Res Chem Intermed (2010) 36:511–522
DOI 10.1007/s11164-010-0162-1

Terminal C$\equiv$C triple bond hydrogenation using immobilized Wilkinson's catalyst

Eliška Leitmannová · Petr Jirásek · Jakub Rak ·
Lucie Potucká · Petr Kačer · Libor Červený

Received: 23 March 2010 / Accepted: 27 May 2010 / Published online: 7 September 2010

Abstract In this work, we try to hydrogenate selectively phenylacetylene to styrene and 3-phenylpropyne to allylbenzene using immobilized or pure Wilkinson's catalyst. The catalyst was immobilized using two approaches—immobilization using ionic exchange and immobilization using covalent bonding. In the first case, the smectite minerals (hectorite and montmorillonite) were used as the supports. In the second case, MCM-41 and SBA-15 were used as the supports. Both types of immobilization were successful and the solid products were characterized. For the covalent bond formation, it was necessary to first modify the surface of the silica material. The modification was carried out using two substances, one adding an amino group to the silica material, and the second adding a phenyl group to the material. The selectivity of hydrogenation of both substances was higher using heterogeneous catalyst in the case of phenylacetylene. In the case of phenylpropyne, no difference in selectivity using Wilkinson's catalyst in homogeneous or heterogeneous arrangement was observed. The type of immobilization has no influence on either activity or selectivity of catalyst.

Keywords Hydrogenation · Immobilization · Phenylacetylene · Wilkinson's catalyst

---

E. Leitmannová · P. Jirásek · L. Potucká · P. Kačer · L. Červený (✉)
Faculty of Chemical Technology, Department of Organic Technology, Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague 6, Czech Republic
e-mail: libor.cerveny@vscht.cz

J. Rak
Faculty of Chemical Engineering, Department of Analytical Chemistry, Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague, Czech Republic

Introduction

Partial hydrogenation of a triple bond to a double bond is a very important synthetic reaction with high utilization both in the laboratory and on the industrial scale. In spite of the existence of a large number of systems with high selectivity to double bond formation (Lindlar catalyst, palladium supported catalysts) there is still a large field for exploring new accesses and catalytic systems using new methods in catalysis.

Rhodium complexes represent a promising class of robust hydrogenation catalysts since, in addition to high catalytic activity, they also show high stability in air as well as high tolerance to the reaction medium and functional groups of reactants [1, 2]. Besides hydrogenation, a particular Rh complex can usually catalyze a few types of other reactions such as hydrocarbonylation, isomerization, hydrosilylation and silylation [1–6], Kharash addition [7], methanation of carbon oxides [8], transformations of diazo compounds [9], and various kinds of polymerizations [2, 10–12]. Therefore, they can be used for the activation of various organic compounds towards a variety of chemical transformations under mild conditions (room or slightly elevated temperature, in solvents from water to hydrocarbons, and in the presence of air), which compensates for the high cost of these catalysts.

The most famous Rh complex is Wilkinson's catalyst ($RhCl(PPh_3)_3$) that is utilized [3, 13–15] in the industrial hydrocarbonylation of olefins and is also known as an effective catalyst of the hydrogenation of unsaturated compounds including the hydrogenation of the $C{\equiv}C$ triple bond to the double bond.

The Wilkinson's catalyst was prepared in situ and used for selective hydrogenation of octynes to octenes and decynes to decenes [14]. As supports, smectites clays were used [16–18] (hectorite and montmorillonite) for immobilization using ionic exchange. Because the silica materials do not have the optimal group for ligand exchange that is the basis for covalent bond formation, it is necessary to add some "spacers" to the material. As a spacer, two different species can be used—aminopropyltriethoxysilane [19], this has the amino group for ligand exchange, and diphenylphosphinoethyltriethoxysilane [20–23], which has the phenyl group for ligand exchange.

In this work, the activity and selectivity of the Wilkinson's catalyst in pure and immobilized forms for the hydrogenation of phenylacetylene to styrene and phenylpropyne to allylbenzene were tested.

Experimental

Materials

Wilkinson's catalyst (pure), phenylacetylene (98%), phenylpropyne (97%) and montmorillonite-K10 were purchased from Aldrich. Aminopropyltriethoxysilane (97%), diphenylphosphinoethyltriethoxysilane (97 %) and hectorite were purchased from ABCR. Hexane, methanol, chloroform and diethylether were purchased from Penta. Materials for immobilization, i.e. MCM-41 and SBA-15, were kindly supplied by J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences, Czech Republic. Hexane, methanol and diethylether were distilled from sodium under argon atmosphere; all other chemicals were used as obtained.

Preparation of heterogeneous catalysts

Catalyst anchored on smectite minerals

Smectite minerals are ionic clays with negative charge on the layers and positive charge in the interlayers carried by alkali metal cations (sodium, potasium etc.). The cationic part of the Wilkinson's can be exchanged with these alkali metals. The mineral (200 mg) was first dried under a nitrogen atmosphere at 300 °C for 6 h and after cooling inserted into a Schlenk vessel under an argon atmosphere. Then, a solution (20 mg in 20 mL) of $[Rh(PPh_3)_3Cl]$ in solvent (methanol, diethylether, hexane) was added with vigorous stirring. After 24 h of stirring, the catalyst was formed. Rh-hectorite or Rh-MTM-K10 was isolated by decantation washed four times with an appropriate solvent and dried under vacuum (4 h).

Catalyst anchored on mesoporous molecular sieve

Because Wilkinson's catalyst only partly and weakly anchors on all-siliceous molecular sieves, the sieve was first modified by reaction with 3-aminopropyltriethoxysilane, $NH_2(CH_2)_3Si(OEt)_3$, or 2-diphenylphosphinoethyltriethoxysilane $PPh_2(CH_2)_2Si(OEt)_3$ to introduce anchoring amino or phosphino groups, respectively, into MCM-41 pores using the procedure described earlier [24–26]. The sieve (1,000 mg) was first dried under a nitrogen atmosphere at 300 °C for 6 h and after cooling was suspended in CH_2Cl_2 (5 mL) in a Schlenk vessel under Ar atmosphere. Then, a solution of $NH_2(CH_2)_3Si(OMe)_3$ (6.0 mmol) or $PPh_2(CH_2)_2Si(OEt)_3$ (6.0 mmol) in $CHCl_3$ (15 mL) was added and the suspension was kept under vigorous stirring at room temperature for 24 h. The white solid obtained, denoted as $MCM\sim NH_2$ or $MCM\sim PPh_2$ or $SBA\sim NH_2$ or $SBA\sim PPh_2$, was separated by decantation, washed four times with 15 mL of $CHCl_3$ and dried under vacuum (4 h).

Anchoring of $[Rh(PPh_3)_3Cl]$ complex was achieved by its direct immobilization on the modified molecular sieve. $MCM\sim NH_2$, $MCM\sim PPh_2$, $SBA\sim NH_2$ or $SBA\sim PPh_2$ (200 mg) was inserted into the Schlenk vessel and an orange solution of $[Rh(PPh_3)_3Cl]$ (20 mg) in $CHCl_3$ (20 mL) was added under vigorous stirring. The sieves turned pale orange while the $CHCl_3$ phase became colorless. After 24 h of stirring, a catalyst formed, $Rh/MCM\sim NH_2$, $Rh/MCM\sim PPh_2$, $Rh/SBA\sim NH_2$ or $Rh/SBA\sim PPh_2$ was isolated by decantation, washed four times with 15 mL $CHCl_3$ and dried under vacuum (4 h).

Hydrogenation experiments

Hydrogenations were carried out in a stainless steel autoclave Parr. Typical reaction conditions were 2 MPa, laboratory temperature and 2.5% of catalyst calculated on active complex. The samples were analyzed on GC Varian 3800 with FID on column VA-1. Nonane was used as internal standard.

Techniques

GC

Varian 3800 instrument was used for GC analysis with FID detector and VA-1 column (60 m, 0.25 mm, 0.25 μm). Nitrogen was used as the carrier gas.

UV/VIS

For the detection of complexes in solvent after immobilization and after the hydrogenation experiments, PE Systems Lambda 35 UV/VIS instrumentation was used. Detection of released amount of catalyst (during immobilization experiments as the same as after hydrogenation experiments) was performed at wavelength 265 nm. Shape of spectrum of Rh specie is visible in Fig. 1.

AAS

For the detection of Rh in solvent after the hydrogenation experiments, a Varian Spectra AA880 instrument was used.

XRD

X-ray powder diffraction data were collected at room temperature with an X'Pert PRO θ–θ powder diffractometer with parafocusing Bragg–Brentano geometry using CuK_α radiation (λ = 1.5418 Å, U = 40 kV, I = 30 mA). Data were scanned with an ultrafast detector X'Celerator (or with a scintilator detector equipped with a secondary curved monochromator) over the angular range 5–60° (2θ) with a step size of 0.02° (2θ) and a counting time of 0.3 s $step^{-1}$. Data evaluation was performed in the software package HighScore Plus.

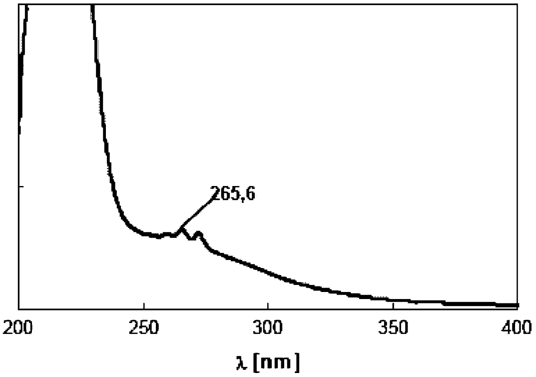

Fig. 1 UV/Vis spectra of Wilkinson's catalyst

Table 1 Characteristics of parent and modified mesoporous molecular sieves used as catalysts support

Sieves	S_{BET} ($m^2\ g^{-1}$)	V_{me} ($cm^3\ g^{-1}$)	D_{me} (nm)
MCM-41	1,140	0.86	3.5
MCM$\sim$NH$_2$	807	0.53	3.0
MCM$\sim$PH$_2$	769	0.44	2.9
SBA-15	720	0.88	7.7
SBA$\sim$NH$_2$	403	0.60	7.0
SBA$\sim$PH$_2$	385	0.48	6.9

S_{BET} BET surface area, V_{me} mesopore volume, D_{me} mean mesopore diameter

Adsorption isotherm of nitrogen

Adsorption isotherm of nitrogen at 77.35 K was measured using Micromeritics ASAP 2010 instrument. Data collected from measurement of supports and modified supports are given at Table 1.

MAS-NMR

Data were collected using Varian Mercury Plus 300 instrument equipped with CP/MAS probe with 5-mm rotors. The ^{31}P spectra were performed at frequency 121.44 MHz.

Results and discussion

The Wilkinson's catalyst was immobilized using two methods—by covalent bonding on a silica mesoporous molecular sieve, and on smectite clay minerals by ionic bonding.

Immobilization using ionic exchange

At first, the dependence of immobilized amount on time was tested. In the literature [14, 16–18], times between 4 and 30 h were used. The Wilkinson's catalyst was immobilized on hectorite using hexane as the solvent, and each hour a sample of the mother liquor was tested using UV to determine the amount of immobilized complex. After 4 h, 96% of the complex was immobilized (only 4% was eluted in the mother liquor), after 5 h, 98% of the complex was immobilized. After 24 h, the amount of the immobilized complex remained the same (98%) indicating that equilibrium of the reaction had been reached. The optimal time for immobilization was 5 h and 19 mg of complex was attached to 200 mg of the hectorite support.

The most important property of the smectite clay minerals is their ability to expand over their monomolecular intercalant dimension. The limit of the interlayer swelling depends on the swelling solvent, exchangeable cation, interlayer charge and the location of the charge. For inorganic systems, water is often used as the solvent, and methanol, ethanol, propan-2-ol and dichloromethane are used for organic systems. In our case, methanol was chosen as the swelling solvent, hexane as a non-polar solvent, and in addition the hydrogenations take place in hexane, and diethylether as the last solvent. Depending on the solvent and minerals (hectorite and montmorillonite K10) used, the amount of immobilized Rh complex was compared.

In chosen minerals, the following exchangeable hydrated cations were detected: Na—interlayer distance 9.9 Å; K—interlayer distance 14 Å; and Ca—interlayer distance 27 Å.

The ionic exchange itself takes place in the movement of the cationic part of the complex to the interlayers, forming the immobilized complex while the anionic counter ion forms a salt with former interlayer cation; in this case, NaCl, KCl or $CaCl_2$ are formed.

The amount of immobilized complex can be detected by several methods. The change in interlayer distance can be detected using XRD [16–18], but the complex must be larger than the hydrated ions and the complex must be inserted into the layers and not simply attached to the mineral surface by nonbonding interactions. The amount of complex on the support can also be quantified using AAS. The amount of metals in the mother liquor after immobilization can also be determined, but there are several limitations in detection of Rh metals from complex substances. The amount of released alkali metals can also be determined, but usually large amounts of alkali metals are presented in the available solvents. Another method to determine the quantity of immobilized complex is the use of UV/VIS spectrophotometry. The amount of the complex in the mother liquor after immobilization is determined in these cases. UV detection, XRD and AAS were used to quantify the amount of metal released.

Solvent effect was examined using both the supports and three solvents described above. From the amount of the Rh complex present in the solvent, the amount of the catalyst immobilized was calculated and is shown in Table 2.

XRD analysis was carried out to determine the real interlayer distance after immobilization. There was only weak intensity peak corresponding to the interlayer distance of the immobilized complex or its crystal structure. Using only hectorite in methanol as a solvent, the structure of Wilkinson's catalyst and the shift of interlayer peak were visible (Fig. 2).

In other solvents, the interlayer distance decreased from 14 Å (hydrated potassium ions) to 9 Å (hydrated sodium ions), this could be explained by the high level of sodium cations in the solvents. We have obtained only a little information about the amount immobilized using XRD, probably due to the attachment of the Wilkinson's catalyst to the surface of the support. The amount of alkali metal in the mother liquor was determined using AAS. It was found that the exchanged amount of alkali metals (Na and K) was distinctively higher using hectorite as a support than in the case of montmorillonite. Use of methanol as the solvent offered the best possibility for ionic exchange as predicted. The results obtained using the detection of released ions (AAS detection, Table 3) were the opposite of the results obtained by detection of immobilized catalyst amount (UV/VIS, Table 2, and AAS detection).

The opposite results can be explained by the ionic exchange taking place in methanol, and in the other solvents, the complex is more attached to the surface. In

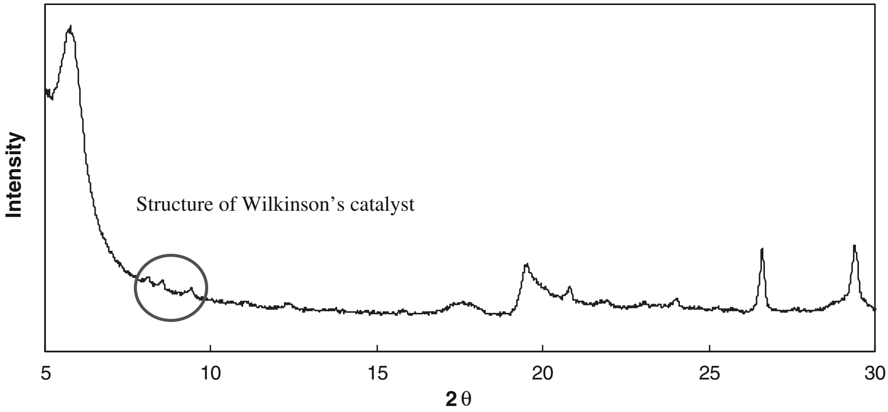

Fig. 2 XRD pattern of immobilized Wilkinson's catalyst on hectorite using methanol as a solvent

Table 2 Immobilized amount of catalyst (%) with respect to supports and solvents used, quantified by UV/VIS spectrometry

Solvent	Support[a]	
	Hectorite	MTM-K10
Methanol	91	90
Diethylether	99	98
Hexane	99	98

[a] 100% of immobilized catalyst = 20 mg/200 mg of the support

spite of this, these interactions are strong enough to hold the complex onto the support under the hydrogenation conditions (see later). Immobilization of the Wilkinson's catalyst was confirmed by ^{13}P MAS-NMR (pure Wilkinson catalyst, see [20]; in the case of immobilized complex, the signals overlap more, but the structure of complex is still visible [17]).

From the results, it is obvious that hectorite is the optimal support for the immobilization of Wilkinson's catalyst with 19 mg of the catalyst immobilized on 200 mg of the support.

Immobilization using covalent bonding

As mentioned above a direct bond between the silica material and Wilkinson's catalyst does not exist. It is necessary to modify the surface of the support using a molecule that can form a covalent bond with the chosen catalyst. Two commonly used silanes, aminopropyltriethoxysilane and diphenylphosphinotriethoxysilane, were chosen as "spacers." These substances have ligands that are able to exchange with triphenylphosphine ligands of Wilkinson's catalyst. Two different supports were chosen: SBA-15 and MCM-41.

Table 3 Amount (%) of released ions (K or Na) from mother liquor after immobilization (calculated from AAS)

Solvent	Support	
	Hectorite	MTM-K10
Methanol	65	46
Diethylether	40	30
Hexane	42	33

The complex was immobilized using the procedure described in the experimental section. The amount of complex immobilized was strongly dependent on the type of spacer used (see Table 4).

The total quantity of the immobilized complex was 19 mg on 200 mg of the support $\sim$PPh$_2$ and 15 mg of the complex on 200 mg of the support $\sim$NH$_2$. Immobilization of the Wilkinson's catalyst by the ligand exchange using MCM$\sim$PPh$_2$ as the support was confirmed by ^{13}P MAS-NMR (see [20]). In contrast to this study, we have found a different intensity of the signals at 25 and 39 ppm; this is solely due to the difference in the immobilization, as the author used two spacers and we only used one. So the shift at 25 corresponds to the attached phosphino group and at 39 to the free group. In any case, the oxidized form of spacer was not confirmed (EA and MAS-NMR [21]).

As shown in Table 4, the amount of the complex immobilized depended only on the type of the spacer employed. Using $\sim$NH$_2$ as the spacer, the immobilized amount was around 75% irrespective of the support [SBA (larger pores) or MCM (smaller pores)]. Using $\sim$PPh$_2$ as a spacer, the amount of catalyst immobilized was significantly higher, about 97% in both cases—using SBA as well as MCM. The higher immobilized amount using the $\sim$PPh$_2$ spacer can be explained by a higher affinity of PPh$_2$ groups to the Rh center of the complex [the PPh$_3$ group of the complex is exchanged with $PPh_2(CH_2)_2Si$– group, the type of the groups is similar]. In contrast, using the $\sim$NH$_2$ spacer, the affinity of Rh center is lower [PPh$_3$ group of the complex is exchanged with $NH_2(CH_2)_3Si$– group, the type of the group is different].

XRD was used for characterization of prepared material. The shift of the typical band of MCM to higher degrees (lower pore size) is visible. The lower intensities of the bands indicate that the rearrangement of the material caused some of the material to become amorphous (Fig. 3).

The dependence of the immobilization using covalent bonding on time was tested. We adopted the same procedure as was used for the immobilization using ionic exchange. Surprisingly, after the first hour of the immobilization, the maximum immobilized amount was achieved, i.e. 75% in the case of Rh/support $\sim$NH$_2$ and 96% in the case of the other Rh/support, $\sim$PPh$_2$. The anchored amount was unchanged 24 h after immobilization, indicating that 1 h is sufficient time for immobilization using covalent bonding.

A molecular sieve (MCM-41 or SBA-15) with $\sim$PPh$_2$ as a spacer for treatment of the surface is optimal for immobilization using covalent bonding.

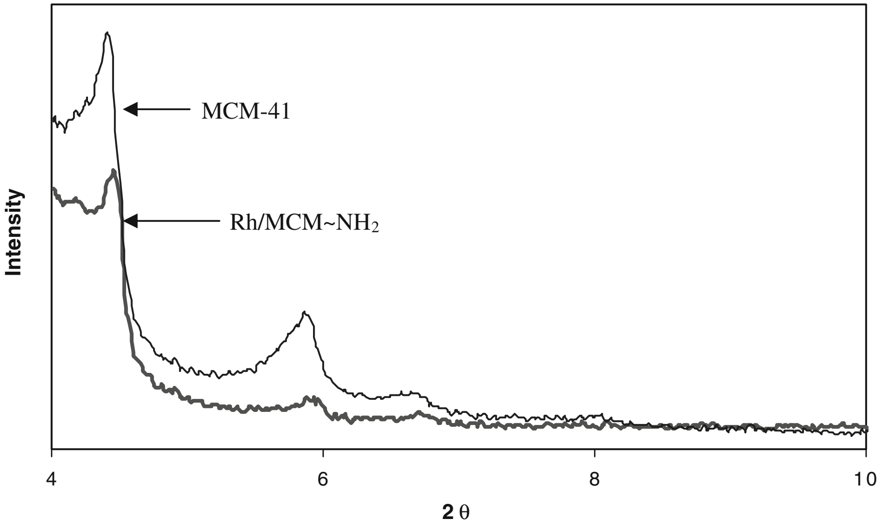

Fig. 3 Representative XRD patterns of immobilized Wilkinson's catalyst using covalent bond

Hydrogenation experiments

Phenylacetylene and 3-phenylprop-1-yne hydrogenation were chosen as model reactions for activity and selectivity tests of the prepared immobilized catalysts. The concentration courses are shown in Figs. 4 and 5. In both cases, the unsaturated compound (styrene or allylbenzene, respectively) is the desired product but is converted to the saturated one (ethylbenzene or propylbenzene). The hydrogenation of phenylacetylene is more selective and faster.

The catalysts prepared by immobilization on the different supports were tested for selective hydrogenation of these two substances and the results were compared with those obtained using the Wilkinson's catalyst in a homogeneous arrangement.

From Table 5, it can be seen that either reaction rates (TOF) or selectivities are very similar to the measurement error is up to 5%. It is probable that the catalytic species still has the structure of Wilkinson's catalyst and no changes occur in the structure of cationic part during the immobilization process either by ionic exchange or by ligand exchange.

When comparing the immobilized catalyst with the catalyst in the homogeneous hydrogenation, surprising results were found. The reaction rate in the heterogeneous conditions was lower, as was expected, but the selectivity in the homogeneous arrangement was over 10% lower than in the heterogeneous one.

The reaction rate in the case of homogeneous hydrogenation of phenylpropyne was 341 h^{-1} with a selectivity of up to 60%. Using immobilized catalyst ($Rh/MCM{\sim}PPh_2$ was chosen as an example), the reaction rate decreased as was expected and the selectivity to allylbenzene remained the same (approximately 60%).

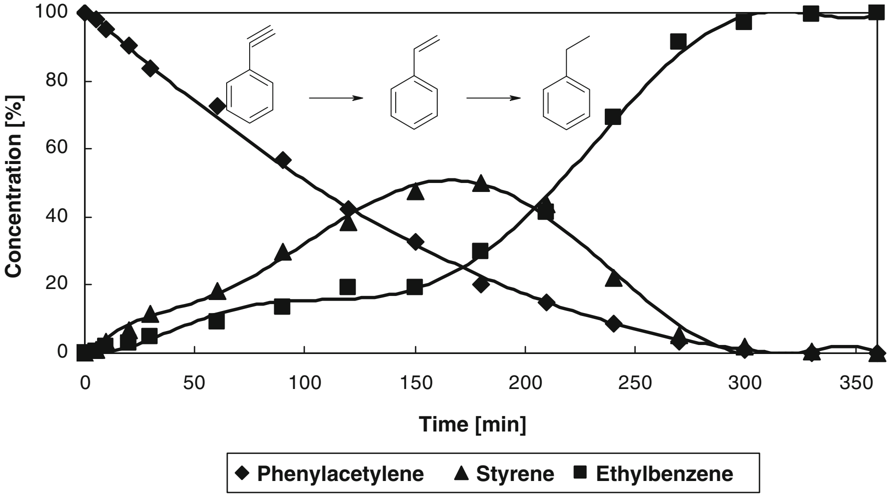

Fig. 4 The concentration course in phenylacetylene hydrogenation (200 mg phenylacetylene, 20 mg Rh-MTM-K10, 100 mg of nonane and 28 mL of hexane)

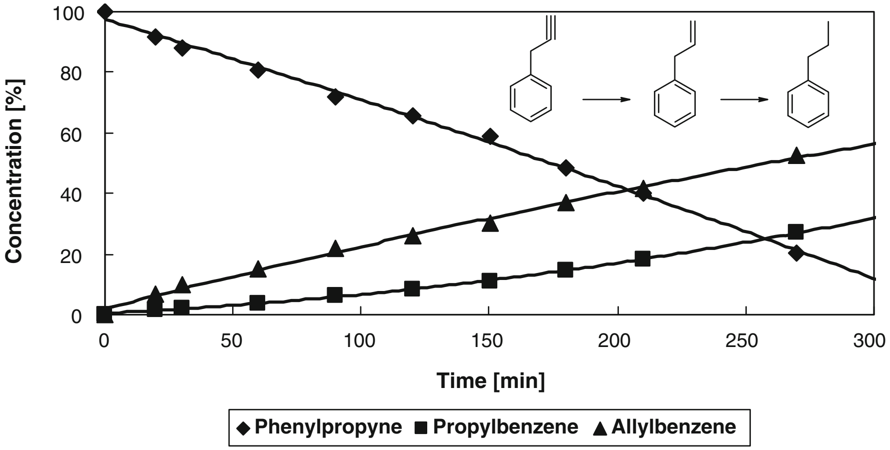

Fig. 5 The concentration course in 3-phenylprop-1-yne hydrogenation (200 mg 3-phenylprop-1-yne, 20 mg Rh-hectorite, 100 mg of nonane and 28 mL of hexane)

Table 4 Immobilized amount (%) of the Wilkinson's catalyst using immobilization by means of covalent bond (UV/VIS)

	Support with spacer			
	SBA ~ NH_2	MCM ~ NH_2	SBA ~ PPh_2	MCM ~ PPh_2
Immobilized amount (%)[a]	75	74	96	97

[a] 100% immobilized amount is 20 mg of the complex on 200 mg of the support (silica material with the spacer)

Table 5 Comparison of TOF and selectivity using the heterogenized catalyst prepared by the different approaches and with the catalysis in the homogeneous arrangement

	Support	Solvent used for catalyst immobilization	$TOF_{initial}$ (h^{-1})	Selectivity toward ST at conversion 50% (%)
Ionic exhange	Hectorite	Methanol	546	72
		Diethylether	428	68
		Hexane	420	68
	Montmorillonite	Methanol	441	72
		Diethylether	520	74
		Hexane	456	75
Covalent bond	$MCM{\sim}PPh_2$	Chloroform	452	77
	$MCM{\sim}NH_2$		403	68
	$SBA{\sim}PPh_2$		443	77
	$SBA{\sim}NH_2$		410	73
Homogeneous arrangement			997	63

After hydrogenations, the extent of eventual Rh leaching from the support into the liquid part of the reaction system was studied. The liquid resulting after the reaction was concentrated by evaporation and analyzed by AAS. No Rh was detected by this method (limit of AAS detection = 0.1 mg/mL; concentration of Rh corresponding to the total leaching = 2 mg/mL). It can be thus concluded, that no or only marginal Rh leaching occurs during followed hydrogenation. This finding was in agreement with no catalytic activity being observed in the liquid phase isolated after finishing the hydrogenation cycle.

Conclusions

The Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ was immobilized by two approaches—ionic exchange and covalent bonding. The ionic exchange was performed using two different supports—hectorite and montmorillonite K10. The selection of a solvent for the immobilization is an important parameter of this process due to possible nonbonding interactions of the catalytic complex and the support (the complex is immobilized to the surface or to the interlayers). The immobilized amount using this approach was 19 mg of the complex on 200 mg of the support. Immobilization using covalent bonding was performed using pretreated silica mesoporous molecular sieves—$MCM{\sim}PPh_2$, $MCM{\sim}NH_2$, $SBA{\sim}PPh_2$ and $SBA{\sim}NH_2$. Treatment with the ${\sim}PPh_2$ spacer was more successful due to the higher immobilized amount of the complex—19 mg on 200 mg of the support; in the other cases, the immobilized amount of complex was lower than 15 mg of complex on 200 mg of the support. A comparison of the two immobilization types was performed and the amount immobilized was the same in both cases, but the immobilization times were different—5 h in the case of ionic exchange and 1 h in the case of ligand exchange. The heterogeneous catalysts were compared in phenylacetylene and phenylpropyne hydrogenations with the Wilkinson's catalyst in the homogeneous arrangement. The significant increase in selectivity in the case of phenylacetylene was observed using heterogenized catalysts, which is caused by the presence of only monomeric species. No change in the coordination of the complex was observed in either of the immobilization types.

Acknowledgments Financial support of the Ministry of Education of the Czech Republic no.: MSM6056137301 and Grant Agency of Czech Republic Grants No: 104/07/1239 and 203/08/H032-1.

References

1. B. Cornils, W.A. Herrmann, R. Schögl, C.H. Wong, *Catalysis from A to Z. A Concise Encyclopedia* (Wiley-VCH, Weinheim, 2000)
2. J. Sedláček, J. Vohlídal, Collect. Czech. Chem. Commun. **68**, 1745 (2003)
3. J.A. Osborn, F.H. Jardine, J.F.Young, G. Wilkinson, J. Chem. Soc. **1**, 1711 (1966)
4. J.V. Crivello, M. Fan, J. Polym. Sci. Polym. Chem. **30**, 1 (1992)
5. I.D. Kostas, K.A. Vallianatou, P. Kyritsis, J. Zedník, J. Vohlídal, Inorg. Chim. Acta **357**(10), 3084 (2004)
6. A. Biffis, E. Castello, M. Zecca, M. Basato, Tetrahedron **57**, 10391 (2001)
7. S. Murai, R. Sugise, N. Sonoda, Angew. Chem. Int. Ed. Engl. **20**, 481 (1981)
8. F. Solymosi, A. Erdöhelyi, in *New Horizons in Catalysis, Studies in Surface Science and Catalysis 7B*, ed. by T. Seiyama, K. Tanabe (Elsevier, Amsterdam, 1980), pp. 1448–1449
9. R. Bertani, R.A. Michelin, M. Mozzon, A. Sassi, M. Basato, A. Biffis, G. Martinati, M. Zecca, Inorg. Chem. Commun. **4**, 281 (2001)
10. A. Nakazato, I. Saeed, T. Katsumata, M. Shiotsuki, T. Masuda, J. Zednik, J. Vohlidal, J. Polym. Sci. Polym. Chem. **43**, 19–4530 (2005)
11. T. Opstal, J. Zedník, J. Sedláček, J. Svoboda, J. Vohlídal, F. Verpoort, Collect. Czech. Chem. Commun. **67**, 1858 (2002)
12. J. Vohlídal, J. Sedláček, N. Patev, O. Lavastre, P.H. Dixneuf, S. Cabioch, H. Balcar, J. Pfleger, V. Blechta, Macromolecules **32**, 6439 (1999)
13. R.D. Gillard, J.A. Osborn, P.B. Stockwell, G. Wilkinson, Proc. Chem. Soc. **1**, 284 (1964)
14. J.A. Osborn, G. Wilkinson, J.F. Young, Chem. Commun. **2**, 17 (1965)
15. J.F. Young, J.A. Osborn, F.H. Jardine, G. Wilkinson, Chem. Commun. 131 (1965)
16. M.M. Taqui Khan, M.R.H. Siddiqui, S.A. Samad, Inorg. Chem. **28**, 4427 (1989)
17. M.M. Taqui Khan, M.R.H. Siddiqui, H.C. Bajaj, G. Ramachandraiah, Polyhedron **10**, 2729 (1991)
18. M. Bartók, G. Szöllösi, Á. Mastalir, I. Dékány, J. Mol. Catal. **139**, 227 (1999)
19. L. Huang, J.Ch. Wu, S. Kavi, React. Kinet. Catal. Lett. 82, 65 (2004)
20. C. Merckle, S. Haubrich, J. Blumel, J. Organomet. Chem. **627**, 44 (2001)
21. J. Kramer, E. Nollen, W. Buis, W.L. Driessen, J. Reedijk, React. Funct. Pol. **57**, 1 (2003)
22. C. Merckle, J. Blumel, Top. Catal. **34**, 5 (2005)
23. I.V. Koptyug, K.V. Kovtunov, S.R. Burt, M.S. Anwar, H.S. Christian, A. Pines, R.Z. Sagdeev, J. Am. Chem. Soc. **129**, 5580 (2007)
24. H. Balcar, J. Sedláček, J. Čejka, J. Vohlídal, Macromol. Rapid Commun. **23**, 32 (2002)
25. H. Balcar, J. Sedláček, J. Svoboda, N. Žilková, J. Vohlídal, M. Pacovská, Collect. Czech. Chem. Commun. **68**, 1861 (2003)
26. P. Kooyman, M. Slabová, V. Bosáček, J. Čejka, J. Rathouský, A. Zukal, Collect. Czech. Chem. Commun. **66**, 555 (2001)