hydrophilic surface of the solid was converted to a hydrophobic one by alkylsilylation, so that the hydrophobic part of the reactant more easily approaches the active site. In the systems described by Kuno et al. [4], the modifiers are assumed to be adsorbed/bonded to the silica or alumina support and not on the platinum surface. This suggests a kind of physical effect of the modifier. In the case of the systems described by Toshima and Takahashi [1], where the colloidal platinum particles are dispersed in the polymer there is also a kind of cage or microenvironmental effect.

We have demonstrated that organometallic fragments (SnR_x) can be grafted by covalent bonding directly onto the metallic surface of rhodium particles supported on silica [5]. In such a system, α–β unsaturated aldehydes were selectively hydrogenated to unsaturated alcohols. It was proposed that this selectivity was due to the steric effect of the alkyl groups which inhibits the flat adsorption of the double bond on the rhodium surface. Since the alkyl groups can create a hydrophobic layer around the rhodium particles, it was proposed that in a hydrophilic medium, the polar head of an unsaturated alcohol remains in the hydrophilic phase and that the hydrophobic tail can reach the metallic surface, through the hydrophobic layer. In this situation, the terminal double bond of the unsaturated alcohol could be hydrogenated much more easily than the internal double bond.

2. Experimental

2.1. Monometallic Rh/SiO$_2$ catalyst

The silica supported rhodium catalyst (Rh/SiO_2) was prepared by the ion exchange method, following the previously described procedure [6]. The specific surface area of the silica support is 200 $m^2\,g^{-1}$. The rhodium precursor is $RhCl(NH_3)_4Cl_2$ from Aldrich. The metal loading is 1.2% (w/w). The average metallic particle size, measured by electron microscopy is close to 1.5 nm. The dispersion of the catalyst (number of surface rhodium atoms per number of rhodium atoms, Rh_s/Rh) measured by hydrogen chemisorption [6] is about 0.9.

2.2. Bimetallic catalysts

The bimetallic samples were prepared by the surface organometallic chemistry on metals route [7]. Tetra *n*-butyl tin, $Sn(n\text{-}C_4H_9)_4$, reacts under hydrogen pressure (30 mbar) in a sealed vessel with the surface of reduced rhodium particles, to give the $Rh_s[Sn(C_4H_9)_x]_y/SiO_2$ species. The values of x and y depend on the temperature, the time of the reaction and on the amount of $Sn(n\text{-}C_4H_9)_4$ introduced [8].

The preparation of the bimetallic catalyst begins with the reduction of the Rh/SiO_2 samples (0.2–0.5 g) under flowing (100 ml min^{-1}) hydrogen at 25–350 °C (1.8 °C min^{-1}), 2 h at 350 °C and then cooling to 25 °C under hydrogen. The reactor is then sealed and the hydrogen pressure is reduced to 30 mbar in order to avoid diffusion limitation of the reactants and products. The desired amount of $Sn(n\text{-}C_4H_9)_4$ is introduced into the reactor via the septum and the temperature of the reactor is kept at 50 or 150 °C during the time t. According to Didillon et al. [8], after reaction of $0.5Sn(n\text{-}C_4H_9)_4/Rh_s$ at 50 °C for 2 h, the catalyst $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ (x and y close to, respectively, 3 and 0.5) is obtained. After reaction at 150 °C during 0.5 h, there are no remaining butyl groups and the catalyst $Rh_sSn_{0.5}/SiO_2$ ($x = 0$ and y close to 0.5) is formed.

A 10 ml of water are then introduced into the reactor via the septum and the suspension is introduced under flowing argon into the hydrogenation reactor.

2.3. Hydrogenation of unsaturated alcohols

The hydrogenation of the two unsaturated alcohols is performed in a 100 ml batch reactor stirred by a magnetic stirrer, under hydrogen pressure of 20 bar.

The reactor is filled with 30 ml of butan-2-ol, 400 mg of *trans*-hex-2en-1-ol and 400 mg of hex-5-ene-1-ol. The catalyst sample prepared in 3.2 is introduced in suspension in water (10 ml) into the reactor. The reactor is then closed and purged three times with hydrogen (20 bar). The kinetics of the reaction are followed by analysis (gas phase chromatography) of samples of solution taken at regular intervals of time.

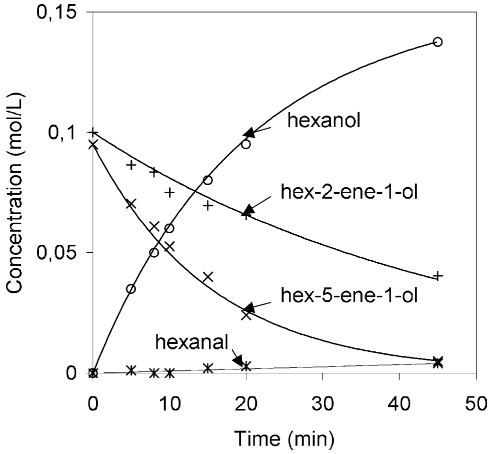


Fig. 1. Hydrogenation of *trans*-hex-2-ene-1-ol (4 mmol) and hex-5-ene-1-ol (3.8 mmol) in butan-2-ol (30 ml) + water (10 ml), under 20 bar of hydrogen at 25 °C on Rh/SiO_2 (0.03 g).

Typical results of the hydrogenation of the mixture of *trans*-hex-2-ene-1-ol and hex-5-ene-1-ol carried out over Rh/SiO_2 catalyst are shown in Fig. 1.

Hydrogenation of the two unsaturated alcohols with formation of hexanol occurs. Isomerization occurs with formation of a small amount of hexanal (reported in Fig. 1) and very small amounts (less than 1%) of hex-4-ene-1-ol, hex-3-ene-1-ol (*cis* and *trans*) or *cis*-hex-2-ene-1-ol (not reported in Fig. 1). The amount of hexanol formed is slightly lower than the amount of hexanol expected from the total amount of unsaturated alcohols consumed. This could be due to dehydroxylation of hexanol to hexane which is effectively observed.

The initial rates of hydrogenation r_0 (for hex-5-ene-1-ol) and r'_0 (for *trans*-hex-2-ene-1-ol) will be used to compare the activities of the catalysts for the two unsaturated alcohols.

As can be seen in Table 1, using the same Rh/SiO_2 catalyst, it was observed that the ratio r_0/r'_0 is close to 3 and varies slightly with the rate of stirring, with the amount of catalyst or whether the sample is used as it or crushed.

3. Results and discussion

The competitive hydrogenation of a mixture of hex-5-ene-1-ol and *trans*-hex-2-ene-1-ol was carried out over Rh/SiO_2 and $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ catalysts. Typical results obtained are reported in Fig. 2.

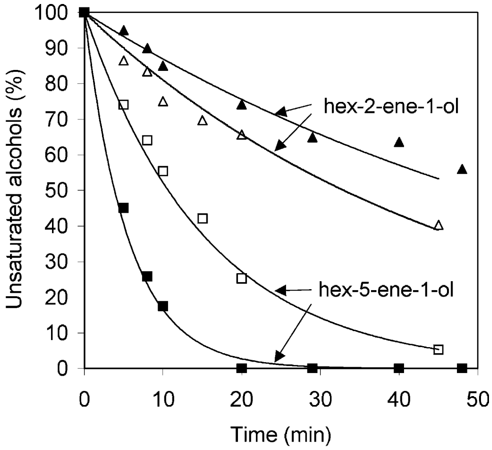


Fig. 2. Hydrogenation of *trans*-hex-2-ene-1-ol (4 mmol) and hex-5-ene-1-ol (4 mmol) in butan-2-ol (30 ml) + water (10 ml), under 20 bar of hydrogen at 25 °C on Rh/SiO_2 (0.03 g) (open symbols) and $Rh_s[Sn(n\text{-}C_4H_9)_3]_{0.5}/SiO_2$ (0.5 g) (filled symbols).

For the Rh/SiO_2, $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ and $Rh_sSn_{0.5}/SiO_2$ catalysts, the values of the initial rates of hydrogenation of hex-5-ene-1-ol (r_0) and *trans*-hex-2-ene-1-ol (r'_0) are reported in Table 2.

It is clear that the ratio r_0/r'_0 drastically increases from monometallic Rh/SiO_2 catalysts to $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ samples. It is worth noting that bimetallic $RhSn_{0.5}/SiO_2$ exhibits less activity but the same ratio r_0/r'_0 compared to Rh/SiO_2. It is obvious that the increase in activity for external double bond hydrogenation as compared to the internal double bond is due to the presence of butyl ligands on the surface of $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ catalysts.

The $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ catalyst can be reused without drastic decrease in activity. After about 1 h of reaction, the liquid phase is removed from the reactor with a syringe and a new quantity of solvent and reactants (4 mmol of *trans*-hex-2-ene-1-ol and 4 mmol of hex-5-ene-1-ol in 30 ml of butan-2-ol + 10 ml of water) is added. The initial rates of hydrogenation of hex-5-ene-1-ol and *trans*-hex-2-ene-1-ol was then, respectively, 1.0 and 0.08 mmol min^{-1} g^{-1}. The slight decrease of the initial reaction rate could be due to the loss of a small amount of catalyst.

From these results, assuming that the remaining alkyl ligands of the organometallic moiety grafted on

Table 1
Initial reaction rate of hydrogenation of hex-5-ene-1-ol (r_0) and *trans*-hex-2-ene-1-ol (r'_0) at 25 °C under 20 bar of hydrogen in butan-2-ol (30 ml) + water (10 ml) with Rh/SiO_2

Stirring speed (rpm)	Catalyst (g)	r_0 (mmol min^{-1} g^{-1})	r'_0 (mmol min^{-1} g^{-1})	r_0/r'_0
1000	0.030	7.5	2.7	2.8
750	0.030	7.2	2.5	2.9
750	0.050	7.5	2.4	3.1
750	0.070	6.9	2.4	2.9
750	0.070 (crushed)	6.5	2.4	2.7

Initial concentration of *trans*-hex-2-ene-1-ol and hex-5-ene-1-ol: 0.1 mol l^{-1}; influence of stirring speed and amount of catalyst.

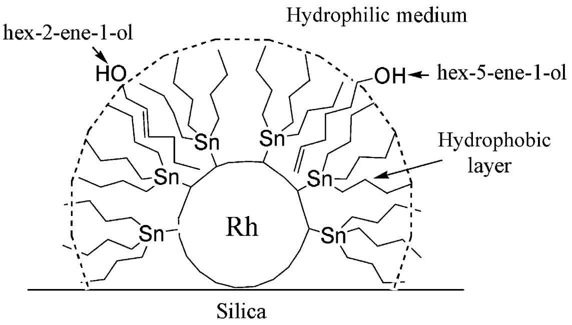
Table 2
Initial reaction rate of hydrogenation of hex-5-ene-1-ol (r_0) and *trans*-hex-2-ene-1-ol (r'_0) at 25 °C under 20 bar of hydrogen in butan-2-ol (30 ml) + water (10 ml) with Rh/SiO_2, $Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$ and $Rh_sSn_{0.5}/SiO_2$ catalysts

Catalyst	Rh/SiO_2	$Rh_s[Sn(C_4H_9)_3]_{0.5}/SiO_2$	$Rh_sSn_{0.5}/SiO_2$
Amount of catalyst (g)	0.03	0.5	0.3
r_0 (mmol min^{-1} g^{-1})	7.2	1.1	0.81
r'_0 (mmol min^{-1} g^{-1})	2.5	0.08	0.27
r_0/r'_0	3 ± 0.2	13 ± 0.2	3 ± 0.2

Initial concentration of unsaturated alcohols: 0.1 mol l^{-1}.

the rhodium surface create a hydrophobic layer around the catalytic sites, it could be suggested that the hydrophobic tail of the unsaturated alcohols is located in this hydrophobic layer and the hydroxyl group is located in the hydrophilic medium which is the solvent. As a consequence, the internal double bond of the unsaturated alcohol could be more remote from the active surface than the terminal double bond, as described in the following Scheme 1.

On both monometallic Rh/SiO_2 and bimetallic $RhSn_{0.5}/SiO_2$ catalysts, there is no hydrophobic layer. In this cases, the two unsaturated alcohols are adsorbed in the same manner on the active surface. It is obvious that the naked tin atoms poisoned the rhodium surface, leading to a drastic decrease of the activity of the sample.



Scheme 1. Rhodium particle covered by grafted $Sn(n\text{-}C_4H_9)_3$ fragments, influence of the hydrophobic layer on the adsorption of hex-2-ene-1-ol and hex-5-ene-1-ol.

4. Conclusion

In this work, we demonstrate that organometallic fragments, grafted on a silica supported rhodium surface can strongly modify the rate of hydrogenation of internal or terminal C–C double bonds of unsaturated primary alcohols. The relative rate of hydrogenation of *trans*-5-hexenol and 2-hexenol at room temperature under 20 bar of hydrogen in butanol + water (30 + 10) solution is four times greater for $Rh_s[Sn(n\text{-}C_4H_9)_3]_{0.5}/SiO_2$ than for Rh/SiO_2 or $Rh_sSn_{0.5}/SiO_2$ catalysts. These results can be explained by the formation of a hydrophobic layer around the modified catalyst which inhibits the adsorption of the unsaturated alcohol by its internal double bond.

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