Catalytic investigation of rhodium nanoparticles in hydrogenation of benzene and phenylacetylene

Jean-Louis Pellegatta, Claudine Blandy, Vincent Collière, Robert Choukroun*, Bruno Chaudret, Pan Cheng, Karine Philippot

Laboratoire de Chimie de Coordination du CNRS (UPR 8241), 205 route de Narbonne, 31077 Toulouse Cedex 4, France

Abstract

Nanoparticles of rhodium embedded in polyvinylpyrrolidone (PVP), as catalyst, were investigated in the hydrogenation of different substrates (benzene, phenylacetylene, norbornene, quinoline, adiponitrile). The solid was used as a heterogeneous catalyst or as a soluble heterogeneous catalyst in biphasic conditions (liquid/liquid) when the catalyst was dissolved in water. In both cases, the kinetics of the catalytic reaction were found to be zero-order in respect to the substrate and first-order with respect to hydrogen and catalyst. The higher hydrogenation reaction rate was found for benzene by using biphasic conditions. The [Rh-PVP] catalyst has shown an efficient activity for the catalytic hydrogenation of norbornene, quinoline and adiponitrile into norbornane, tetrahydroquinoline and 6-aminocapronitrile. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Biphasic catalysis; Colloids; Hydrogenation; Kinetics; Rhodium nanoparticles

1. Introduction

The discovery of new catalytic pathways is presently a fascinating challenge. Recent works have pointed out the interest of working in water as a practical solution for the future in homogeneous and heterogeneous catalysis [1]. Therefore, the immobilization of nanoparticles of metals (colloids) in a water soluble polymer material such as polyvinylpyrrolidone (PVP) or their stabilization with a water soluble surfactant may lead to significant progress in catalysis. Previous works for this kind of systems have been reported and different catalytic systems have been considered [2–17]. Recently, we have prepared and characterized nanoparticles of rhodium embedded in PVP [18]. This material designed as [Rh-PVP] is soluble in methanol and water and some insights into its catalytic properties were evidenced. Different substrates were tested in hydrogenation catalysis in an attempt to evaluate the potentiality of our catalyst and to evaluate if our new synthetic strategy for the preparation of colloids M^0, starting from an organometallic M^I, is able to compete with other synthetic procedures.

2. Results and discussion

The rhodium colloids were prepared from the reaction in THF of $[RhCl(C_2H_4)_2]_2$ with two equivalents of Cp_2V as a reducing agent in the presence of K30-PVP, polymer used to trap the colloids. A black solid is filtered from the THF solution and characterized as [Rh-PVP]. According to different syntheses and to the different amounts of PVP added, the analysis of the rhodium concentration embedded

* Corresponding author.

in the polymer can be found between 5 and 10 wt.%. For each catalytic reaction described here above, the same [Rh-PVP] catalyst batch was used. The solid was used as an heterogeneous catalyst or as a soluble heterogeneous catalyst [11] in biphasic conditions (liquid/liquid) when the catalyst was dissolved in water.

The hydrogenation of benzene was selected as a test reaction for the colloidal catalyst system [19]. Preliminary series of catalytic hydrogenation of benzene into cyclohexane were performed at 80 °C under 20 or 40 bar H_2 without added solvent in a heterogeneous system with [catalyst]/[C_6H_6] ratio of 1/34,000. The linear plot of hydrogen uptake versus time over 6 days indicated a dihydrogen consumption of 0.45 and 1 bar h^{-1}, respectively, for the same initial kinetic conditions. This indicates first-order kinetics with respect to dihydrogen. The formation of cyclohexane for the experiment carried out under 20 bar H_2 was followed by GC. A linear variation of the concentration with time was obtained which corresponds to zero-order in C_6H_6 (Fig. 1). A different series of benzene hydrogenation reactions was carried out under 7 bar H_2 at 30 °C in water/C_6H_6 biphasic reaction. The experimental conditions correspond to a [Rh-PVP] catalyst dissolved in 5 ml H_2O and a [catalyst]/[C_6H_6] ratio of 1/2000. The influence of the amount of water on the catalytic activity was tested. Increasing the amount of water four times (5–20 ml H_2O) for the same stirring rate speed (700 rpm) has no effect on the catalytic
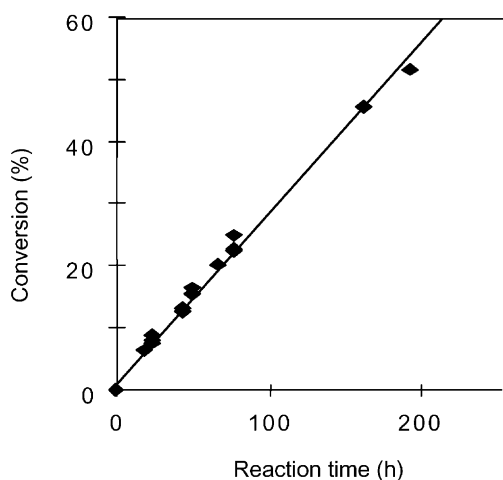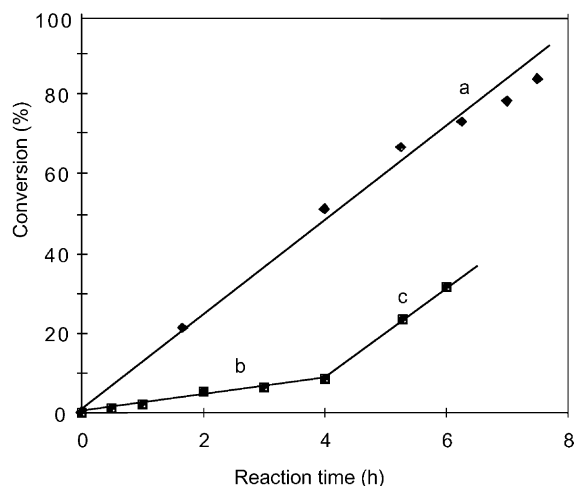

Fig. 2. Hydrogenation of benzene catalyzed by [Rh-PVP] (Rh contents, 10.2%): 7 bar H_2; 30 °C; [catalyst]/[substrate] = 1/2000. Under biphasic conditions (water, 5 ml): curve a; under monophasic conditions: curve b; with 5 ml water added after 4 h: curve c.

efficiency (nearly 5% h^{-1}). In these experimental conditions, the linear plot of the cyclohexane formation rate shows that zero-order kinetics in C_6H_6 is maintained within the biphasic system. The turnover frequency (TOF), defined as mol of C_6H_6 consumed per mol of rhodium per hour, is 250 for a [substrate]/[catalyst] ratio of 2000. As shown in Fig. 2, for the same value of [substrate]/[catalyst] ratio (2000), the TOF decreases from nearly 250 (curve a) for the biphasic system to nearly 40 for the monophasic system (curve b) in heterogeneous conditions. It is interesting to observe that when H_2O is added to the heterogeneous system after 4 h, the catalytic activity of the biphasic system is recovered (TOF = 235; curve c). After completion of the reaction, the catalyst dissolved in water was removed from the reactor, evaporated to dryness under vacuum and a small amount of the solid was dissolved in methanol for deposition onto microscopy grids. The presence of Rh nanoparticles after hydrogenation catalysis in water is demonstrated by TEM in Fig. 3. The particles are polydisperse in size and display irregular shapes, most likely resulting from the coalescence of small particles (ca. 2–3 nm). Some spherical individual particles are also visible. HREM images evidence the presence of atomic columns characteristic of the fcc structure of Rh (selected area electron diffraction (SAED)
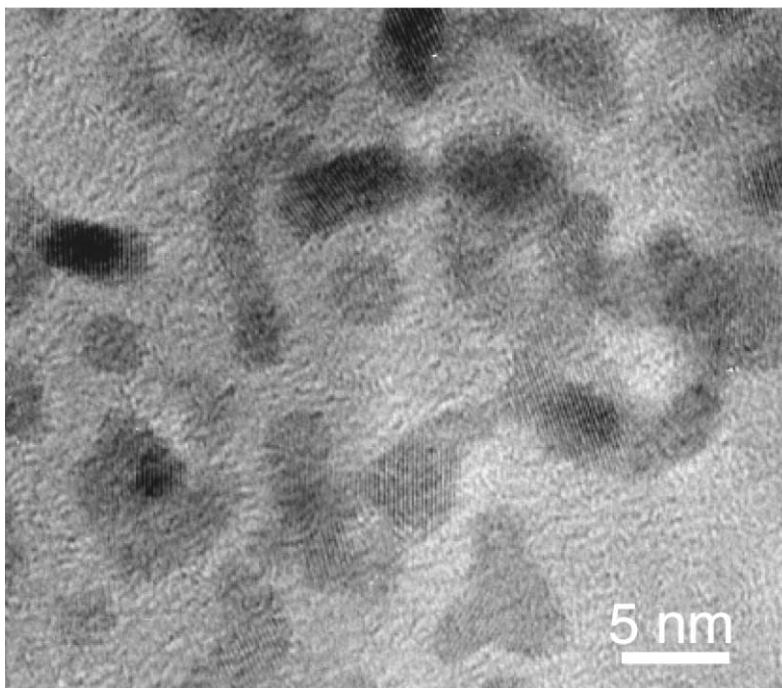

Fig. 1. Hydrogenation of benzene catalyzed by [Rh-PVP] (Rh contents, 8.9%): 20 bar H_2; 80 °C; [catalyst]/[substrate] = 1/34,000.

Fig. 3. TEM image of [Rh-PVP] catalyst after benzene hydrogenation in biphasic conditions (7 bar H_2; 30 °C).

experiments performed on this grid gave ring pattern typical of fcc Rh: the mean metal–metal distance of 0.268 nm observed is very close to the 0.269 nm of the bulk value). Therefore, no oxidation of Rh has occurred in water. A similar hydrogenation reaction was performed with the same [catalyst]/[substrate] ratio (1/2000); after which the organic layer was removed and a new run was performed with the same catalyst and a ratio of 1/4000. The plot of the formation of cyclohexane versus time is reported in Fig. 4 and indicates a first-order with respect to the solid catalyst (the rate of the reaction decreasing by a factor of 2 from curve a to b). Note that the re-used catalyst has nearly the same activity. So the rate expression for the cyclohexane formation is given by $r = k[H_2][catalyst][C_6H_6]^0$.

No hydrogenation of benzene was observed using the same experimental conditions in methanol as a solvent, where the catalyst is soluble. However, the rhodium colloids still may be active in methanol since the hydrogenation of hexene to hexane is obtained when hexene is added to the reaction mixture.
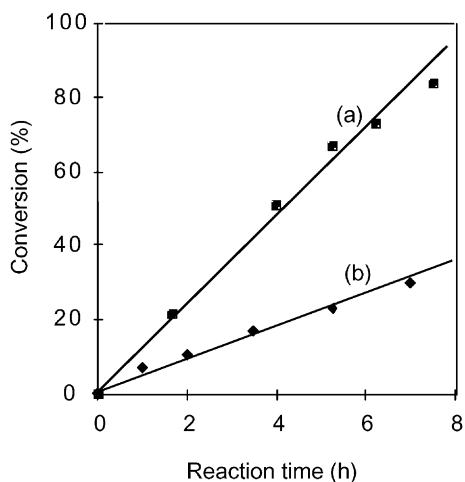

Fig. 4. Hydrogenation of benzene catalyzed by [Rh-PVP] (Rh contents, 10.2%): 7 bar H_2; 30 °C. Curve a: [catalyst]/[substrate] = 1/2000; curve b: [catalyst]/[substrate] = 1/4000.

Additional experiments on benzene hydrogenation were performed using C_6D_6 or D_2O in the catalytic reactions. Under the following experimental conditions: 40 bar H_2, 80 °C, 2 g C_6D_6, and a [catalyst]/[substrate] ratio (1/1000), the formation of deuterated cyclohexane $C_6H_{6+x}D_{6-x}$ ($x = 1$–6) was characterized as the main product by gas chromatography–mass spectrometry (GC–MS) of the solution. Only $C_6H_7D_5$ at MS = 91 can be observed after 3 days reaction. The hydrogenation of C_6H_6 was also performed in a biphasic medium with 5 ml D_2O (40 bar H_2, 80 °C, [catalyst]/[substrate] ratio: 1/1000). In this case, at 60% conversion, no deuterium incorporation into unreacted benzene was found and some multiple deuterium incorporation into cyclohexane as $C_6H_{6+x}D_{6-x}$ ($x = 1$–6) were observed by GC–MS analysis. The reaction was carried out for 3 days in order to completely convert benzene into cyclohexane (MS = 84–92; we could note the presence of $C_6H_5D_7$ and $C_6H_4D_8$ at MS = 91 and 92). In this case, the deuterium atoms have to come from the deuterated water. The H/D exchange between H_2 and D_2O, expected for a rhodium catalyst, was also detected by mass spectroscopy in the gas phase (HD and D_2) when the colloids were dissolved in D_2O and left to react with 40 bar H_2. But the reaction between D_2O and C_6H_6, carried out for 1 week at 80 °C under argon in the presence of the [Rh-PVP] catalyst, does not lead to catalytic H/D exchange in the absence of H_2. This blank experiment shows that H_2O does not participate with the catalysis but participates in the H/D exchange. Similar observations have already been discussed by Blum et al. [20–22] and recently reviewed in detail by Finke et al. using $RhCl_3$, $[(C_8H_{17})_3NCH_3]Cl$ catalyst [19]. A mechanism for benzene hydrogenation was proposed which involves η^3–η^2–η^1 interconversions [20]. Significantly, we have demonstrated that the Rh nanoparticles, synthesized by an organometallic route between a Rh^I precursor and Cp_2V could be used for heterogeneous catalysis, as a solid or in biphasic solution.

The catalytic studies and kinetic measurements of the hydrogenation of phenylacetylene and styrene were also performed at 60 °C under a hydrogen pressure of 7 bar, in the absence of solvent, using a [catalyst]/[substrate] ratio of 3800. In this case, the substrate does not dissolve the catalyst and the reaction is performed in a heterogeneous system as above. From the kinetic data corresponding to Fig. 5,
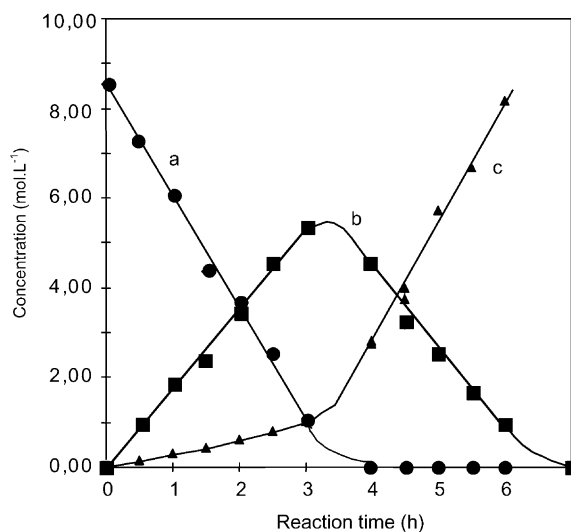

Fig. 5. Hydrogenation of phenylacetylene catalyzed by [Rh-PVP] (Rh contents, 5.7%): 7 bar H_2; 60 °C; [catalyst]/sub-[strate] = 1/3800 ((a) phenylacetylene; (b) styrene; (c) ethylbenzene).

we obtain a linear variation of the concentration with time, indicating a zero-order with respect to PhC≡CH ($r_1 = 2.5$ mol l^{-1} h^{-1} which defines the rate of disappearance of PhC≡CH) and when all the alkyne is consumed- a zero-order in PhCH=CH$_2$ ($r_2 = 2.9$ mol l^{-1} h^{-1}). An experiment involving the colloids and styrene, using the same experimental conditions, confirms the formation of ethylbenzene ($r_2 = 2.7$ mol l^{-1} h^{-1}; Fig. 6) with nearly the same hydrogenation rate as that obtained above in the hydrogenation of PhC≡CH. Therefore, the kinetic investigations of the hydrogenation of phenylacetylene to styrene and of styrene to ethylbenzene revealed that the reaction rates do not depend on the concentration of the substrates. A further experiment was carried out under 3.5 bar H_2 to identify the order with respect to hydrogen. From the data shown on Fig. 7, we obtain a rate value of $r_1 = 1.1$ mol l^{-1} h^{-1} and $r_2 = 1.3$ mol l^{-1} h^{-1} for PhC≡CH and PhCH=CH$_2$ hydrogenation, respectively (after the alkyne has been consumed). These results indicate that the reaction is first-order in dihydrogen and zero-order in phenylacetylene. So the rate law can be written as $r = k$ [catalyst][H_2] with a first-order in respect to the solid catalyst. We note that the reduction of styrene
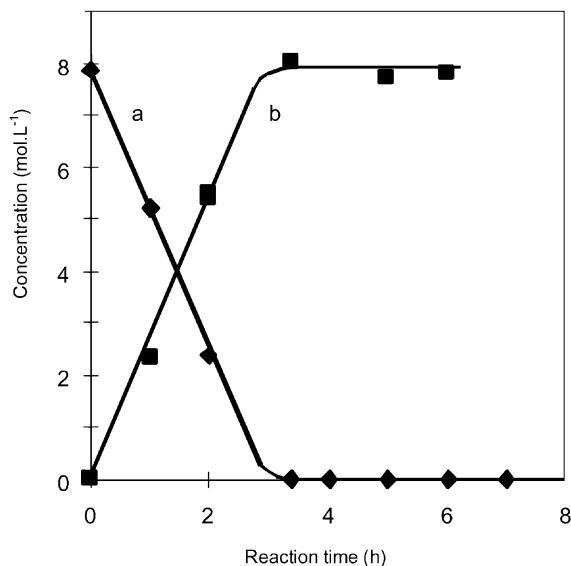
Fig. 6. Hydrogenation of styrene catalyzed by [Rh-PVP] (Rh contents, 5.7%): 7 bar H_2; 60 °C; [catalyst]/[substrate] = 1/3400 ((a) styrene; (b) ethylbenzene).
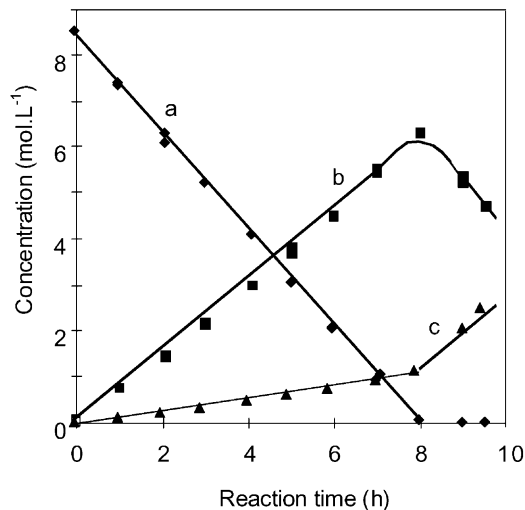

Fig. 7. Hydrogenation of phenylacetylene catalyzed by [Rh-PVP] (Rh contents, 5.7%): 3.5 bar H_2; 60 °C; [catalyst]/[substrate] = 1/3800 ((a) phenylacetylene; (b) styrene; (c) ethylbenzene).

into ethylbenzene depends on the concentration of phenylacetylene still present in solution. There is a strong preference for catalyst-alkyne bonding in such a manner that phenylacetylene has to be converted into styrene before the transformation of the latter in ethylbenzene.

Finally, we intended to learn about the influence of ligands on the catalytic activity and selectivity and in particular on phosphines. Similar experiments were conducted in the presence of 10 equivalents of phosphine (PPh$_3$, PPh$_2$Me, PPhMe$_2$, PMe$_3$) with respect to rhodium. In Table 1, the percentages of phenylacetylene, styrene and ethylbenzene found in the reaction mixture after 2 and 6 h of reaction times are listed.

The kinetic study shows by comparing entry 1 (experiment without phosphine) with 2–5, that the formation of ethylbenzene versus styrene is lowered in the presence of phosphine and that the selectivity of styrene is particularly increased in presence of PPh$_3$ (which has the highest Tolmann's angle and the lowest basicity among the phosphines used in this work). Unfortunately, at this stage, we were unable to obtain selectively styrene from phenylacetylene. This result demonstrates nevertheless the availability of the particle surface to phosphine coordination and suggests that the selectivity of catalytic reactions could be tuned using different ligand systems.

In all these experiments the absence of ethylcyclohexane was also confirmed by ^{1}H NMR and GC.

Table 1
Hydrogenation data of phenylacetylene [PhC≡CH] (8.52 mol l^{-1} h^{-1}) using [Rh-PVP] as catalyst, at 60 °C and 7 bar H_2 for 2 and 6 h

Entry	PR$_3$	PhC≡CH (%)		PhCH=CH$_2$ (%)		PhCH$_2$CH$_3$ (%)		[PhC≡CH]/[catalyst]
		2	6	2	6	2	6	
1		48	0	45	10	7	90	3800
2	PPh$_3$	83	42	16	54	1	4	3450
3	PPh$_2$Me	87	82	11	15	2	3	3300
4	PPhMe2	89	67	10	30	1	3	3350
5	PMe$_3$	92	77	7	19	1	4	3550

Hydrogenation of the phenyl group in toluene and styrene as methylcyclohexane and ethylcyclohexane, respectively, was found when Rh colloids of 3.6 nm diameter were used [13]. By comparison, the initial mean size of our particles is 1.3 nm [18] and this difference in size could explain the behavior observed in the total hydrogenation of the phenyl group by others which occurs under 1 bar H_2. The formation of methylcyclohexane from toluene under 7 bar H_2 at 30 and 60 °C was not observed and was only possible under forcing conditions, i.e. 40 bar H_2 and 80 °C.

The catalytic activity of the rhodium colloids is not limited to the hydrogenation of phenylacetylene and benzene. With the same experimental conditions (7 bar H_2, 30 °C), solid norbornene ([catalyst]/[substrate] ratio: 1/3500) dissolved in dodecane as solvent (and used as reference for GC analysis), gives norbornane (TOF = 265). Other functional groups have been hydrogenated. Quinoline was hydrogenated into tetrahydroquinone. In this case, the quinoline dissolves the [Rh-PVP] catalyst and a soluble heterogeneous solution of the catalyst is obtained. The reaction was monitored by ^{1}H NMR. At 5 bar H_2, 80 °C and a [catalyst]/[substrate] ratio of 1/1200, 50% conversion was observed in 3 h (100% in 9 h). The reduction of different functional groups is under investigation. For example, partial hydrogenation of the adiponitrile $NC(CH_2)_4CN$, an industrial goal [23], has been performed at 80 °C under 5 and 40 bar H_2, with a ratio [catalyst]/[substrate] = 1/1500 for 9 h. The conversion of the adiponitrile into 6-aminocapronitrile $H_2N(CH_2)_5CN$ is 33 and 85%, respectively, as shown by ^{1}H NMR. The total reduction of adiponitrile into hexamethylenediamine $H_2N(CH_2)_6NH_2$ is in progress.

3. Conclusions

The catalytic potential of the [Rh-PVP] colloids synthesized by an organometallic route has been explored in heterogeneous and biphasic conditions for the hydrogenation of different types of substrates (benzene, phenylacetylene, norbornene, quinoline, adiponitrile). Two different substrates, benzene and phenylacetylene, have mainly been studied. In both cases and for heterogeneous conditions, the kinetics of the catalytic reaction were found to be zero-order with respect to the substrate and first-order with respect to hydrogen and catalyst. Little information is still available concerning the kinetic studies of colloids in catalysis and efforts will be developed in our group in this direction.

4. Experimental

The rhodium colloids were prepared by a previously published method [18]. The rhodium contents of the catalyst used is specified for each experiment. GC analyses were performed on a Shimadzu GC 14B equipped with a Nukol ID fused silica column (Supelco 15 m) and on a HP 4890 equipped with a HP5 column (15 m). ^{1}H NMR spectra were recorded on a AC 200 (Brucker). Hydrogen C grade was supplied by Air Liquide. GC–MS was performed using a Nermarg R10–10 with a ionizing voltage of 70 eV (for an H/D exchange studies, an ionizing voltage of 17 eV was recommended [19,20]). Transmission electron microscopy (TEM) was performed on a JEM 2010 operating at an accelerating voltage of 200 kV with point resolution 0.23 nm. Samples were prepared in a glove box (Vacuum Atmospheres Company) under argon and were examined at magnification between 100 and 400 K. Samples were prepared using carbon coated copper grids. One drop of the MeOH solution of the [Rh-PVP] before and after catalysis was placed on the carbon-coated grid using a syringe.

4.1. Hydrogenation experiments at 20 and 40 bar H_2

The catalytic reactions were carried out in a 100 ml stainless steel autoclave under constant pressure (40 or 20 bar). The temperature was maintained at 80 °C by circulation of oil through a double jacket. The gas was contained in a tank connected to the autoclave. The fall in pressure in the tank was monitored with a pressure gauge connected to an electronic unit. A deliberated stirring at 300 rpm was used to avoid projection of the solid catalyst above the reactant on the wall of the reactor (in this case, the effect of diffusional limitations upon the observed reaction rate was not tested). The [catalyst]/[substrate] ratio was calculated according to the concentration of rhodium atoms contained in the [Rh-PVP] catalyst.

In a typical experiment, colloids (7.6 mg [Rh-PVP], 9% Rh content) is introduced under hydrogen into the autoclave preheated at 80°C; then benzene (5.18 g) is added and the gas is admitted (40 bar). The rates of the hydrogenation were calculated from the plots of hydrogen consumption versus time. Samples for GC were also removed from time to time.

4.2. Hydrogenation experiments at 7 bar H_2

The catalytic reactions were carried out in a 250 ml Fisher–Porter bottle connected to the H_2 tank and maintained at 30 or 60 °C in an oil bath. Several experiments using different stirring rate were carried out in order to eliminate mass transfer limitations during our studies. The [catalyst]/[substrate] ratio was calculated according to the concentration of rhodium atoms contained in the [Rh-PVP] catalyst.

In a typical experiment, colloids (9.7 mg [Rh/PVP], 10.2% Rh content) and H_2O (4.92 g) were stirred at 700 rpm during 30 min until complete dissolution of the catalyst took place. The substrate (benzene: 1.55 g) is then added. Samples of the organic phase were removed from time to time for GC analyses. For the hydrogenation of quinoline and adiponitrile into tetrahydroquinoline and 6-aminocapronitrile, respectively, the catalysis was monitored by ^{1}H NMR.

Acknowledgements

References

[1] B. Cornils, W.A. Herrsmann, Aqueous Phase Organometallic Catalysis, Wiley, Weinheim, 1998.
[2] G. Schmid, Clusters and Colloids, VCH, Weinheim, 1994.
[3] G. Schmid, V. Maihack, F. Lantermann, S. Peschel, J. Chem. Soc., Dalton Trans. 5 (1996) 589.
[4] H. Hirai, J. Macromol. Sci. Chem. A13 (1979) 633.
[5] H. Bönnemann, W. Brijoux, in: A. Fürnstner (Ed.), Active Metals, VCH, Weinheim, 1996, pp. 339–376.
[6] H. Bönnemann, G. Braun, W. Brijoux, R. Brinkmann, A. Schulze Tilling, K. Seevogel, K. Siepen, J. Organomet. Chem. 520 (1996) 143.
[7] H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, J. Mol. Catal. 74 (1992) 323.
[8] T. Yonezawa, T. Tominaga, D. Richard, J. Chem. Soc., Dalton Trans. 5 (1996) 783.
[9] J.D. Aiken III, R.G. Finke, J. Mol. Catal. 145 (1999) 1.
[10] J.D. Aiken III, G. Finke, J. Chem. Soc. 120 (1998) 9545.
[11] J.D. Aiken III, Y. Lin, R.G. Finke, J. Mol. Catal. 114 (1996) 29.
[12] J.D. Aiken III, R.G. Finke, J. Am. Chem. Soc. 121 (1999) 8803.
[13] J. Schulz, A. Roucoux, H. Patin, J. Chem. Soc., Chem. Commun. 6 (1999) 535.
[14] C. Larpent, E. Bernard, F. Brisse-Le Menn, H. Patin, J. Mol. Catal. 116 (1997) 277.
[15] C. Larpent, H. Patin, J. Mol. Catal. 61 (1990) 65.
[16] S. Xu, X. Xi, J. Shi, S. Cao, J. Mol. Catal. 160 (2000) 287.
[17] K.E. Gonsalves, H. Li, R. Perez, P. Santiago, M. Jose-Yacaman, Coord. Chem. Rev. 206/207 (2000) 607.
[18] R. Choukroun, D. de Caro, B. Chaudret, P. Lecante, E. Snoeck, N. J. Chem. 25 (2001) 525.
[19] K.S. Weddle, J.D. Aiken III, R.G. Finke, J. Am. Chem. Soc. 120 (1998) 5653, and references therein.
[20] J. Blum, I. Amer, K. Volhardt, H. Schwarz, G. Hoöhne, J. Org. Chem. 52 (1987) 2804.
[21] I. Amer, H. Amer, J. Blum, J. Mol. Catal. 34 (1986) 221.
[22] I. Amer, H. Amer, R. Ascher, J. Blum, Y. Sasson, K. Vollhardt, J. Mol. Catal. 39 (1987) 185.
[23] K. Weissermel, H-J. Arpe, Industrial Organic Chemistry, VCH, Weinheim, 1993, p. 235.