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Letter

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Selective Hydrogenation of Carboxylic Acids to Alcohols or Alkanes Employing a Heterogeneous Catalyst

*Johannes Ullrich and Bernhard Breit**

Institut für Organische Chemie

Albert-Ludwigs Universität Freiburg

Albertstraße 21, 79104 Freiburg i. Brg., Germany

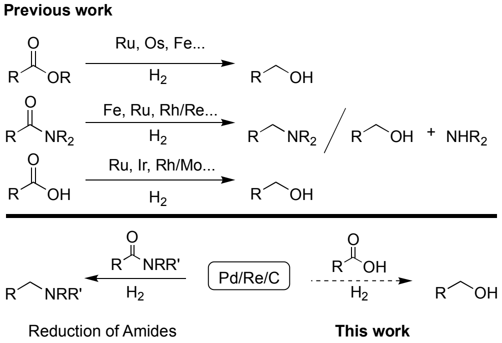
Abstract: The chemoselective hydrogenation of carboxylic acids to either alcohols or alkanes is reported employing a heterogeneous bimetallic catalyst consisting of rhenium and palladium supported on graphite. α-Chiral carboxylic acids were hydrogenated without loss of optical purity. The catalyst displays a reverse order of reactivity upon hydrogenation of different carboxylic functions with esters being less reactive than amides and carboxylic acids. This allows for chemoselective hydrogenation of an acid in the presence of an ester or an amide function.

Keywords: Hydrogenation • Heterogeneous • Carboxylic acid • Alcohol • Alkane

Alcohols are important building blocks for the fine chemical industry and in laboratory synthesis. Among the many ways of their synthesis reduction of carboxylic acids and their derivatives employing stoichiometric amounts of metal hydrides is a reliable and common procedure. However, disadvantages are safety issues as well as generation of stoichiometric amounts of waste. A “greener“, more attractive solution to this problem would be a catalytic reduction using molecular hydrogen. In particular, the catalytic hydrogenation of esters[1] and amides[2] has seen a lot of progress in the past and a variety of efficient catalytic systems were found to generate the respective alcohols or amines under convenient reaction conditions (Scheme 1).

Carboxylic acids are abundant building blocks available also from bio mass resources (e.g. fatty acids) but their hydrogenation has been found to be more difficult. Nevertheless, several homogeneous catalyst systems for acid to alcohol hydrogenation have been reported based on different transition metals such as Cu, Cd, Ru, Rh/Mo, Ru/Mo, Ir, Re or Co.[2i, 3] From a practical point of view heterogeneous catalysts are advantageous, since they allow for easy substrate separation through filtration. Indeed, research on heterogeneous catalytic hydrogenation of carboxylic acids reaches back to the early 20th century when Norman and Schrauth reported about Ni/Cu catalysts almost simultaneously.[4,5] A number of subsequent reports mirrors the high interest in this field, with rhenium being a very frequent metal, [6h-k] especially as part of synergistic compositions of two or three metals.[6a-g] However, all reported catalyst systems share the disadvantage for the need of harsh reaction conditions such as high reaction temperatures and/or high pressure of hydrogen gas.

We recently reported, that amides could be hydrogenated to the corresponding amines under mild reaction conditions applying a heterogeneous catalyst consisting of 2 w% palladium and 10 w% rhenium supported on high surface area graphite (HSAG).[7] We herein report that the same catalyst allows for hydrogenation of carboxylic acids to give either alcohols or alkanes, respectively.



Scheme 1. Hydrogenation of carboxylic acids and its derivatives.

The catalyst was prepared by sequential incipient wetness impregnation of activated HSAG with [$Pd(NO_3)_2$] and [Re_2O_7].[8] The final catalyst composition was confirmed by EDX (energy dispersive X-ray spectroscopy). The surface was measured by N_2-adsorption/desorption to be 19.6 m^2/g according to BET. Following our interest in the oxidation state of the metals we performed XPS (X-ray photoelectron spectroscopy) measurements of the catalyst before and after treatment with hydrogen (Figure 1). For evaluation, the resulting binding energies (BE) were compared with the literature. The spectrum of the native catalyst shows two distinct peaks for the $3d_{3/2}$ and the $3d_{5/2}$ signals of Pd(II) and $4f_{5/2}$ and $4f_{7/2}$ of Re(VII), proving that both metals are still oxidized. After hydrogenation, the Pd $3d_{5/2}$ signal shifted from 337.7 eV to 335.7 eV, indicating that the palladium was reduced from Pd(II) to Pd(0). For the rhenium signals however, no shift could be observed, implying that the oxidated rhenium is the active species. It might therefore act as a Lewis acid, though its exact role in the catalytic process cannot be elucidated.

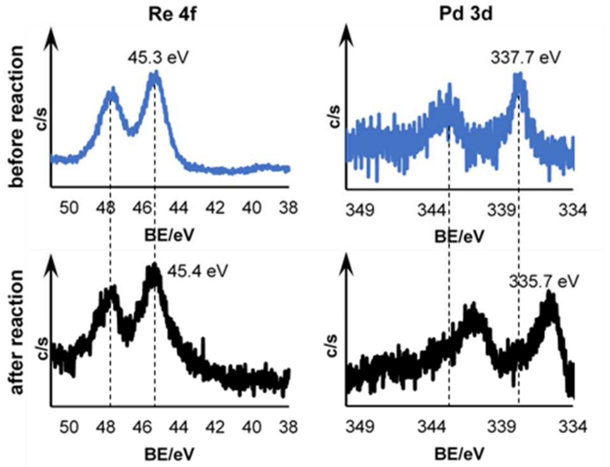
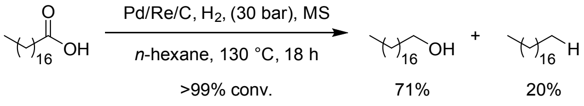


Figure 1. Binding Energies (BE) of Re and Pd in XPS before reaction (top line) and after reaction (bottom line) with hydrogen.

Initial reactivity assays were performed with stearic acid. To our delight we obtained the desired alcohol in promising yields (Scheme 2). However, while optimizing the reaction conditions,[8] we also observed significant amounts of the deoxygenated alkane, a sort of defunctionalisation that has been reported by others as well.[6e,9,10]



Scheme 2. Reduction of stearic acid (MS: molecular sieve, 4 Å).

To gain more insight into that process, we monitored the reaction kinetics of this hydrogenation via GC (Figure 2).[8] For a more convenient GC-analysis (higher volatility of products) octanoic acid was chosen a substrate. The conversion was determined after transforming the starting material to its methyl ester by addition of TMS-diazomethane. Temperature and pressure were selected such that the measurement could be performed in a reasonable time frame. During the first two hours of the reaction the alcohol as the primary product is formed with the starting material simultaneously decreasing. Interestingly, only when all of the starting material (carboxylic acid) was consumed the hydrogenation of the alcohol to furnish the corresponding alkane started to proceed. After six hours of reaction time the alcohol was entirely consumed leaving only the alkane as the final product. This profile allows for two conclusions: First, it shows that the alkane is generated from the alcohol and not in a parallel reaction pathway. Secondly, it seems as that the presence of carboxylic acid substrate suppresses hydrogenation of the alcohol to the alkane.[11]

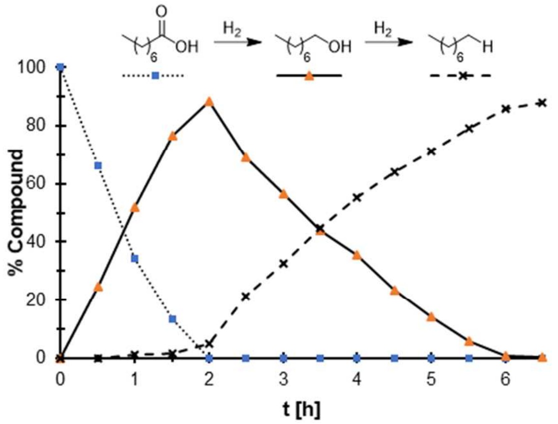
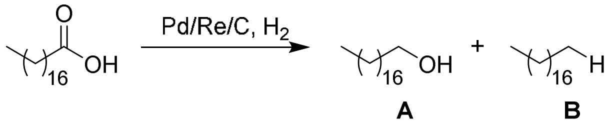


Figure 2. Hydrogenation profile of octanoic acid, conditions: 3 mmol octanoic acid, 2 mol% Pd/ 7 mol% Re, *n*-hexane (0.2 M), 160 °C, H_2 (30 bar).

We next explored the influence of reaction temperature, pressure and solvent (Table 1).[8] Thus, optimal yields for the alcohol reduction product were obtained at 130 °C and 20 bar hydrogen pressure (entry 2). Changing to ethereal solvents led to strong decrease of conversion (entries 6, 7), which has been reported for the heterogeneous hydrogenation of amides as well.[2f] The superior solvation properties of aliphatic solvents for hydrogen could explain that observation.[12] Using these conditions in a catalyst recycling experiment revealed a significant drop in conversion to 36% after four runs (for more information see SI), which is an aspect of this system, that still needs to be improved. During these optimization studies, we also performed reactions with single metal catalysts containing either only supported palladium or rhenium, respectively. While there was almost no conversion for Pd/C, the catalyst Re/C showed at least some, therefore confirming the already reported hydrogenation capability of rheniumoxides. It also emphasizes the synergistic effect of the bimetallic mixture, though the exact contribution of each compound remains subject for further investigations. So far, we can state that palladium is known for activating molecular hydrogen at low pressures und temperatures while obviously being unsuitable for carboxylic acid activation, whereas Rhenium(oxide) on the other hand is in principle able to do both. Hence, it can be assumed that its main role in the reaction is to activate the acid while palladium provides the activated hydrogen.

Table 1. Optimizing reaction conditions.[a]

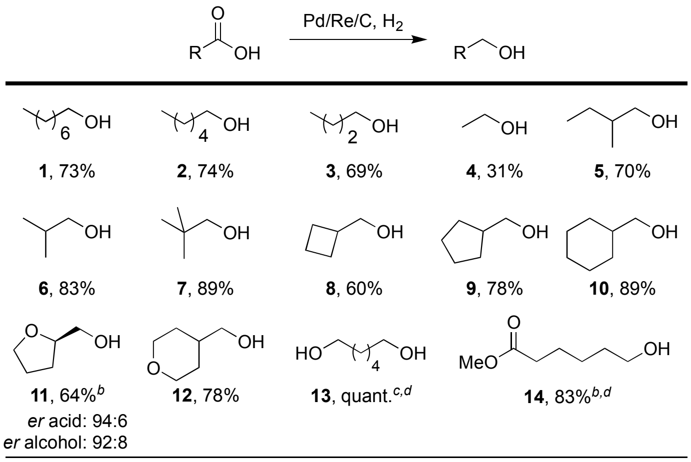


#	T [°C]	p [bar]	Solvent	% conv.	% **A**	%**B**
1	140	20	*n*-Hex	100	70	20
2	130	20	*n*-Hex	100	87	Traces
3	120	20	*n*-Hex	41	34	Traces
4	130	10	*n*-Hex	69	56	Traces
5	130	30	*n*-Hex	100	71	20
6	130	20	DME	0	0	0
7	130	20	THF	46	44	0
8[b]	130	20	H_2O	72	15	0

[a] 1 mmol substrate, 2 mol% Pd/7 mol% Re, solvent (0.2 M), 18 h, 200 mg MS 4 Å, [b] 56% ester from starting material and product alcohol

With optimized reaction conditions in hand we set out to test the reduction of a series of carboxylic acids to the alcohol (Table 2). Primary aliphatic acids could be reduced in good yields (**1-4**) with the yield only dropping in the case of acetic acid **4**, which is likely to happen during depressurization due to the volatility of the product. Different secondary and tertiary acids with cyclic or acyclic structures were smoothly hydrogenated (**5-12**). If the secondary center is part of a carbocycle, the yields increased from 4- to 6-membered rings (**8**-**10**). Heteroatoms within the ring are tolerated (**11** and **12**), but seem to lower the yield. Interestingly tetrahydrofuranyl alcohol **11**, obtained from hydrogenation of enantiomerically enriched starting material, was obtained without loss or optical purity. This structural motif **11** is prevalent in several medicinally relevant inhibitors.[13] A diacid such as adipic acid could be reduced to the diol **13** in quantitative yield. Such diols are valuable monomers for polymer chemistry.[14] Interestingly, hydrogenation of mono-methyl adipate furnished the alcohol **14** while the ester function remained untouched. This represents another result, where the earlier stated reactivity order of carboxylic acid derivatives in hydrogenation[15] is questioned. Other examples have been reported by different groups in homogeneous[3k] as well as heterogeneous hydrogenations. [6b, 6k]

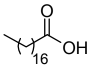
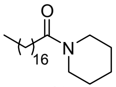
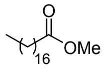
Table 2. Hydrogenation of saturated carboxylic acids[a]



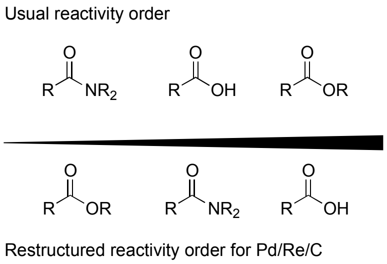
[a] 1 mmol substrate, 2 mol% Pd/ 7 mol% Re, *n*-hexane (0.2 M), 130 °C, 20 bar H_2, 18 h, 200 mg MS 4 Å, all yields are GC-yields using *n*-decane or *n*-dodecane as internal standard, [b] reaction in THF, [c] H_2O, 160 °C, 30 bar, [d] isolated yield.

Interested in this behaviour we had a closer look into reactivity differences with respect to hydrogenation between carboxylic acids, esters and amide functions (Table 3). As test substrates we chose stearic acid **15**, its amide **16** derived from piperidine and its methylester **17**. Each of these compounds was subjected to the standard conditions from table 1 (cond. A) as well as more harsh ones (cond. B). The crude mixtures were analysed for their conversion to the alcohols/alkanes in the case of acid and ester or the respective amine in the case of the amide. From table 3 it is evident that the substrate reactivity upon hydrogenation with the Pd/Re/C catalyst decreases from the carboxylic acid over the amide to the ester (Scheme 3).

Table 3. Hydrogenation of carboxylic acid derivatives.[a]

Conv. for:	 **15**	 **16**	 **17**
Cond. A[b]	100	41	0
Cond. B[c]	100	100	89

[a]Conv. was determined by NMR with TMB as internal standard, [b]Cond. A: 1 mmol substrate, 2 mol% Pd/ 7 mol% Re, *n*-hex (0.2 M), 130 °C, 20 bar H_2, 18 h, 200 mg MS 4 Å, [c]Cond. B: 1 mmol substrate, 2 mol% Pd/ 7 mol% Re, *n*-Hex (0.2 M), 160 °C, 30 bar H_2, 18 h, 200 mg MS 4 Å.

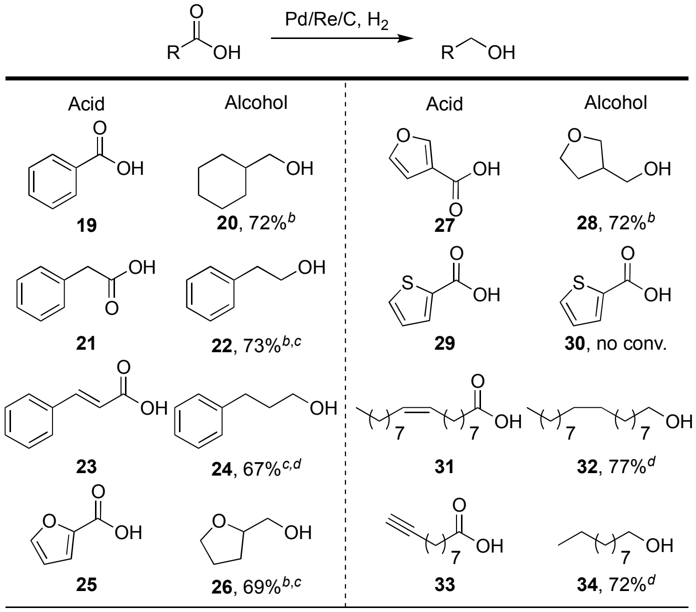


Scheme 3. Reactivity of carboxylic acid derivatives for hydrogenation with the Re/Pd/C catalyst system.

When attempting the reduction of benzoic acid **19** (Table 4), we observed reduction of the acid commitend with hydrogenation of the phenyl ring. However, employing homologeous phenylacetic acid **21**, hydrogenation furnished the alcohol **22** with the phenyl-substituent untouched. Hydrogenation of cinnamic acid **23** led to alcohol **24**. Thus, alkene and carboxylic acid function were hydrogenated. This result indicates that the alkene might be reduced most easily, which leaves the carboxylic acid separated from the phenyl substituent by an alkyl spacer similar to **21**. Furoic acids **25** and **27** were converted to the saturated alcohols **26** and **28**, respectively. Conversely, 2-thiophene carboxylic acid **29** showed no reactivity at all. In a control experiment, stearic acid **15** was attempted to hydrogenate in the presence of **29**. However, none of the two substrates reacted which may suggest a poisoning effect of sulfur for our catalyst.

Isolated alkene and alkyne functions were hydrogenated as well as shown in the examples of **31** and **33**.

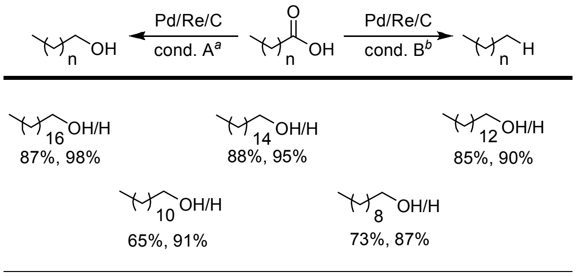
Table 4. Hydrogenation of unsaturated carboxylic acids.[a]



[a]1 mmol substrate, 2 mol% Pd/ 7 mol% Re, *n*-hexane (0.2 M), 130 °C, 20 bar H_2, 18 h, 200 mg MS 4 Å, [b]GC-yield using *n*-decane as internal standard, [c]Solvent: EtOAc, [d]isolated yield.

Long chain fatty acids constitute an attractive class of renewable feedstocks. Besides their usage as carboxylates in soaps and cosmetics[16] they are also further derivatized to alcohols or alkanes which are of high value as lubricants and fuels.[17,18] Regarding our initial hydrogenation profile, we proposed, that it should be possible to generate both alcohols and alkanes chemoselectively by choice of the proper reaction conditions. As illustrated in table 5 we could obtain the alcohols with the general reaction conditions A in good yields. However, increasing reaction temperature and pressure allowed us to obtain the respective alkanes as single products in excellent yields. Hence, our catalyst allows the selective preparation of either the alcohol or the alkane from a single feedstock.

Table 5. Selective hydrogenation of fatty acids to either alcohols or to the alkanes.



^{a}Cond. A: 1 mmol substrate, 2 mol% Pd/ 7 mol%Re, *n*-hexane (0.2 M), 130 °C, 20 bar H_2, 18 h, 200 mg MS 4 Å, ^{b}Cond. B: 1 mmol substrate, 2 mol% Pd/ 7 mol% Re, *n*-hexane (0.2 M), 160 °C, 30 bar H_2, 18 h, 200 mg MS 4 Å, all yields are isolated.

In conclusion, we report on a bimetallic heterogeneous catalyst system consisting of rhenium and palladium supported on HSAG that allows for the selective hydrogenation of carboxylic acids under mild conditions. The reaction allows the inclusion of α-stereocenters without racemization. Aromatic rings can be reduced or retained depending on their structural activation. The pool of natural fatty acids was made accessible for the production of industrially relevant alcohols or alkanes by choosing the appropriate reaction conditions.

AUTHOR INFORMATION

Corresponding Author

E-Mail: bernhard.breit@chemie.uni-freiburg.de

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures and analytical data.

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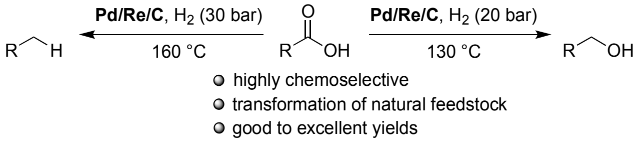
TOC-Graphic:


Pd/Re/C, H2 (30 bar)
160 °C
R
H
O
R
OH
Pd/Re/C, H2 (20 bar)
130 °C
R
OH
highly chemoselective
transformation of natural feedstock
good to excellent yields