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Catalytic transfer hydrogenation of hydrophobic substrates by water-insoluble hydrogen donors in aqueous microemulsions

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ABSTRACT

In the course of our attempts to replace harmful organic solvents used in organic processes by environmentally favored media, we investigated the transfer hydrogenation of various, unsaturated substrates by cyclohexene and similar water-insoluble hydrogen donors. The catalyst in these reactions was Pd(0) in form of nanoparticles, stabilized by hydrophobic silica sol–gel which can be reused at least 4–6 times without significant loss of activity. The process was shown to depend on the electronic nature of the surfactants. Marlipal® 24/70 gave in most experiments the best results. Except for the hydrolysable 1-chloromethylnaphthalene, where chlorine can be substituted by a hydroxyl group, the aqueous medium does not take part in the catalytic process.

1. Introduction

Transfer hydrogenation of unsaturated compounds is a “green” version of the conventional hydrogenation. It may avoid the danger associated with the transport of hydrogen in cylinders [1]. When the hydrogen donors (such as alcohols or formic acid derivatives) as well as the unsaturated acceptors are water-soluble, the reactions can be conducted in aqueous media [2] (see also the comprehensive monographs on organic synthesis in water [3,4]). When however, the reaction components are water-insoluble, most industrial plants prefer the application of organic media. In the course of our attempts to replace as much as possible of the large quantities of the harmful solvents by environmentally favored aqueous media, we have already shown that the use of either aqueous emulsions [5] or microemulsions [6] obtained in the presence of micelle-forming surfactants, enables the performance of a variety of organic catalyses in aqueous media even if all the reaction components are water insoluble [7–10]. The use of sol–gel entrapped pre-catalysts gives emulsion/sol–gel transport systems (EST) [6] applicable to some different hydrogen transfer processes and to C–C couplings of water-insoluble substrates. We now find that in the presence of the palladium acetate pre-catalyst the EST system is also applicable to catalytic transfer hydrogenation reactions of a variety of lipophilic acceptors from water insoluble donors. The reactions shown in Schemes 1-6a were usually very efficient. Except for a few exceptions, the turnover frequencies (TOF) were between 100 and 5200 h^{-1}. The turnover numbers (TON) extended under our conditions to 1300 and the catalyst could be recycled easily.

In the absence of a surfactant the formation of the microemulsions did not take place (checked by the laser light scattering analysis) and consequently the heterogenized catalyst failed to promote any transfer hydrogenation.

2. Experimental

2.1. Instruments

NMR spectra were recorded with either a Bruker DRX-400 or a Bruker Avance II 500 in $CDCl_3$. Infrared spectra were obtained with a Perkin-Elmer 65 FTIR spectrometer. Mass spectral measurements were performed with a Q-TOF-II spectrometer. ICP-MS analyses were carried out with a Perkin-Elmer model Elan DRC II instrument. Gas chromatographic separations and analyses were carried out on a Hewlett Packard model Agilent 4890D equipped with either a 30 m long column packed with Carbowax 20 M-poly(ethylene glycol) in fused silica (Supelco 25301-U) or with a 15 m long column

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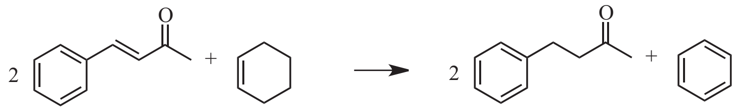
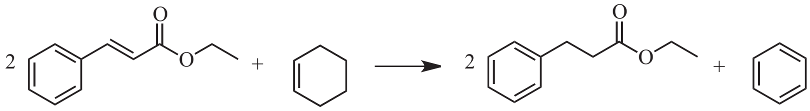
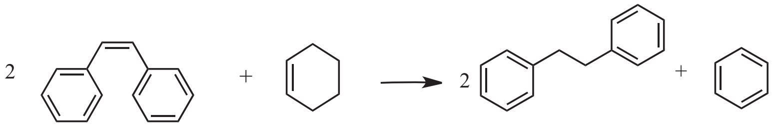


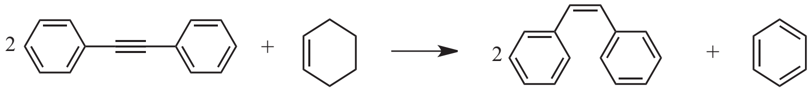
Scheme 1. Transfer hydrogenation of benzylidene acetone.



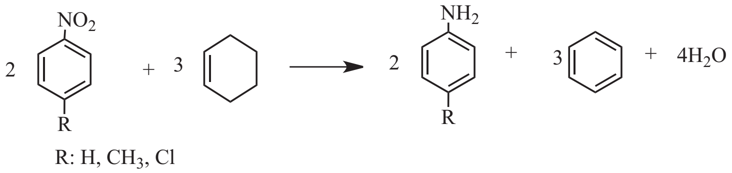
Scheme 2. Transfer hydrogenation of ethyl cinnamate.



Scheme 3. Transfer hydrogenation of (*Z*)-stilbene.



Scheme 4. Transfer hydrogenation of diphenylacetylene.



Scheme 5. Transfer hydrogenation of some nitrobenzene derivatives.

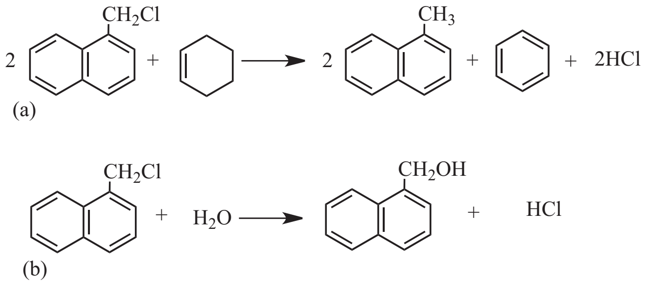
packed with a bonded crosslinked (5% phenyl) methylpolysiloxane [HP-5]. XPS measurements were performed with a Kratos Axis ultra X-ray photoelectron spectrometer. The spectra were acquired with monochromated AlKα (1486.7 eV) X-ray source with 0° take off angle. The pressure in the test chamber was maintained at 1.5×10^{-9} Torr during the acquisition process. High resolution XPS scans were collected for Pd 3d and C 1s peaks with pass energy of 20 eV. The XPS binding energy was calibrated with respect to the peak position of C 1s as 285.0 eV. Data analysis was performed with Vision processing data reduction software (Kratos Analytica Ltd. and Casa SPX Software Ltd.). Transmission electron microscopy (TEM) was done with a Scanning Transmission Electron Microscope Technai G^2 F20 (FEI Company, USA) operated at 200 kV and equipped with an EDAX-EDS device for identification of the elemental composition. Initial powders were dispersed in ethanol and dropped onto a standard 400 mesh carbon coated copper TEM grid.

2.2. Chemicals

All the substrates and reference compounds, as well as palladium acetate, cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) were purchased from the Sigma–Aldrich Company. Tetramethoxysilane (TMOS), propyltrimethoxysilane (PTMOS), octyltriethoxysilane (OTEOS) and phenyltriethoxysilane (PhTEOS) were obtained from ABCR (Glest, Inc.). Sodium dodecyl sulfate (SDS) was purchased from Riedel de Haën. C_{12}–C_{14} alcohols polyoxyethyleneglycol ethers (7-EO-Marlipal 24/70) was obtained from the Sasol Company.

2.3. Preparation of the heterogenized palladium catalyst

Typically, the alkoxysilane $RSi(OR^1)_3$, where $R = n\text{-}C_3H_7$ or $n\text{-}C_8H_{17}$ and R^1 = Et or Me (6.68 mmol), was hydrolyzed by stirring with a mixture of EtOH (73 mmol) and triply distilled water (TDW, 22 mmol) for 24 h. Separately TMOS (3.6 ml, 24.2 mmol) was hydrolyzed with TDW (2.0 ml) by stirring for 10 min. The solutions of the two hydrolyzed silicon compounds were united and stirred magnetically for 10 min at 25 °C and added to a solution of $Pd(OAc)_2$ (30 mg, 0.134 mmol in 4 ml CH_2Cl_2). The stirring was



Scheme 6. (a) Palladium catalyzed transformations of 1-chloromethylnaphthalene in aqueous microemulsion by cyclohexene. (b) Hydrolysis of 1-chloromethylnaphthalene in the aqueous medium.

continued until the gelation was completed (usually 1–3 days). The resulting gel was dried for 24 h at 100 °C and 0.1–0.5 Torr. Then it was washed and sonicated with warm CH_2Cl_2 (3× 10 ml) and redried to obtain a constant weight. For the entrapment of the palladium compound within phenylated sol–gel, the TMOS and PhTEOS could be hydrolyzed together in the same vessel for 24 h. The organic solvent used to wash the sol–gel and the dried sol–gel material was subjected to ICP-MS analyses. The exact palladium content of the sol–gel matrix was calculated from these analyses.

2.4. *General procedure for the transfer hydrogenation process*

Typically, to a stirred mixture (stirring rate 400 rpm) of the unsaturated hydrogen acceptor (0.893 mmol) and the hydrogen donor (3.572 mmol), calculated to make the combination of the acceptor and the donor 1.65 wt.% of the emulsion, was added in a preheated pressure tube (or a mini-autoclave) with a mixture of a surfactant (3.27 wt.%), a co-surfactant (usually 1-PrOH, 6.54 wt.%) and TDW (88.54 wt.%). In most cases, this operation formed transparent microemulsions that dispersed laser beams. To this mixture was added the immobilized palladium pre-catalyst (containing e.g., 0.067 mmol Pd). Following this addition the reaction vessel was heated up to the desired reaction temperature. After the desired reaction period the reaction mixture was cooled to 20 °C and the sol–gel material was filtered off. The filtrate was separated into two phases by addition of NaCl (2 g). The solid material was sonicated with hexane (8 ml) and the aqueous layer of the filtrate was extracted with hexane (2× 8 ml). The combined organic layers were dried ($MgSO_4$) concentrated and analyzed by GC and ^1H NMR. Some of the products were separated by column chromatography. The used catalyst was dried over P_2O_5 and reused in further runs.

3. Results and discussion

We chose benzylidene acetone, ethyl cinnamate, (*Z*)-stilbene, nitrobenzene, diphenylacetylene and 1-chloromethylnaphthalene as representative hydrogen acceptors and cyclohexene, S(−)-limonene, rac-α-phellandrene and tetralin as typical lipophilic hydrogen donors. Palladium acetate which is known to be converted into recyclable Pd(0) nanoparticles during its entrapment within sol–gel materials [10], has been used as our standard pre-catalyst. For the solubilization of the water-insoluble reaction components, we used differently charged, micelle-forming surfactants: Anionic (SDS), cationic (CTAB, DTAB) as well as the non-ionic Marlipal 24/70. Suitable reaction conditions that led usually to quantitative transfer hydrogenation of the aforementioned hydrogen acceptors were achieved by heating the microemulsified substrates for 0.25–6 h together with the cyclohexene at 140 °C (the ratio of acceptor/donor was ∼1/4). Under standard conditions the molar ratio catalyst/acceptor was 7.5/92.5 and the surfactant, together with the co-surfactant were 3.3 wt.% of the microemulsion. A detailed study with the different types of surfactants is summarized in Table 1.

Table 1 indicates that in most cases, the non-ionic surfactant is the most efficient one. Generally, though not always, SDS is second in its efficiency. The cationic surfactants have shown usually the lowest activity. Among the two cationic surfactants investigated, the shorter C_{12}-based one, DTAB, proved more efficient than the C_{16}-CTAB compound. This order of efficiency resembles the order observed in the disproportionation of dihydroarenes by a rhodium (but not by a palladium) catalyst [10], and differs from the order in some other hydrogen transfer reactions [9] and in catalytic C–C couplings in microemulsions [7]. Since the substrates in the EST system have to penetrate the pores of the sol–gel in which the catalyst is located, the bulkiness of the hydrogen acceptor plays an important role on the efficiency of the reaction (cf. e.g., entries 13, 17

Table 1

Dependence of the transfer hydrogenation of hydrophobic acceptors in aqueous microemulsion on the nature of the surfactant.[a]

	Entry substrate (H-acceptor)	Surfactant[b]	Reaction times, h	Products (yield, %)[c]
1	Benzylideneacetone	CTAB	1	1-Phenyl-3-butanone (42)
2	Benzylideneacetone	DTAB	1	1-Phenyl-3-butanone (60)
3	Benzylideneacetone	SDS	1	1-Phenyl-3-butanone (40)
4	Benzylideneacetone	Marlipal	1	1-Phenyl-3-butanone (100)
5	Ethyl cinnamate	CTAB	0.5	Ethyl 3-phenylpropionate (51)
6	Ethyl cinnamate	DTAB	0.5	Ethyl 3-phenylpropionate (55)
7	Ethyl cinnamate	SDS	0.25	Ethyl 3-phenylpropionate (37)
8	Ethyl cinnamate	Marlipal	0.25	Ethyl 3-phenylpropionate (100)
9	(*Z*)-Stilbene	CTAB	0.5	Bibenzyl (59)
10	(*Z*)-Stilbene	DTAB	0.5	Bibenzyl (51)
11	(*Z*)-Stilbene	SDS	0.5	Bibenzyl (80)
12	(*Z*)-Stilbene	Marlipal	0.5	Bibenzyl (74)
13	Nitrobenzene	CTAB	3	Aniline (49)
14	Nitrobenzene	DTAB	3	Aniline (92)
15	Nitrobenzene	SDS	1	Aniline (72)
16	Nitrobenzene	Marlipal	1	Aniline (75)
17	4-Chloronitrobenzene	CTAB	3	1-Chloroaniline (23)
18	4-Nitrotoluene	CTAB	3	4-Toluidine (5)
19	1-Chloromethylnaphthalene	CTAB	4	1-Methylnapthalene (45) 1-Napthalenemethanol (36)
20	1-Chloromethylnaphthalene	DTAB	4	1-Methylnapthalene (39) 1-Napthalenemethanol (49)
21	1-Chloromethylnaphthalene	SDS	4	1-Methylnapthalene (67) 1-Napthalenemethanol (16)
22	1-Chloromethylnaphthalene	Marlipal	4	1-Methylnapthalene (86) 1-Napthalenemethanol (12)

[a] Reaction conditions: a microemulsion of the unsaturated substrate (0.893 mmol), cyclohexene (3.572 mmol), the triply distilled water (adjusted to 88.54 wt.% while the acceptor + the donor were 1.65 wt.%), surfactant (adjusted to 3.27 wt.%), 1-propanol (6.54 wt.%), $Pd(OAc)_2$ (15 mg, 0.067 mmol) entrapped within octylated silica sol–gel [prepared from 3.6 TMOS and 2.1 ml OTEOS], 140 °C.

[b] For the meaning of the abbreviations see Section 2.2. “Marlipal” refers to Marlipal 24/70.

[c] The yields were deduced from GC and ^1H NMR analyses and were average of at least two experiments that did not differ by more than ±3%.

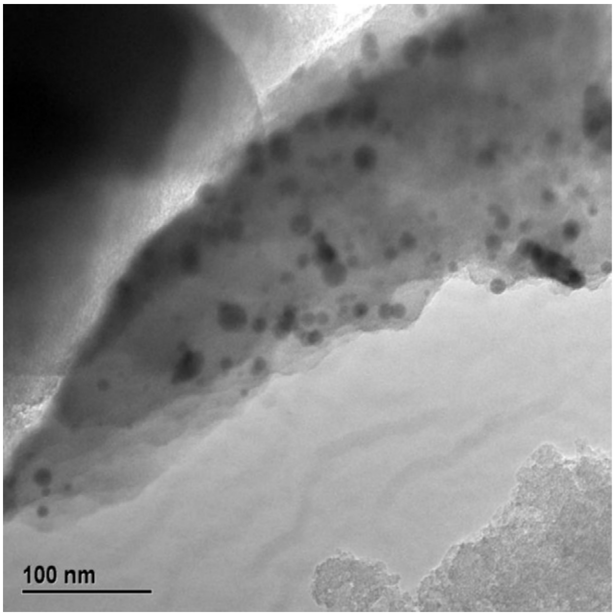


Fig. 1. TEM micrograph of a typical silica sol–gel support section after transfer hydrogenation of (*Z*)-stilbene by cyclohexene at 140 °C under EST conditions.

and 18 in Table 1). Thus, unsubstituted nitrobenzene reacts faster than both bulkier electron rich and electron poor derivatives of the nitro-compound.

Transfer hydrogenation of C–C double bonds (as for example (*Z*)-stilbene, Table 1 entries 9–12) leads readily to the formation of the saturated hydrocarbon, bibenzyl. The analogous alkyne (e.g., diphenylacetylene) is however converted initially into (*Z*)-stilbene and transferred to bibenzyl only after most of the starting alkyne has been consumed. Thus, after 6 h the major products were (*Z*)- and (*E*)-stilbenes (36 and 41, respectively). Only after 24 h the bibenzyl started to accumulate in the reaction mixture.

As mentioned above, a part of the Pd(OAc)$_2$ is transferred under the EST conditions (above ~80 °C) into metallic palladium particles (cf. also the behavior of other metal catalysts [11]). We assume that these particles represent the "true catalyst" in the transfer hydrogenation process. The formation of Pd(0) does not take place at low temperature (<60 °C) nor in the presence of metal-carbonyl ligands. For this reason the Pd(0) could be traced, e.g., when Pd(OAc)$_2$ was used as catalyst under the EST conditions in the regioselective hydroformylation of styrene derivatives at 50 °C [12]. The part of the sol–gel-entrapped palladium salt that had not been converted into metallic particles during its entrapment is reduced at the beginning of the first catalytic run. Consequently, a short induction period is usually observed in the initial stage of the first catalytic process. The metallic particles formed during the entrapment in the sol–gel matrix and those produced during the transfer hydrogenation in the first run differ in their sizes [13]. While the aggregates formed before the catalytic reaction are mostly between 40 and 50 nm, the diameters of the particles that are added during the transfer hydrogenation [of (*Z*)-stilbene] are of the order of 5–8 nm (see Fig. 1, which exhibits the images of both kinds of the dark metallic palladium particles).

The oxidation state of the palladium species before and after the catalyst reactions were studied by X-ray photoelectron spectroscopy (XPS). The starting non-encaged Pd(OAc)$_2$ revealed binding energy peaks (BE) centered at 336.80 and 342.11 eV which are typical for Pd(II) 3d$_{5/2}$ and Pd(II) 3d$_{3/2}$ species [14]. During the entrapment process these BE peaks disappear almost completely forming new signals centered at 335.55 and 340.81 eV which are characteristic for palladium 3d$_{5/2}$ and 3d$_{3/2}$ of Pd(0) [15]. At this stage of our research we were unable to provide clear evidence for the exact kind of the metallic particles which are responsible for the catalytic transfer hydrogenations and to what extent.

Another major factor which has been found to influence the transfer hydrogenation is the hydrophobicity of the sol–gel support in which the pre-catalyst had been entrapped. Non-hydrophobicized silica sol–gel usually caused metal leaching together with the formation of catalytically inactive metal mirrors. We have investigated three types of hydrophobic sol–gel matrices: one which was doped with n-propyl moieties by co-polycondensation of TMOS (78%) with PTMOS (22%); the second one was hydrophobicized with n-octyl groups (using 22% OTEOS), and the third one was modified with phenyl moieties (by 22% PhTEOS). As in the case of the isomerization of some allylarenes by a rhodium pre-catalyst [9] (but opposite to the disproportion of dihydroarnes, and to the Suzuki and Heck reactions in aqueous microemulsions [7,10]), the doping of the support with propyl groups led to the highest activity and by the phenyl functions to the lowest. Transfer hydrogenation of nitrobenzene in the presence of phenylated sol–gel did not take place at all.

Table 2
Dependence of the transfer hydrogenation of unsaturated hydrogen acceptors under EST conditions on the hydrophobicity of the sol–gel support.[a]

Entry	Substrate (H-acceptor)	Sol–gel hydrophobic moiety	Reaction time, h	Products (yield, %)[b]
1	Benzylidene acetone	n-C_3H_7	1	1-Pheny-3-butanone (97)
2	Benzylidene acetone	n-C_8H_{17}	1	1-Pheny-3-butanone (42)
3	Benzylidene acetone	C_6H_5	1	1-Pheny-3-butanone (19)
4	Ethyl cinnamate	n-C_3H_7	0.5	Ethyl 3-phenylpropionate (49)
5	Ethyl cinnamate	n-C_8H_{17}	0.5	Ethyl 3-phenylpropionate (51)
6	Ethyl cinnamate	C_6H_5	0.5	Ethyl 3-phenylpropionate (21)
7	(*Z*)-Stilbene	n-C_3H_7	4	Bibenzyl (100)
8	(*Z*)-Stilbene	n-C_8H_{17}	2	Bibenzyl (96)
9	(*Z*)-Stilbene	C_6H_5	4	Bibenzyl (79)
10	Nitrobenzene	n-C_3H_7	3	Aniline (100)
11	Nitrobenzene	n-C_8H_{17}	3	Aniline (49)
12	Nitrobenzene	C_6H_5	3	Aniline (0)
13	1-Chloromethylnaphthalene	n-C_3H_7	4	1-Methylnaphthalene (37) 1-Naphthalenemethanol (40)
14	1-Chloromethylnaphthalene	n-C_8H_{17}	4	1-Methylnaphthalene (32) 1-Naphthalenemethanol (49)
15	1-Chloromethylnaphthalene	C_6H_5	4	1-Methylnaphthalene (18) 1-Naphthalenemethanol (43)

[a] Reaction conditions as in Table 1, except that the sol–gel support was prepared from 78% TMOS and 22% RSi(OR^1)$_3$ where R = n-C_3H_7, n-C_8H_{17} or C_6H_5 and R^1 = CH_3 or C_2H_5 and the surfactant was CTAB.

[b] The yields were the average of at least two experiments that did not differ by more than ±3%.

Except for the disproportionation of dihydroarenes, where, we noticed very slow hydrogen exchange between a substrate and the water [10], we have not yet observed any participation of the aqueous medium of the EST system in the catalytic reactions. However, now we have found that during the transfer hydrogenation of 1-chloromethylnaphthalene (Scheme 6a) that undergoes easy hydrolysis (Scheme 6b), part of the substrate reacts with the aqueous medium to form 1-naphthalenemethanol (Table 2, entries 13–15).

As in all other catalyses under EST conditions studied so far, the catalyst could be recycled for several runs. The metallic particles generated during the transfer hydrogenations listed in Table 1, entries 1–18 proved recyclable. They could be isolated and reused at least 4–6 times, without significant loss of their catalytic potencies. Thereafter the catalytic activity drops gradually in most cases. For example, in the transfer hydrogenation of (*Z*)-stilbene under the conditions of Table 2 entry 7, the yields of bibenzyl in the presence of CTAB for 2.5 h were in the first five runs 97, 97, 96, 93 and 58%. The drop in the activity has often been observed when the pores in the sol–gel become clogged by the substrates and/or the products [16].

Replacement of the cyclohexene by some other well known lipophilic hydrogen donors proved to be less efficient. The transfer hydrogenation of (*Z*)-stilbene that yields 96% of bibenzyl after 2 h at 140 °C, dropped to 34, 5 and 2%, respectively, under the same conditions when α-phellandrene, tetralin and rac-limonene were employed.

Finally, it should be noted that transfer hydrogenation is often substantially enhanced by the addition of a base [17]. Under our conditions however, the addition of either $KHCO_3$ or K_2CO_3 has only a marginal effect. We assume that the reactions in microemulsions differ in their mechanism from that in other media. Therefore, our reactions were performed in the absence of an added base.

4. Conclusions

Transfer hydrogenation of the water-insoluble alkenes, alkynes, α,β-unsaturated ketones and esters, and nitroarenes by cyclohexene takes place in a selective manner in aqueous microemulsion at 100–140 °C in the presence of sol–gel entrapped palladium acetate. During the entrapment process and during the first catalytic cycle, the palladium compound is reduced to metallic particles. These particles can be recycled 4–6 times without seriously affecting their catalytic potencies. Thus, we regard the ligand-free metallic particles as the true catalyst in the “green” hydrogenation process. In comparison to the molecular hydrogenation, a big advantage of the transfer hydrogenation process is that there is no need for high hydrogen pressures to overcome the mass-transport-limitations due to the low hydrogen concentration at higher temperatures. Furthermore, the concentration of the hydrogen donor and the transferred molecules of hydrogen can be easily adjusted to the concentration of the substrate. Although the transfer hydrogenation in aqueous microemulsions is applicable to many water-insoluble acceptors, the latter should be inert to water. Water-sensitive substrates as, for example, benzylic halides form in addition to the hydrogenated products, also, the hydrolyzed compounds.

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References

[1] A. Robertson, T. Matsumoto, S. Ogo, Dalton Trans. 40 (2011) 10304–10310, and references cited therein.
[2] B. Cornils, W.A. Herrmann, Aqueous Phase Organometallic Catalysis: Concepts and Applications, Wiley-VCH, Weinheim, 2004.
[3] U.M. Lindström (Ed.), Org. Reactions in Water: Principles Strategies and Applications, Blackwell Publishing, Singapore, 2007.
[4] S. Kobayashi (Ed.), Water in Organic Synthesis, vol. 1, Thieme, Stuttgart, 2012.
[5] R. Abu-Reziq, D. Avnir, J. Blum, Angew. Chem. Int. Ed. 41 (2002) 4132–4134.
[6] R. Abu-Reziq, D. Avnir, Chem. Eur. J. 10 (2004) 958–962.
[7] A. Rozin-Ben Baruch, D. Tsvelikhovsky, M. Schwarze, R. Schomäcker, M. Fanun, J. Blum, J. Mol. Catal. A: Chem. 323 (2010) 65–69.
[8] D. Tsvelikhovsky, J. Blum, Eur. J. Org. Chem. (2008) 2417–2422.
[9] D. Meltzer, D. Avnir, M. Fanun, V. Gutkin, I. Popov, R. Schomäcker, M. Schwarze, J. Blum, J. Mol. Catal. A: Chem. 335 (2011) 8–13.
[10] T. Yosef, R. Schomäcker, M. Schwarze, M. Fanun, F. Gelman, J. Blum, J. Mol. Catal. A: Chem. 351 (2011) 46–51.
[11] F. Alonso, P. Rente, H. Yus, Acc. Chem. Res. 44 (2011) 379–391.
[12] Z. Nairoukh, J. Blum, J. Mol. Catal. A: Chem. 358 (2012) 129–133.
[13] D. Tsvelikhovsky, I. Popov, V. Gutkin, A. Rozin, A. Shvartsman, J. Blum, Eur. J. Org. Chem. (2009) 98–102.
[14] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, J. Catal. 114 (1988) 23–33.
[15] R.J. Bird, P. Swift, J. Electron Spectrosc. Relat. Phenom. 21 (1980) 227–240.
[16] J. Blum, D. Avnir, in: S. Sakka (Ed.), Handbook of Sol–Gel Science and Technology (Chapter 24), vol. 3, Kluwer Scientific Publishers, Boston, 2005, pp. 507–526.
[17] W. Baratta, K. Siega, P. Rigo, Chem. Eur. J. 13 (2007) 7479–7486.