

Immobilization of $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ catalyst: Application for sorbic acid hydrogenation and comparison with homogeneous and two-phase catalysis

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Abstract

The Ru complex active for selective sorbic acid hydrogenation to *cis*-hex-3-enoic acid had been immobilized by means of hydrogen bonds using direct procedure. The immobilized catalyst was tested for selective hydrogenation and gave almost the same results in selectivity as the catalysis in homogeneous phase. The characterization, kinetic experiments and comparison tests were carried out. The stability of the catalyst was increased by the immobilization.

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Keywords: Immobilization; Ru complex; Selective hydrogenation; Silica; Sorbic acid

1. Introduction

Sorbic acid can be hydrogenated to large amount of products, but only two of them (in a pure state) are useful for fragrant compound synthesis—*trans*-hex-2-enoic acid and *cis*-hex-3-enoic acid. These acids can be used for leaf alcohols syntheses. *trans*-Hex-2-enoic acid (rather methyl-*trans*-hex-2-enoate, ester are more active than acids) can be prepared [1–3] by sorbic acid (methyl sorbate) hydrogenation using standard metal catalysts with high selectivity (Pd/C, Ni/Al₂O₃). Few years ago, a very selective catalyst for sorbic acid hydrogenation to *cis*-hex-3-enoic acid was discovered [4–6]. The $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ catalyst (Cp^* = pentamethylcyclopentadienyl) is capable to catalyze the hydrogenation of sorbic acid with very high selectivity (up to 96%) under mild conditions (1 MPa, 60 °C). *cis*-Hex-3-enoic acid can be used for *cis*-hex-3-ene-1-ol preparation. This product is very intensively used in fragrance and flavor chemistry for its very intensive fragrant properties.

Catalyst immobilization represents nowadays an important research area. The ability of catalyst regeneration and recycling

is the most important aspect. However, $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ catalyst was used only in homogeneous and two-phase hydrogenation [4,5]. Two-phase hydrogenation may be considered as a type of immobilization but in this case the recycling of catalyst phase was not possible and the catalyst appeared in the product phase too. The active catalyst gives only a few possibilities to be immobilized by means of its attaching to the solid support. One of them is immobilization by means of hydrogen bonds. A few papers using immobilization of catalyst by means of hydrogen bonds to the silica support via triflate group of complex were published [7–10]. On the silica surface two interesting types of “places” which can be used for immobilization exist [11,12]—silanol and siloxane groups, the former is used for triflate group immobilization.

2. Experimental

2.1. $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ preparation

The ruthenium active catalyst was prepared by the method described in literature [4–6,13]. The $[\text{Cp}^*\text{RuCl}_2]_n$ (0.013 g) was dissolved in ether (5 ml) with excess of sorbic acid (0.15 g), zinc powder (0.15 g) and silver triflate (0.02–0.03 g) and stirred under laboratory conditions for 2.5 h. The orange solution of $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ (0.08 mmol) was obtained.

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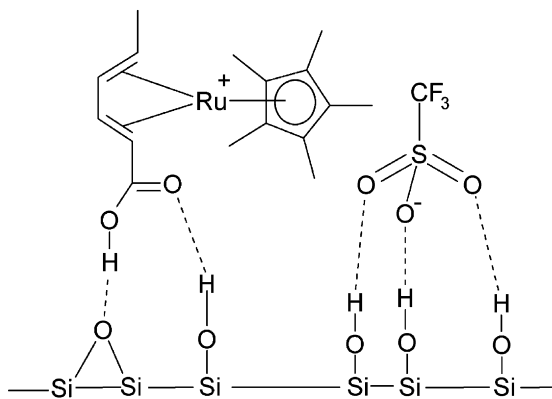


Fig. 1. Immobilization of $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ by means of hydrogen bonds.

2.2. $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3/\text{SiO}_2$ preparation

The silica (Aldrich, 200 m²/g) was at first dried at 300 °C in the air, then stirred with deionized water for 6–7 h and finally dried under N₂ at 250 °C for 24 h. This procedure was used for preparation of silica with the highest amount of silanol groups. The catalyst solution was filtered to the pretreated silica. The suspension was stirred for at least 1 h (usually for 3 h). The solution, which was initially orange, was decolorized and the silica took on the same color. The solvent was filtered off and the solid washed with ether. The solvent was analyzed by AAS in order to distinguish the amount of Ru on the support. After that the immobilized catalyst on silica was dried under vacuum for at least 12 h and stored under argon atmosphere until use. Typically, theoretical loadings of 2 wt.% of ruthenium were used.

2.3. Kinetic experiments

The hydrogenations were carried out in a glass reactor adapted for pressure measurement up to 0.35 MPa, equipped with a sampling probe; or in stainless steel autoclave equipped with glass insertion piece. The stirring was in both apparatus provided by magnetic stirrer.

3. Results and discussion

3.1. Characterization

Ru(II) is usually unstable and in this complex was even in 16e⁻ state, so the low stability of the catalyst was expectable. Complex was relatively stable in the air but very unstable in polar solvents (in nonpolar solvents was not soluble). The immobilization could be one of the ways how to stabilize the active complex.

At the first step of immobilization (Fig. 1), the appropriate support was chosen. The silica materials were tested for their ability to attach the complex by hydrogen bonds. The pretreated silica was chosen because of the low catalyst leaching and a

good availability. The support had no influence to the following hydrogenation. The time of immobilization was optimized in range of 1–18 h. In this range, the difference in leaching was almost negligible, however after 18 h the catalyst changed its color (was deactivated) because of the long contact with ether. The optimal amount of support was tested from leaching point of view. The optimal amount 20 mg of catalyst on 200 mg of silica was chosen because when the amount of the support was lower the leaching was much higher. With higher amount of the silica the leaching was almost the same. It was found that silica has adsorption capacity for sorbic acid (approximately 65 mg of acid on 100 g of silica, but the amount was dependent on a number of silanol and siloxane groups), and during the kinetic experiments, it was necessary to deal with higher amount of hydrogenated acid.

The infrared spectroscopic analysis of the prepared catalyst had shown decrease in the immobilized catalyst spectra of –O–H bond vibration (Fig. 2) and significant increase of band at around 1200 cm⁻¹. The first change could prove the immobilization of complex to the support by means of hydrogen bonds (some surface –O–H functions bonds are occupied by triflate groups) and the second showed the strong band of –C–F vibration in the triflate anion of the complex. In the physical mixture of the complex and the support, no decrease of –OH vibration was present and the vibration around 1200 cm⁻¹ was very significant.

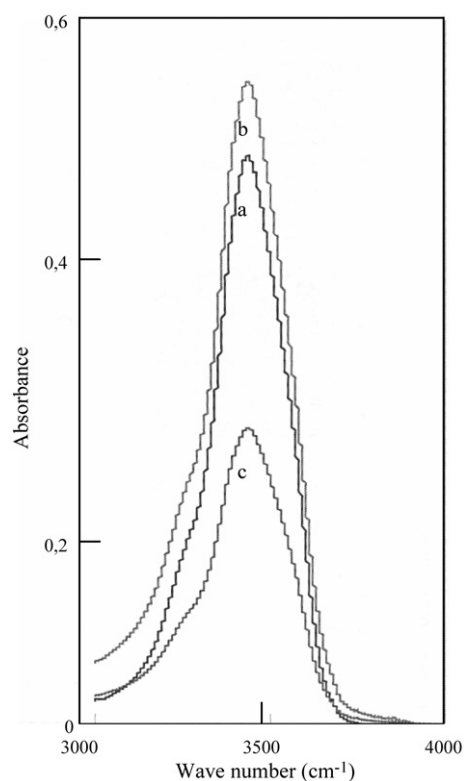


Fig. 2. IR spectra in the $\nu(\text{OH})$ region at room temperature: (a) activated silica; (b) physical mixture of $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3$ and activated silica; (c) $[\text{Cp}^*\text{Ru}(\text{sorbic acid})]\text{CF}_3\text{SO}_3/\text{SiO}_2$.

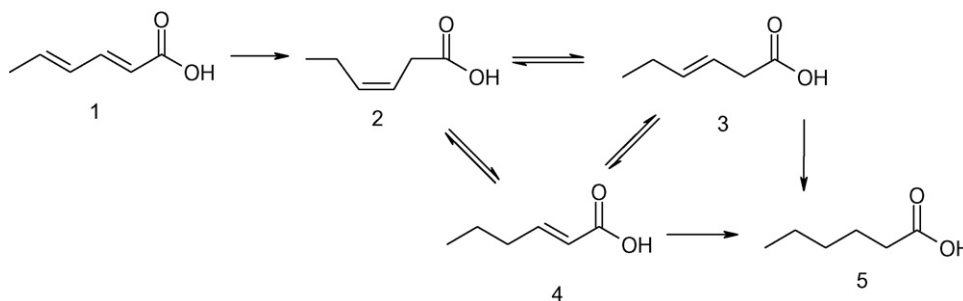


Fig. 3. Proposed mechanism of sorbic acid hydrogenation designed by calculation: (1) sorbic acid; (2) *cis*-hex-3-enoic acid; (3) *trans*-hex-3-enoic acid; (4) *trans*-hex-2-enoic acid; (5) hexanoic acid.

3.2. Sorbic acid hydrogenation using immobilized complex

The kinetic experiments using immobilized catalyst were carried out in order to find out the influence of reaction conditions on activity and selectivity and to compare the results with homogeneous and two-phase hydrogenation. The reactions were carried out in different solvents and it was necessary, not to exceed the saturated solution of sorbic acid in the solvent. The pressure influence of catalyst activity and selectivity on sorbic acid hydrogenation to *cis*-hex-3-enoic acid was measured in the range 0.35–5 MPa and the temperature influence in the range 35–85 °C. It was found that the pressure and the temperature have almost no influence to the selectivity and activity, expressed by TOF (turn over frequency), depended proportionally on these conditions. Only in the case of 5 MPa and temperature of 85 °C, the hydrogenation was very fast and the catalyst was deactivated during the reaction. The influence of the catalyst amount was measured in the range 5–20 wt.% of catalyst on the substrate amount, the selectivity was almost the same and the TOF values was also same. The same TOF, which is dependent on catalyst amount, means that the reaction rate is dependent on the catalyst amount proportionally. The solvent influence was also tested, as optimal the methyl-*tert*-butylether (MTBE) was chosen. Ethyl-*tert*-butylether (ETBE), diethylether (DEE), dibuthylether (DBE) and combination of MTBE and dibuthylether were tested. Lower activity and selectivity was found in all solvents, in the case of DBE and MTBE with DBE even in low concentrations the catalyst was totally deactivated. Selectivity in DEE was the lowest because of high degree of hexenoic acid polymerization and in other solvents was comparable with selectivity in MTBE. The leaching of the catalyst after reaction was about 0.5% approximately except in “drastic” conditions (5 MPa, 85 °C) where about 6% was observed.

The most interesting aspect was the recycling of the supported catalyst. The same catalyst was used in three hydrogenations and it was found, that the activity and selectivity significantly decreased. That could be caused by active catalyst sensitivity to solvents and its deactivation.

3.3. Comparison of homogeneous, two-phase and heterogeneous hydrogenation

Comparison of catalyst activity and selectivity in sorbic acid hydrogenation in homogeneous state, two-phase [14] (ethy-

Table 1

Comparison of homogeneous, two-phase and heterogeneous hydrogenation at optimal conditions (50 °C, 2 MPa, solvent MTBE)

	TOF (h ⁻¹)	Selectivity
Homogeneous	21.3	0.98
Two-phase (second cycle)	15.9 (8.5)	0.94 (0.61)
Heterogeneous (second cycle)	12.5 (9.4)	0.96 (0.68)

lene glycol—MTBE) and heterogenized state was carried out (Table 1). The reaction mechanism (Fig. 3) was the same in all these cases that can prove the hydrogenation by the same active species. The active complex catalyzed only hydrogenation of sorbic acid to *cis*-hex-3-enoic acid and in small range the following isomeration to the others hexenoic acid. Hydrogenations of monounsaturated acid to hexanoic acid were probably catalyzed by deactivated complex or metal Ru formed during reaction by reduction. The most active was the catalyst in the homogeneous phase, as was originally supposed. The difference between heterogeneous and two-phase hydrogenation was probably caused due to the attachment of sorbic acid to the support or due to the higher leaching of catalyst from glycol phase in two-phase hydrogenation. The highest influence of the conditions was found in two-phase hydrogenation, probably due to the solubility changes of catalyst depending on temperature and pressure. The selectivity was not affected by that type of hydrogenation. Using the immobilized catalyst no leaching was observed during the hydrogenation (the hydrogenation of sorbic acid by immobilized catalyst and there was no occurrence of homogeneous hydrogenation) and it is possible to remove almost all from the reaction mixture in opposite to the catalyst in two-phase arrangement.

The immobilized catalyst is more stable than the homogeneous catalyst prepared pure or in the solution and it is not necessary to prepare new catalyst before each reaction. The silica is very hygroscopic and the air humidity is “caught” by the support and the catalyst is not deactivated as quickly as in the case of pure catalyst and the deactivation by solvents is mentioned above.

4. Conclusion

The [Cp*₂Ru(sorbic acid)]CF₃SO₃ catalyst used for sorbic acid hydrogenation to *cis*-hex-3-enoic acid, was successfully

immobilized on silica material. The immobilization was carried out by means of hydrogen bonds on silanol groups of the support. The kinetic experiments for comparison with homogeneous and two-phase hydrogenation using the same catalyst were carried out. The immobilized catalyst demonstrated the same selectivity and the lower activity for desired hydrogenation, but was more stable against the air and humidity. The recycling of the catalyst was not successful, but the catalyst separation from reaction mixture was very simply carried, that is very important for further manipulation with the reaction mixture.

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