Controlled distribution of solid catalysts into two immiscible liquid phases – synthesis and catalytic applications

Markus Gruber[a], Michael Wagner[a], Roland Heidenreich[a], Jürgen G.E. Krauter[b],
N. Coskun[b], and Klaus Köhler[a,*]

[a]*Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany*
[b]*Degussa AG, Catalysts & Initiators, Rodenbacher Chaussee 4, 63403 Hanau, Germany*

Received 11 November 2003; accepted 19 February 2004

A new concept for the separation of heterogeneous catalysts is presented. Against gravity, surface modified catalysts are located only in one of two immiscible liquid phases. The catalyst phase can be separated by simple decantation. Advantages of this multiphase system were demonstrated for hydrogenations and CC coupling reactions.

KEY WORDS: multiphase catalysis; catalyst separation; supported palladium; hydrogenation; CC coupling.

1. Introduction

Batch hydrogenations carried out in industry either use heterogeneous powder catalysts or homogeneous catalysts. Heterogeneous slurry phase catalysts need to be separated from the reaction by filtration. It is possible that filtration takes as long as the chemical reaction. In case of homogeneous catalysts, catalyst separation is especially a challenge since product and catalyst are dissolved in the same phase [1].

An innovative already well-established solution for separation of homogeneous catalysts is liquid–liquid two-phase catalysis where catalyst and product are dissolved in two immiscible liquid phases and separated by simple phase segregation [2].

The basic idea of this paper is to use heterogeneous catalysts in a liquid–liquid two-phase system. The approach is to modify the surface polarity of the support, so that the heterogeneous catalyst will be located only in the liquid phase that has the same polarity. Then it should be possible to separate catalyst phase from product phase by simple decantation instead of filtration. Although heterogeneous catalysts have been described in liquid–liquid two-phase systems [3–6] to the best of our knowledge the high relevance for overcoming fundamental problems in catalyst separation was not the focus of the corresponding reports.

Additional advantages of this new concept can be: (i) salt by-products can be easily removed if one phase solubilizes the salt which prevents the catalyst from being blocked by precipitated salt (increase of catalyst lifetime); (ii) ease of catalyst re-use (simple re-use of catalyst containing phase); (iii) increased safety since phase separation “switches off” the catalyst by phase separation in case of power supply interruption. Depending on the reaction the following advantages may arise: (iv) higher activity or (v) higher selectivity due to removal of product from catalyst phase [7].

2. Experimental

Palladium on activated carbon catalysts (Pd/C: E 105 CA/W 5% or E 1002 NN/W 5% with 5.0% Pd and 50% water content) and oxidic supports were received from Degussa AG. All chemicals were used without special treatment.

Four grams of support or palladium catalyst were dried in vacuum at 140 °C for 24 h. Under argon atmosphere 15 mL *n*-hexane were transferred and the mixture was stirred for 10 min. *n*-octyldimethylsilylchloride was dropped to the suspension within 1 min and the mixture was stirred for 24 h, filtered off and washed six times by *n*-hexane. The silylated product was dried under vacuum for 24 h.

A 0.99 g of support were suspended in 20 mL water/THF (= 80 vol% : 20 vol%). 2.00 g of 0.5 wt% $PdCl_2$ in HCl solution were added. Palladium was precipitated by addition of a base (e.g. NaOH). The catalyst was filtered off and washed four times with 1 mL of water [8].

0.27 mol% of palladium catalyst, 70 mmol of *N*-benzylaminoethanol, 2500 mg of *n*-hexadecane (as internal standard), 120 mL of water/toluene (mostly 75 vol% : 25 vol%), and 0.5 mL 25 wt% HCl were introduced in a 300 mL autoclave with multiple paddle mixers. The reactor was flushed three times by hydrogen, heated to 120 °C and pressurized by 10 bar of H_2. After 2 h at 1000 rpm the reaction mixture was cooled and analyzed by GC.

---

[*] To whom correspondence should be addressed.
E-mail: klaus.koehler@ch.tum.de

1011-372X/04/0500–0177/0 © 2004 Plenum Publishing Corporation

A 0.1 mol% of palladium catalyst, 50 mmol of bromobenzene, 60 mmol of NaOAc, 2500 mg of *n*-hexadecane, 80 mL of water/toluene (mostly 62.5 vol% : 37.5 vol%), 75 mmol of styrene, and 60 mmol of Bu_3N (as internal standard) were introduced in a 300 mL autoclave with multiple paddle mixers. The reactor was flushed three times by argon and heated to 140 °C. After 6 h at 1000 rpm the reaction mixture was cooled and analyzed by GC.

For re-use experiments the liquid phases were decanted. The catalyst phase was introduced into the autoclave again. Fresh educts were added and the reactions performed as described above. Comparative re-use tests were performed by filtration of the catalyst.

The different phases were filtered and analyzed by GC-FID and GC-MS (organic phase: HP-1, 30 m × 0.25 mm × 0.25 μm; water phase: HP-5, 30 m × 0.25 mm × 0.25 μm). Conversion and selectivity were calculated by the method of internal standard as described elsewhere [9].

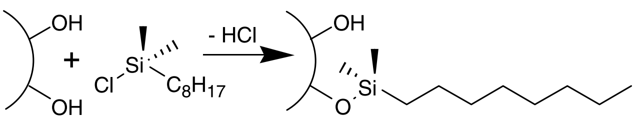
Carbon was analyzed by the apparatus vario EL from the company Elementar-Analysensysteme. Silicon was detected by a Shimadzu UV-160 ($\lambda = 810$ nm). Palladium was quantitatively determined by AAS with a Varian SpectrAA 400.

3. Results and discussion

3.1. Preparation of catalysts

Since the partition of a heterogeneous catalyst between two immiscible phases (e.g. water/toluene) should depend on the hydrophilicity/hydrophobicity of the surface of the catalyst, tuning of the surface polarity could allow the determination in which phase the catalyst will be kept. For this purpose either unmodified or modified support material can be used. In this work unmodified activated carbon (hydrophobic surface) and (un)modified oxides (silica, alumina, and titania) were used. The surface modification of the oxides was done by silylation with *n*-octyldimethylsilyl chloride (scheme 1).

Additionally, commercially available hydrophobic titania (T 805, Degussa AG) was used. Precipitation from $PdCl_2$/HCl solution on these hydrophobic oxides [8] led to hydrophobic Pd catalysts. Direct silylation of supported Pd catalysts was also conducted. The presence of the *n*-octyldimethylsilyl groups on the oxide or catalyst surface was confirmed by IR spectroscopy and elemental analysis. Pd content was determined by elemental analysis (table 1).



Scheme 1. Silylation of oxides.

3.2. Phase separation experiments

The various materials were suspended in water/toluene and in water/hexane. In fact, the original pure oxides and Pd/oxide catalysts are dispersed in the water phase and the hydrophobic ones in the organic phase after phase separation (figure 1, chosen examples). The phase separation occurs against gravity within a few seconds or minutes.

3.3. Catalytic model reactions

The catalysts were used in the *N*-debenzylation of *N*-benzylaminoethanol with H_2 to aminoethanol (AE) (scheme 2) and the *Heck* reaction between bromobenzene and styrene (scheme 3).

In the *N*-debenzylation the activity and selectivity were higher for the mixture of water and toluene than for the pure solvents (table 2, entries 4–6) with an optimum volume ratio of 75 : 25 (high conversion and yield obtained in few hours). This is attributed to a combination of the high availability of the reactants

Table 1
Elemental analyses of chosen hydrophobic carriers and silylated Pd catalysts[a]

Entry	Catalyst	Content (Pd) (%)	Content (Si) (%)	Content (C) (%)	σ (C) (%)[b]
1	Al_2O_3_H[c]	–	0.26	0.79	16
2	Pd/Al_2O_3_A[d]	4.6	0.54	1.40	8
3	Pd/Al_2O_3_B[e]	0.9	0.52	0.76	4

[a] Dried oxide (140 °C, 0.1 mbar, 24 h) was reacted with *n*-Octyldimethylsilylchloride (RT, Argon, 24 h).
[b] σ(C) = degree of silylation, calculated on C.
[c] Silylated hydrophobic oxides.
[d] Silylation after precipitation of palladium.
[e] Silylation before precipitation of palladium.

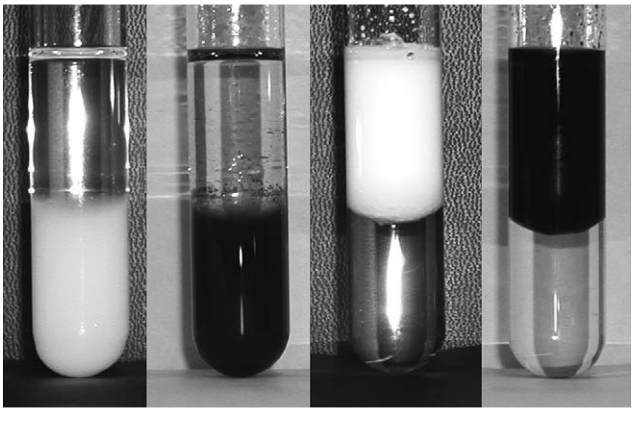
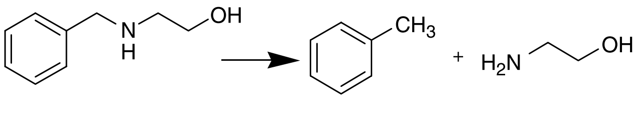
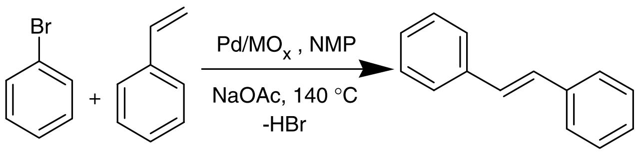


Figure 1. Controlled distribution of different solid oxides or catalysts in toluene (top)/water (bottom) (from left to right: Al_2O_3, Pd/TiO_2, TiO_2_H (=Hydrophobic titania), and Pd/C).



Scheme 2. Palladium catalyzed *N*-debenzylation.



Scheme 3. Palladium catalyzed *Heck* reaction.

Table 2
Catalytic tests in the *N*-debenzylation[a]

Entry	Catalyst	Conversion (%)[b]	Yield (AE) (%)[b]	Selectivity (AE) (%)[b]
1[c]	10% Pd/Al_2O_3	23	19	81
2[c]	10% Pd/Al_2O_3_B	49	26	54
3[d]	Pd/C_1[e]	100	74	74
4[d]	Pd/C_2[f]	94	69	73
5[g]	Pd/C_2[f]	63	0	0
6[h]	Pd/C_2[f]	76	38	51

[a] 300 mL PARR autoklave, 70 mmol *N*-benzylaminoetahnol, 120 mL water/toluene = 75 : 25, 0.5 mL HCl, 0.27 mol% Pd, 10 bar H_2, 120 °C, 1000 rpm.

[b] Determined by GLC-FID and GC-MS, diethyleneglycol-*n*-butylether as internal standard.

[c] 8 h.

[d] 2 h.

[e] Pd/C (E 105 XNE/W 10%).

[f] Pd/C (E 1002 NN/W 10%).

[g] 120 mL toluene.

[h] 120 mL water.

Table 3
Re-use of Pd/C in the *N*-debenzylation[a]

Entry	Run	Conversion (%)[b]	Yield (AE) (%)[b]	Selectivity (%)[b]
1	1. Run	94	59	63
2	2. Run	100	72	72
3	3. Run	100	79	79
4	4. Run	97	73	74

[a] 300 mL PARR autoklave, 70 mmol *N*-benzylaminoetahnol, 120 mL water/toluene = 75 : 25, 0.5 mL HCl, 0.27 mol% PdC (E 1002 NN/W 10%), 10 bar H_2, 120 °C, 1000 rpm, 1 h.

[b] Determined by GLC-FID and GC-MS, diethyleneglycol-*n*-butylether as internal standard.

(*N*-benzylaminoethanol and H_2) in the organic phase and the high solubility of the product in water. The hydrophobic catalysts showed higher activity than their hydrophilic counterparts (table 2, entry 1 and 2). This indicates that the reaction takes place in the organic phase probably due to the higher solubility of H_2 in toluene [10,11]. Best results showed a Pd/C catalyst (table 2, entry 3).

The re-use of the catalyst was possible by filtration or phase separation with comparable results. Until the third run the conversion and selectivity increased before it diminished due to an incrementing loss of catalyst (table 3). This increase (especially in selectivity) is ascribed to an accumulative adsorption of only slightly water soluble by-products which change the selectivity behavior of the catalyst. The product AE is only dissolved in water while the hydrophobic catalyst is only dispersed in toluene. A great part of the main by-product benzylalcohol is located in the organic layer which facilitates the product refining.

The second example is the application of the concept to CC-coupling reactions, e.g. *Heck* reaction (scheme 3). Highly active heterogeneous catalysts are known for this reaction [9]. This reaction is characterized by the production of stoichiometric amounts of insoluble salt (which can causes re-usability problems) and a limited number of suitable and relatively expensive solvents. Indeed, if using the cheap solvent mixture water/toluene (optimum for volume ratio 62.5 : 37.5) the *Heck* reaction runs well (yield of *E*-stilbene 67% after 6 h) in contrast to the pure solvents (yield of *E*-stilbene in toluene 3% and in water 17%, respectively). In addition, it is possible to decant the water phase which contains the inorganic by-products (remaining base and salt which arises in stoichiometric amounts).

4. Conclusions

The outlined concept to use heterogeneous catalysts in liquid–liquid two-phase systems demonstrated clear advantages for both reactions. The tests revealed (i) higher activity and (ii) higher selectivity compared to the pure (more expensive) solvents. (iii) Easier and faster product separation and (iv) catalyst re-usability by phase separation is possible while allowing (v) additional filtration for product refining or catalyst recycling. In principal, this concept can be applied to a variety of reactions like hydrogenations, oxidations or coupling reactions.

References

[1] *Handbook of Heterogeneous Catalysis*, Vol. 5, eds. G. Ertl, H. Knoezinger and J. Weitkamp (Wiley-VCH, Weinheim, 1997).

[2] *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*, eds. B. Cornils and W.A. Herrmann (Wiley-VCH, Weinheim, 1998).

[3] G.D. Yadav and S.S. Naik, Catal. Today 66 (2001) 345.

[4] R. Ben-Daniel, A.M. Khenkin and R. Neumann, Chem. A Eur. J. 6 (2000) 3722.
[5] W.D. Bossaert, D.E. de Vos, W.M. van Rhijn, J. Bullen, P.J. Grobet and P.A. Jacobs, J. Catal. 182 (1999) 156.
[6] H. Nur, S. Ikeda and B. Ohtani, J. Catal. 204 (2001) 402.
[7] M. Nobis and B. Driessen-Hoelscher, Angew. Chem. Int. Ed. 21 (2001) 3983.
[8] W.P. Pearlman, Tetrahedron Lett. 17 (1967) 1663.
[9] K. Koehler, R.G. Heidenreich, J.G.E. Krauter and J. Pietsch, Chem. A Eur. J. 8 (2002) 622.
[10] M. van der Zon, P.J. Hamersma, E.K. Poels and A. Bliek, Catal. Today 48 (1999) 131.
[11] H. Vinke, P.J. Hamersma and J.M.H. Fortuin, Eng. Sci. 48 (1993) 2197.