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Selective hydrogenations on heterogenized ruthenium complexes

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Abstract

The heterogenized versions of $[RuCl_2(PPh_3)_3]$ and $[\{RuCl_2(TPPMS)_2\}_2]$ were prepared and applied in the selective hydrogenation of α,β-unsaturated aldehydes. Depending on the conditions the above heterogenized catalysts could hydrogenate selectively either the C=O or the C=C bonds, similar to the results obtained in aqueous biphasic systems. Meanwhile the heterogenized catalysts show all the advantages that we can expect from a heterogeneous catalyst: good performance, easy separation, and the possibility of recycling. The effect of H_2 pressure on the selectivity was also studied.

Keywords: Chemoselectivity; Heterogenized catalyst; Hydrogenation; Ru complex; α,β-Unsaturated aldehydes

1. Introduction

During the last decade there has been a dramatic development within the field of selective catalysis for the production of fine chemicals. Among these processes, selective hydrogenations with soluble catalysts have become more and more important in the pharmaceutical industry, and consequently in catalytic research. Both the activity and the selectivity of these soluble complexes are excellent, but the difficulties of recovering and recycling limit the usefulness of these catalysts. Due to these limitations, an increased demand has developed toward the application of heterogeneous catalysts. The heterogeneous systems could be modified heterogeneous catalysts [1–3] or heterogenized homogeneous complexes [4]. The importance of the heterogenized homogeneous catalysts is shown by the large number of recent publications [5].

A new and highly efficient method for the heterogenization of homogeneous hydrogenation catalysts has recently been introduced by Augustine and co-workers [6]. The procedure involves the attachment of a preformed metal complex to a solid support using a heteropoly acid (HPA: phosphotungstic, phosphomolybdenic, or silicotungstic acids) as the anchoring agent. The heteropoly acids are attached to the support by the interaction of the protons of the acid with the basic sites of the support (alumina, carbon). Either ion pairing or direct bonds between surface oxygen atoms of the HPA and the metal center of the complex have been suggested to account for the immobilization of the metal complex onto the heteropoly acid. However, the true nature of this linkage is still unclear. Nevertheless, the resulting catalyst is at least as active as the homogeneous one, and in addition it has the advantages of a heterogeneous system [7,8].

The selective hydrogenation of α,β-unsaturated aldehydes has attracted much interest in homogeneous catalysis because of the synthetic value of the corresponding allylic alcohols [9]. It is also an industrially important process dealt with in several patents and papers such as the one from Degussa [10]. In that study the authors used the Ru complexes $[RuCl_2(TPPTS)_3]$ and $[H_2Ru(TPPTS)_3]$ (TPPTS,

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tris(3-sulfonatophenyl)phosphane trisodium salt) together with their supported aqueous-phase (SAPC) heterogenized analogs. It is believed that the immobilization of the SAPC catalysts (used mainly for the hydroformylation of long-chain alkenes [11]) is due to the strong interactions between the sulfonated phosphane ligands and the silanol groups of the silica support within a surface water film. 3-Methyl-2-butenal (prenal) was hydrogenated on these catalysts in hexane with 95% selectivity. When the hydrogenation was carried out in methanol, low activity and rapid deactivation were observed. Since a high percentage of the metal was recovered in the solution, it was suggested that the rapid deactivation was caused by the dissolution of the metal complex in the polar media. Even in the nonpolar media it was difficult to recycle the catalyst, because of the poisonous adsorption of organic compounds at the catalyst surface. Supported iridium–phosphane catalysts appeared more promising. These catalysts were chemoselective for several unsaturated aldehydes, including 3-methyl-2-butenal and all-*trans*-retinal, producing a suitable unsaturated alcohol and in the latter case they were stereoselective, too. Recovery was easy and it was possible to use the supported catalysts in polar reaction media. However, the activity of the heterogenized catalysts was one or two orders of magnitude less than that of the corresponding homogeneous catalyst. Although recycling could be achieved, the productivity of these heterogenized catalysts is still to be improved in order to make them reasonable alternatives to unsupported (soluble) homogeneous catalysts in the hydrogenation of α,β-unsaturated aldehydes. These difficulties point out the importance of the heterogenization of $[RuH_2(PPh_3)_4]$ and/or $[RuH_2(TPPTS)_4]$ on solid supports and the application of these heterogenized systems in the above-noted reaction.

Similar water-soluble Ru complexes, such as $[\{RuCl_2(TPPMS)_2\}_2]$ (TPPMS, (3-sulfonatophenyl)diphenylphosphane sodium salt). were applied in the hydrogenation of α,β-unsaturated aldehydes, and depending on the pH, various Ru–hydride complexes were established as active catalytic species [12]. At pH < 6 the $[HRuCl(TPPMS)_3]$ (**1a**) was the dominant Ru(II) complex and it catalyzed a slow but selective hydrogenation of the C=C bond in *trans*-cinnamaldehyde. Conversely, at pH > 8 the $[H_2Ru(TPPMS)_4]$ (**2a**) was found to be an active and selective catalyst for the C=O reduction. Consequently, changing the pH of the solution could shift the equilibrium between the two Ru species and invert the selectivity of the hydrogenation of *trans*-cinnamaldehyde.

Considering all of these former results and the environmental and economic aspects, heterogenization of the above-noted catalytic systems has become a challenge. In this paper we report our efforts to heterogenize onto a zeolite support the $[RuCl_2(PPh_3)_3]$ and $[\{RuCl_2(TPPMS)_2\}_2]$ complexes and to apply them in the hydrogenation of α,β-unsaturated aldehydes. NaY zeolite was chosen as a support, since our former experience in this field has shown that the three-dimensional zeolite is generally applicable for the heterogenization of soluble complexes [13], either by synthesizing the complex inside the zeolite or by anchoring it onto the surface [14].

2. Experimental and methods

2.1. Materials: preparation of the catalysts

$[RuCl_2(PPh_3)_3]$ was purchased from Aldrich and used as received. $[\{RuCl_2(TPPMS)_2\}_2]$ was prepared from TPPMS and $RuCl_3 \times 3H_2O$ as described in the literature [12].

The purity of the TPPMS ligand was checked by NMR spectroscopy, using a Bruker AVANCE DRX 500 MHz instrument. The NMR spectra showed that the sulfonated triphenylphosphane has one SO_3 group in position 3.

2.2. Anchoring the soluble complexes

The amount of 1.5 g of NaY zeolite (Aldrich) was suspended in 30 mL of 96% ethanol, and 288.0 mg (0.1 mmol) of phosphotungstic acid hydrate (PTA) was dissolved in 25 mL of ethanol. This solution was added dropwise into the zeolite suspension with efficient stirring. The stirring was continued for 2 days at room temperature, under an Ar atmosphere. The mixture was filtered and the solid residue was suspended in 30 mL of ethanol. Ninety-six milligrams (0.1 mmol) of $[RuCl_2(PPh_3)_3]$ was dissolved in 40 mL of deoxygenated ethanol and this solution was dropped slowly, with stirring to the suspension. The stirring was continued for another 2 days. The mixture was filtered and washed with ethanol, until a colorless solution was obtained. The light brown solid material (1.6 g) was dried at 30 °C for 2 h in vacuum and for 1 day under argon. A 1.45 g catalyst was obtained, with a Ru content of 36.3 µmol/g.

The heterogenized $[\{RuCl_2(TPPMS)_2\}_2]$ catalyst was prepared analogously using 1.5 g NaY zeolite and (0.1 mmol) PTA; 90.1 mg (0.1 mmol Ru) of $[\{RuCl_2(TPPMS)_2\}_2]$ complex was applied; and 1.5 g of the heterogenized catalyst was obtained with a Ru content of 2.0 µmol/g.

2.3. Catalyst characterization

FTIR spectra of the support, the Ru complexes, and the heterogenized samples were recorded on a Bio-Rad FTS–65 A spectrophotometer, in the range of 400–4000 cm^{-1}, in KBr pellets. XRD spectra were obtained on a Philips PW–1830 diffractometer. The metal content of the anchored catalysts was determined using a JOBIN YVON 24-type ICP-AES instrument; 250 mg catalyst samples were dissolved in 4 mL conc HNO_3.

2.4. Hydrogenation experiments

Trans-cinnamaldehyde and crotonaldehyde were hydrogenated in a batch reactor of 30 mL capacity, at 65 °C and 0.4 MPa hydrogen pressure. For the hydrogenation of the C=C bond, acidic conditions were applied: 10 mg (10.42 µmol) [$RuCl_2(PPh_3)_3$] or 300 mg (10.89 µmol Ru) [$RuCl_2(PPh_3)_3$]/NaY was added to 3 ml of 96% ethanol, followed by 3 µL (20 µmol) Et_3N and 7.8 mg (30 µmol) PPh_3. The catalyst precursors were prehydrogenated overnight. Then 50 µl of substrate (0.396 mmol *trans*-cinnamaldehyde or 0.603 mmol crotonaldehyde) was injected and the reactor was pressurized with H_2 and the reaction was initiated by starting the stirring. For the C=O reduction, we have adjusted a basic condition, with the same amount of Ru precursor and 13.5 mg (0.05 mmol) PPh_3 together with 6 µL (0.04 mmol) Et_3N. Samples were taken every hour from the reaction mixture, and the products were analyzed by capillary gas chromatography (Hewlett Packard 5890 Series II) using a DB-5 column at 145 °C. Reactions with the TPPMS-containing catalysts were done the same way using 12.3 mg (0.03 mmol) or 20.5 mg (0.05 mmol) TPPMS for the two different conditions.

2.5. Catalysts recycling

The heterogenized catalysts were used in several subsequent runs. After the reactions the catalyst was recovered by filtration under Ar, washed with ethanol, dried in Ar, and then reused.

3. Results and discussion

With the aim of developing active, chemoselective heterogeneous catalysts, we have prepared the anchored [$\{RuCl_2(TPPMS)_2\}_2$] and [$RuCl_2(PPh_3)_3$] catalysts, using the method developed by Augustine and co-workers [7]. In all cases phosphotungstic acid was used as anchoring material. The heterogenized complexes were characterized by spectroscopic methods and applied as catalysts in the hydrogenation of α,β-unsaturated aldehydes. To our knowledge this is the first example of heterogenization of these complexes by this relatively new method and applying them for catalysis of hydrogenation reactions.

3.1. Physical properties of the catalysts

The heterogenized catalysts were characterized with the usual spectroscopic methods. The FTIR spectra of the support (PTA/NaY), the [$\{RuCl_2(TPPMS)_2\}_2$] and the [$RuCl_2(PPh_3)_3$] complexes, and the heterogenized samples were all taken.

The comparison of these spectra (Fig. 1) shows convincingly that [$RuCl_2(PPh_3)_3$] is anchored on the NaY support. The spectrum of the heterogenized catalyst displays the bands at 1493, 1440, 1076 cm^{-1}, which are characteristic for the [$RuCl_2(PPh_3)_3$] complex.

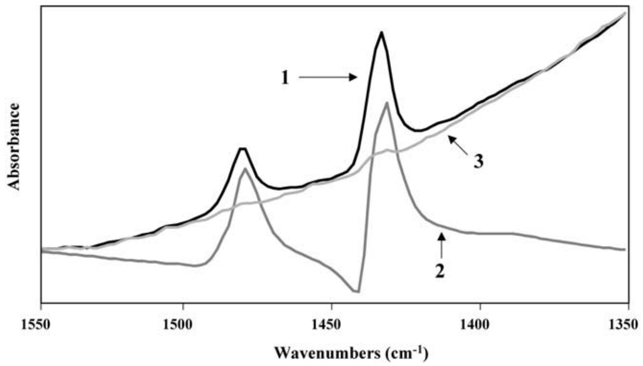


Fig. 1. The FTIR spectra of [$RuCl_2(PPh_3)_3$] and [$RuCl_2(PPh_3)_3$]/PTA/NaY: 1, [$RuCl_2(PPh_3)_3$]; 2, [$RuCl_2(PPh_3)_3$]/PTA/NaY; 3, PTA/NaY.

Similar spectra were obtained for [$\{RuCl_2(TPPMS)_2\}_2$] and its heterogenized analog. The comparison of the spectra leads to the same conclusion as that for [$RuCl_2(PPh_3)_3$].

The XRD spectra of the zeolite and the heterogenized samples were taken as well. The similarity of these spectra shows no change of the zeolite structure during the catalyst preparation.

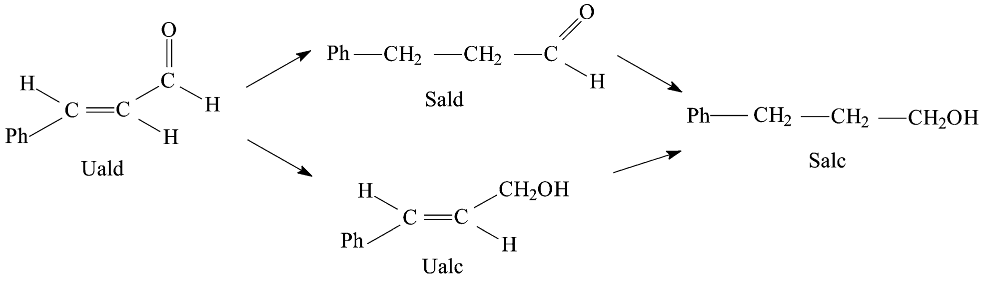
In order to determine the metal complex concentration of the heterogenized catalysts, samples were dissolved in conc HNO_3. The metal content of these solutions were determined by ICP-AES. The solid catalysts were found to contain 36.3 µmol/g and 2.0 µmol/g Ru in the case of the anchored [$RuCl_2(PPh_3)_3$] and [$\{RuCl_2(TPPMS)_2\}_2$], respectively. This is a fairly large difference in view of the same heterogenization procedure. It seems that the neutral [$RuCl_2(PPh_3)_3$] can be more easily incorporated to the PTA layers containing large polytungstate anions than the bulky [$\{RuCl_2(TPPMS)_2\}_2$] which carries negatively charged sulfonated ligands.

3.2. Catalytic properties of the catalysts

[$\{RuCl_2(TPPMS)_2\}_2$] is water soluble and in aqueous (biphasic) systems under H_2 a pH-dependent equilibrium exists between its monohydrido [$HRuCl(TPPMS)_3$] (**1a**) and dihydrido [$H_2Ru(TPPMS)_4$] (**2a**) derivatives. These two Ru–hydrides have different selectivities in the hydrogenation of α,β-unsaturated aldehydes. Namely, the monohydrido derivative hydrogenates the C=C double bond, while the dihydrido species is a selective catalyst for the hydrogenation of the C=O double bond [12]. Consequently, simply adjusting the pH of the aqueous phase can change the selectivity of the hydrogenation of *trans*-cinnamaldehyde.

3.3. Hydrogenation of *trans*-cinnamaldehyde

The purpose of this study was the synthesis of heterogenized ruthenium–phosphane catalysts having all the advantages of heterogeneous systems, i.e., easy handling and the possibility of recycling. The properties of the heterogenized catalysts, [$\{RuCl_2(TPPMS)_2\}_2$]/PTA/NaY and



Scheme 1. The hydrogenation reaction of *trans*-cinnamaldehyde. Abbreviations: Uald, unsaturated aldehyde (*trans*-3-phenylprop-2-enal); Sald, saturated aldehyde (3-phenylpropanal); Ualc, unsaturated alcohol (3-phenylprop-2-en-1-ol); Salc, saturated alcohol (3-phenylpropan-1-ol).

Table 1
The product distribution of the hydrogenation of *trans*-cinnamaldehyde on homogeneous and heterogenized Ru–phosphane catalysts under basic conditions

Catalyst	Time (h)	Conversion (%)	TOF	Product distribution (%)		
				Sald	Salc	Ualc
(**2a**)	1	22.1	8.5	11.5	0	88.5
	3	68.4		9.1	0	90.9
(**2a**)/NaY	1	5.8	38.3	12.1	0	87.9
	3	15.0		12.0	0	88.0
(**2b**)	1	30.7	11.7	7.0	10.5	82.5
	3	93.9		5.5	11.6	82.9
(**2b**)/NaY	1	32.7	11.9	4.7	10.4	84.9
	3	92.3		3.0	11.9	85.1

Experimental conditions: 0.4 MPa H_2, 65 °C, 0.05 mmol PPh_3 or TPPMS, 0.04 mmol Et_3N, 0.396 mmol substrate, 10.28 µmol (**2a**) or 0.6 µmol (**2a**/Na), 10.42 µmol (**2b**), 10.89 µmol (**2b**/NaY).

Table 2
The product distribution for three subsequent runs of the hydrogenation of *trans*-cinnamaldehyde on (**2b**)/NaY catalyst

Runs	Time (h)	Conversion (%)	Product distribution (%)		
			Sald	Salc	Ualc
1	1	32.7	4.7	10.4	84.9
2	1	27.8	3.1	11.7	85.2
3	1	25.7	2.1	12.0	85.9

$[RuCl_2(PPh_3)_3]$/PTA/NaY were investigated in the hydrogenation of *trans*-cinnamaldehyde. During this study we have examined the existence of the Ru–hydride complexes—(**1a**), (**2a**), as well as $[HRuCl(PPh_3)_3]$ (**1b**) and $[H_2Ru(PPh_3)_3]$ (**2b**)—on the support and their catalytic effect on the hydrogenation of *trans*-cinnamaldehyde.

3.3.1. Selective hydrogenation of C=O bonds

For the hydrogenation reaction we have applied two slightly different conditions, based on the results obtained under homogeneous conditions [12]. In our ethanolic solutions the basicity was adjusted by Et_3N. For the C=O reduction, basic conditions were applied (see Experimental). The catalyst mixture was prehydrogenated for sufficient time to ensure the formation of the catalytically active Ru–hydrides. The products of the reaction are shown on Scheme 1 (no other products were found during the hydrogenation reaction), and the results are collected in Table 1.

It is seen that the heterogenized catalysts—both the sulfonated and the nonsulfonated derivatives—were active in the hydrogenation of *trans*-cinnamaldehyde in alcoholic solution. Comparing the performance of the heterogenized and the homogeneous catalysts, we must use the TOF values, since the concentrations of Ru complexes are different for different catalysts. Considering these values the heterogenized catalysts have about the same or higher activity than the homogeneous analogs. The higher activity of (**2a**)/NaY is in a good agreement with our earlier findings [13,14], i.e., that the heterogenized catalysts showed about the same or higher reaction rate than the homogeneous counterparts, leading to higher specific activities than those of the homogeneous analogs. Indeed, in the present experiments, the sulfonated derivative had substantially higher specific activity than its homogeneous counterpart while with the PPh_3-containing derivatives no difference could be seen (Table 1). Although in the present case this behavior still awaits explanation; however, these observations are not without precedent [15].

Considering the selectivity in the above conditions all the catalysts have a fairly good selectivity for the C=O hydrogenation. In other words, the synthetically important product, the unsaturated alcohol, is formed in high yields. However, in addition to the C=O hydrogenation, all catalysts showed some activity in C=C hydrogenation, too.

As it was expected on the basis of the biphasic experiments, the consecutive reaction did not take place on the sulfonated catalysts, while on the other catalyst the complete hydrogenation has occurred, especially with higher conversions.

3.3.2. Catalyst recycling

The main advantage of using heterogenized catalysts is the possibility of recycling. We have used our $[RuCl_2(PPh_3)_3]$/NaY catalyst in several subsequent runs and the results were collected in Table 2.

As Table 2 shows, in the three subsequent runs, the performance of the catalyst has not changed significantly. A slight decrease in conversion was observed, due to the minor loss of catalyst from run to run. However, the selectivity is about the same in each subsequent run; as a matter of fact, a slight increase in selectivity was observed.

Table 3
The product distribution in the hydrogenation of *trans*-cinnamaldehyde on homogeneous and heterogenized Ru–phosphane catalysts under acidic conditions

Catalyst	Time (h)	Conversion (%)	TOF	Product distribution (%)		
				Sald	Salc	Ualc
(**1a**)	1	22.1	8.5	63.1	8.9	28.0
	3	54.5		62.2	9.5	28.3
(**1a**)/NaY	1	10.1	66.7	58.8	19.7	21.5
	3	30.6		58.5	19.8	21.7
(**1b**)	1	9.5	3.6	43.8	5.8	50.4
	3	25.5		41.6	6.7	51.8
(**1b**)/NaY	1	10.8	3.9	55.8	9.8	34.4
	3	32.7		53.9	10.4	35.7

(**1a**), [HRuCl(TPPMS)$_3$]; (**1b**), [HRuCl(PPh$_3$)$_3$]. Experimental conditions: 0.4 MPa H_2, 65 °C, 0.03 mmol PPh_3 or TPPMS, 0.02 mmol Et_3N, 0.396 mmol substrate, 10.28 µmol (**1a**) or 0.6 µmol (**1a**/NaY), 10.42 µmol (**1b**), 10.89 µmol (**1b**/NaY).

This set of experiments allows us to conclude that our heterogenized catalysts have the expected advantages, namely good performance—approximately the same activity and similar selectivity as that of the homogeneous counterparts—together with easy handling and efficient recycling.

3.3.3. Selective hydrogenation of C=C bonds

Under acidic conditions (see Experimental), the selective hydrogenation of C=C was expected. Table 3 shows the results obtained under these conditions.

Table 3 shows clearly that all of the catalysts were active in the hydrogenation reaction under this condition, too. Similar to the case of C=O hydrogenation, the specific activities on the heterogenized catalysts were about the same or higher than in the homogeneously catalyzed reactions. Both the sulfonated catalysts and the heterogenized nonsulfonated catalyst showed some selectivity in favor of the hydrogenation of C=C bond, with 3-phenylpropanal (the saturated aldehyde) as the major product. However, with (**1b**) the C=O hydrogenation remained predominant, even under acidic conditions.

3.3.4. The effect of hydrogen pressure on the selectivity

Under aqueous/organic biphasic conditions [12] the hydrogenation of *trans*-cinnamaldehyde catalyzed by water-soluble Ru(II)–phosphane complexes at pH 3.04 produced a 51:49 mixture of cinnamyl alcohol and 3-phenylpropanal at 1 bar H_2 pressure. However, with increasing H_2 pressure this ratio increased, too, and at 10 bar H_2 pressure it reached 93:7. This dramatic pressure effect on selectivity could be explained by the different pressure dependence of the rate of C=C hydrogenation, catalyzed by [RuHCl(TPPMS)$_3$] and that of C=O hydrogenation, catalyzed by [RuH$_2$(TPPMS)$_4$]. The increase in H_2 pressure changes the molecular distribution of Ru among its various hydride species. However, it is also possible that some other Ru complexes, e.g., [RuH(H$_2$)(TPPMS)$_4$]$^+$, can also take part in the hydrogenation reaction [20].

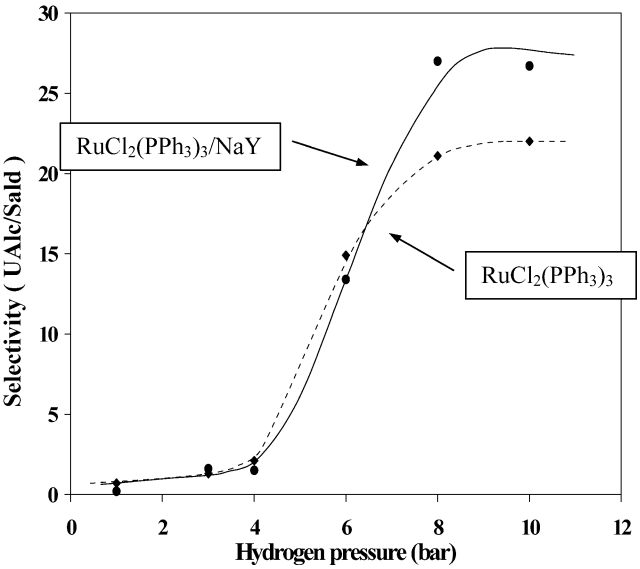


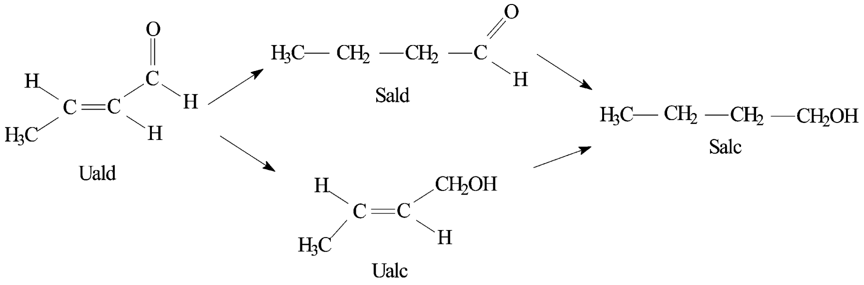
Fig. 2. The effect of H_2 pressure on the selectivity of the hydrogenation of *trans*-cinnamaldehyde catalyzed by (**1b**) and (**1b**)/NaY. Selectivity: unsaturated alcohol (Ualc)/saturated alcohol (Sald).

Under the conditions of Fig. 2 (ethanolic solution, acidic conditions) at 4 bar H_2 pressure, we have obtained a product ratio of cinnamyl alcohol:3-phenylpropanal = 36:54 in the hydrogenation of *trans*-cinnamaldehyde with the heterogenized catalyst (**1b**)/NaY. Based on the results obtained in aqueous biphasic systems, we have also studied the effect of H_2 pressure on the catalysts' selectivity, and—indeed—these measurements showed a remarkable pressure effect on the selectivity. For comparison, experiments were made under the same conditions with the soluble (**1b**) catalyst, too (Fig. 2).

It can be seen from the data of Fig. 2 that the increase in hydrogen pressure caused a substantial increase in the selectivity of both the soluble and the heterogenized catalysts toward the formation of the unsaturated alcohol product. This also implies, though does not prove unequivocally, that the same ruthenium–hydride complexes, [HRuCl(PPh$_3$)$_3$] and [H$_2$Ru(PPh$_3$)$_4$], act as catalytic species on the surface of the support, which are already known from solution phase hydrogenations of *trans*-cinnamaldehyde. As a result, the selectivity in this system can be affected not only by manipulating the basicity of the solution phase, but by varying the hydrogen pressure, as well. Consequently, the synthetically important unsaturated alcohol, 3-phenylprop-2-en-1-ol can be produced either by using basic conditions or under acidic conditions using a higher H_2 pressure.

3.4. Hydrogenation of crotonaldehyde

The hydrogenation of an unsaturated aliphatic aldehyde, crotonaldehyde, was also studied to examine the effect of the structure of the starting material. It was interesting to



Scheme 2. The hydrogenation of crotonaldehyde. Abbreviations: Uald, unsaturated aldehyde (*trans*-but-2-en-1-al); Sald, saturated aldehyde (butanal); Ualc, unsaturated alcohol (but-2-en-1-ol); Salc, saturated alcohol (butan-1-ol).

Table 4
The product distribution in the hydrogenation of crotonaldehyde under basic conditions with soluble and heterogenized Ru(II)–phosphane complexes

Catalyst	Time (h)	Conversion (%)	TOF	Product distribution (%)		
				Sald	Salc	Ualc
(**2a**)	1	64.0	37.5	0.6	3.6	95.8
	3	100		1.6	7.2	91.2
(**2a**)/NaY	1	12.0	120.6	6.9	10.6	82.5
	3	35.9		7.8	11.7	80.5
(**2b**)	1	13.8	8.0	10.6	1.8	87.6
	3	42.0		11.0	2.3	86.7
(**2b**)/NaY	1	28.5	15.8	2.0	7.4	90.6
	3	91.1		2.2	8.1	89.7

Experimental conditions: 0.4 MPa H_2, 65 °C, 0.05 mmol PPh_3 or TPPMS, 0.04 mmol Et_3N, 0.603 mmol substrate, 10.28 µmol (**2a**) or 0.6 µmol (**2a**/NaY), 10.42 µmol (**2b**), 10.89 µmol (**2b**/NaY).

Table 5
Product distribution in the hydrogenation of crotonaldehyde under acidic conditions with soluble and heterogenized Ru(II)–phosphane catalysts

Catalyst	Time (h)	Conversion (%)	TOF	Product distribution (%)		
				Sald	Salc	Ualc
(**1a**)	1	14.9	8.7	90.5	8.5	1.0
	3	50.8		90.0	9.0	1.0
(**1a**)/NaY	1	14.8	148.7	86.5	9.5	4.0
	3	49.8		84.2	11.2	4.6
(**1b**)	1	11.0	6.4	81.0	9.0	10.0
	3	42.4		78.2	10.3	11.5
(**1b**)/NaY	1	12.0	6.6	63.0	11.4	25.6
	3	43.4		60.0	12.5	27.5

Experimental conditions: 0.4 MPa H_2, 65 °C, 0.03 mmol PPh_3 or TPPMS, 0.02 mmol Et_3N, 0.603 mmol substrate, 10.28 µmol (**1a**) or 0.6 µmol (**1a**/NaY), 10.42 µmol (**1b**), 10.89 µmol (**1b**/NaY).

see whether the same phenomena can be observed as in the hydrogenation of *trans*-cinnamaldehyde.

For a better comparison we have used the same experimental protocol for this substrate as in the case of *trans*-cinnamaldehyde. Table 4 shows the product distribution of the hydrogenation of crotonaldehyde under basic conditions.

As seen in Table 4 both the soluble, (**2a**) and (**2b**), and the heterogenized (**2a**)/NaY and (**2b**)/NaY catalysts were active in the hydrogenation of crotonaldehyde. Generally the activities were somewhat higher than they were in the case of *trans*-cinnamaldehyde. In this system both of the heterogenized catalysts—(**2a**)/NaY, (**2b**)/NaY—had higher TOF than the homogeneous catalysts. The product distribution is about the same as that of the homogeneously catalyzed reactions. On the (**2b**)/NaY catalyst not only the activity was higher but also the selectivity.

The heterogenized catalyst (**2b**)/NaY was used in three subsequent runs and we had similar observations as in the case of trans-cinnamaldehyde. In these recycling experiments the heterogenized catalyst did not loose its activity to a significant extent and the product distributions were very similar from run to run. In other words the selectivity did not change considerably; as a matter of fact, it increased slightly in favor of the formation of the unsaturated alcohol. Considering the conversion, we have observed a similar trend as in the case of *trans*-cinnamaldehyde, which can be caused by some loss of catalyst.

We have also tested the hydrogenation of crotonaldehyde under acidic conditions. The results are shown in Table 5.

As shown by the data in Table 5, the C=C selectivity is much better than in the case of *trans*-cinnamaldehyde under the same conditions. In the hydrogenation of crotonaldehyde the saturated aldehyde is the major product on all catalysts, under the acidic conditions. The selective C=C bond hydrogenation is definitely pronounced on the sulfonated catalysts, where all the other products amount to less than 20%. This is in contrast to the selectivity of the same catalyst under basic conditions where the C=O hydrogenation is dominant. The results obtained with the two different starting materials show the generality of the selectivity change, which becomes even more pronounced with crotonaldehyde. It is noted here, that in the hydrogenation of *trans*-cinnamaldehyde, the C=O hydrogenation remains predominant even under acidic condition.

Once again, it can be concluded, that these heterogenized Ru–phosphane catalysts deliver all the expected advantages: good performance, easy separation, and the possibility of efficient recycling.

3.5. General remarks on the hydrogenation of α,β-unsaturated aldehydes with Ru–triphenylphosphane catalysts anchored on NaY zeolite

Selective hydrogenation of α,β-unsaturated aldehydes is an industrially important process. In the case of aldehydes with short carbon chains (e.g., 3-methyl-2-butenal) the catalyst recycling problem, which is a main drawback of homogeneous catalysis, has been overcome by the use of a biphasic process in which the reactants are in the organic phase and the water-soluble catalyst, $[RuCl_2(TPPTS)_3]$, is found in the aqueous phase. However, in the case of aldehydes with long carbon chains the use of liquid–liquid biphasic systems leads to poor results, probably caused by the low solubility of the reactant in the aqueous phase.

In our study we have prepared the heterogenized analogs of $[RuCl_2(PPh_3)_3]$ and $[\{RuCl_2(TPPMS)_2\}_2]$. In the hydrogenation of *trans*-cinnamaldehyde and crotonaldehyde these catalysts showed good activity and selectivity (both comparable to the homogeneous catalysts), easy separation, and the possibility for recycling with no appreciable loss of performance. In some instances, the heterogenized catalysts had higher activity and selectivity than the homogeneous counterparts (e.g., (**2b**)/NaY for both aldehydes and (**1b**)/NaY for *trans*-cinnamaldehyde). This latter finding is in accord with our earlier observations [13,14].

In the literature there are various experimental results and theories concerning the relation of the activity of a catalyst in its dissolved and heterogenized state [16]. Immobilization generates catalysts that are generally more complex than their homogeneous analogs. It is therefore not surprising that, in practice, the effect of immobilization is still very unpredictable. Unfortunately, most heterogenized homogeneous catalysts are less active, than in homogeneous solutions and/or loose part of their activity upon recycling [17]. However, in some cases the activities and the chemo- and enantioselectivities of the heterogenized systems were found superior to those of the corresponding homogeneous catalysts [18]. Thomas et al. [19] suggest that in some cases the improved performance of a heterogeneous catalyst can be explained by the "confinement concept," according to which the substrate's favorable interaction with both the pore wall and the catalyst molecule is the key point. Conversely, lower activities can be due to the reduced or even blocked mass transport in the small pores, imposing limits to the effective range of the substrates that can be utilized [16]. "Site isolation," i.e., attaching a catalyst to a support in a way that the catalytic sites can no longer interact with each other, is another concept that might explain the better performance of heterogenized catalysts [18b]. In this case, effective functional site isolation, and thus the formation and protection of highly active catalytic species, was strongly dependent on the tight attachment of the ligand to the support, the low surface concentration of the ligands, and the chemical nature of the catalyst precursor.

The fact that the heterogenized samples were active under both basic and acidic conditions shows that both of the two different Ru–hydride complexes were able to form during the prehydrogenation. The red, monohydrido derivative catalyzes a slow C=C hydrogenation, while the yellow dihydrido complex selectively hydrogenates the C=O bond; this latter reaction is much faster with the heterogenized catalysts than with the homogeneous analogs.

The observed similarities in the selectivity of the homogeneous and the heterogenized samples suggest that the mechanism of hydrogenation is also similar [20].

4. Conclusions

We have prepared the heterogenized $[\{RuCl_2(TPPMS)_2\}_2]$ and $[RuCl_2(PPh_3)_3]$ catalysts, using a heteropoly acid (phosphotungstic acid) as an anchoring medium. To our knowledge this is the first example of preparing these catalyst via this heterogenization method. These catalysts were applied successfully in the hydrogenation of *trans*-cinnamaldehyde and crotonaldehyde. In general, there was no substantial difference in the performance of the homogeneous and the heterogenized catalysts in the hydrogenation of these two substrates. In particular, the heterogenized catalysts showed about the same activity as their homogeneous counterparts and at the same time their selectivity toward the formation of the unsaturated alcohol product was found approximately twice as high as the selectivity of the corresponding homogeneous catalysts. In addition, it was possible to use these heterogenized catalysts in three subsequent runs, without any significant loss of activity, and even with a slight increase in selectivity.

The hydrogen pressure had a dramatic effect on the selectivity of the hydrogenation of *trans*-cinnamaldehyde with both the soluble and the heterogenized catalysts. Under acidic conditions, with increasing H_2 pressure the C=O selectivity was increased significantly. Presently, this pressure effect is not completely clear and further studies are in progress in our laboratories in order to establish its mechanistic background.

At this stage of the study no data exist on solvent effects in this reaction. Nevertheless, we expect that our heterogenized complexes work in aqueous solutions, too. This could extend the use of these Ru–phosphane catalysts, considering that only $[\{RuCl_2(TPPMS)_2\}_2]$ is soluble in water. The basic finding, though, is that the method of heteropoly acid-mediated anchoring of soluble complexes onto heterogeneous supports, introduced by Augustine et al. [6,7], is indeed a viable method for the preparation of heterogenized homogeneous catalysts with no noticeable alteration of the chemistry and the catalytic performance of the homogeneous catalysts. Therefore—despite the lack of complete understanding of the molecular mechanism of the catalyst–support interaction—the use of heteropoly acids can be expected to yield further active and stable heterogenized homogeneous (solid) catalysts.

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