



Priority Communication

Metal–support interaction in Pt/alumina: Inversion of diastereoselectivity by tuning the acid–base properties of the support

Erik Schmidt, Fatos Hoxha, Tamas Mallat, Alfons Baiker*

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, HCI, CH-8093 Zürich, Switzerland

ARTICLE INFO

Article history:

Received 14 June 2010

Revised 6 July 2010

Accepted 10 July 2010

Available online 8 August 2010

Keywords:

Metal–support interaction

Diastereoselective hydrogenation

Cinchonidine

Adsorption geometry

ABSTRACT

The role of metal–support interaction in the hydrogenation of cinchonidine (CD) was studied on acid- and base-doped flame-made Pt/alumina. Analysis of the product distribution revealed that on Pt/alumina and Pt/alumina–silica CD adsorbs on Pt in pro(*S*) geometry, but doping the support with only 0.25 wt.% Cs₂O is sufficient to invert the major adsorption mode to pro(*R*). The origin of differences between the effect of an acidic additive and support acidity is discussed.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

Supported metal catalysts are widely used in hydrogenation reactions, and their activity and selectivity can be influenced by the support composition. The origin of the phenomenon has been the topic of intensive research in the past decades [1–3]. The support effect on the electronic properties of Pt particles has been investigated by Koningsberger and co-workers, using X-ray absorption spectroscopy and DFT calculations [4,5]. The shift in the Pt 6s and p and 5d orbitals upon interaction with the support was correlated with a higher Pt–H bond strength on ionic (basic) supports to explain the different activity in hydrogenolysis and hydrogenation reactions. The observation of a decreasing hydrogen coverage on Pt particles supported on zeolites and on promoted Pt/Al₂O₃ of increasing acidity confirmed these predictions experimentally [6,7]. The reactivity of larger molecules on heterogeneous catalysts, however, is more complex. The reason is that the (stereo)selectivity and reactivity depend not only on the adsorption strength but also on the three dimensional orientation of complex, bulky substrates on the metal surface [8,9], which behavior is expected to be influenced by the electronic properties of the metal.

Hydrogenation of the quinoline unit of the natural alkaloid cinchonidine (CD) is the most important side reaction in enantioselective hydrogenations on Pt-group metals, since this part of the molecule “anchors” the chiral modifier close to parallel to the metal surface (π -bound) [10–16]. The analysis of the chemo- and diastereoselectivity in this reaction (Scheme 1) is a unique tool to

investigate in situ the orientation of the alkaloid on the metal surface [17–20]. The most relevant conformations of CD on Pt have been described as the groups of “Surface Open” (SO), “Surface Closed” (SC) as well as “Surface Quinuclidine Bound” (SQB) [21], which can be sub-classified with respect to their prochiral orientation at C(4’).

Here, we report on the effect of support acidity/basicity on the adsorption geometry of CD at the surface of supported Pt nanoparticles. The model catalysts were prepared by a single step flame spray pyrolysis route to minimize the disturbing effect of impurities originating from the catalyst synthesis [22]. The acid/base properties of Pt/Al₂O₃ were fine tuned by doping the support with SiO₂ or Cs₂O [22].

2. Experimental

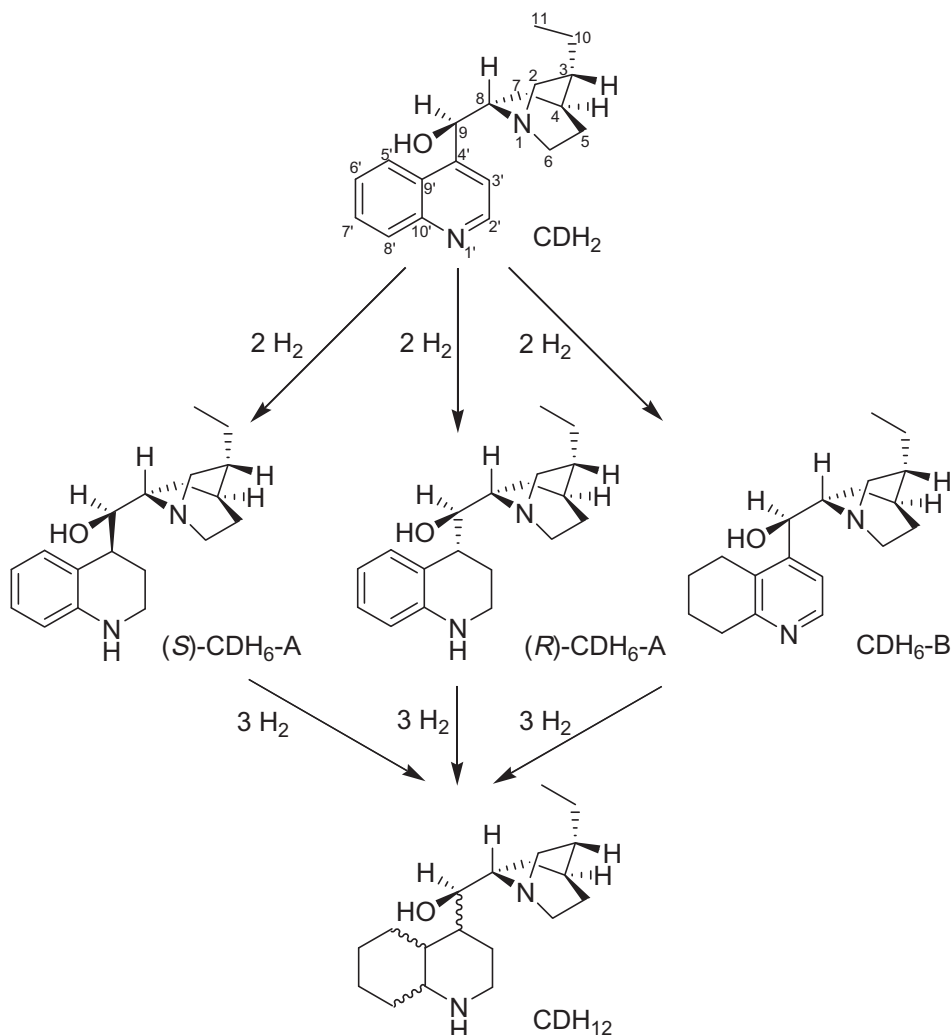
Generally, analytical grade reagents and solvents were used. Toluene (Fluka, >99.7%) was dried over activated molecular sieve 4A; CD (Fluka, >98% alkaloid) was used as received. The 5 wt.% Pt/alumina reference catalyst (Pt/Al₂O₃ (ref)) was purchased from Engelhard (Engelhard 4759).

The preparation and characterization of the model catalysts prepared by flame spray pyrolysis were described elsewhere [22]. Aluminum sec-butoxide (Aldrich, >98%), hexamethyldisiloxane (Fluka, >98%), and cesium acetylacetonate (Fluka) dissolved in 2-ethylhexanoic acid (Aldrich, >98%) were used as precursors. The key characteristics of the catalysts are collected in Table 1.

The catalysts were always pretreated prior to use in a fixed bed reactor. They were heated under flowing nitrogen up to 400 °C in

* Corresponding author.

E-mail address: baiker@chem.ethz.ch (A. Baiker).



Scheme 1. Chemo- and diastereoselective hydrogenation of CDH_2 .

Table 1

Chemical and textural properties of the catalysts (from [22,23]) and the reference Pt/ Al_2O_3 catalyst (from [22]).

Catalyst	Pt content (wt.%)	Promoter in support (wt.%)	BET surface area ($m^2 g^{-1}$)	Average Pt particle size (nm)
Pt/ Al_2O_3	4.7	0	138	1.9
Pt/ Al_2O_3 - Cs_2O	4.7	0.25	208	2.0
Pt/ Al_2O_3 - Cs_2O	4.7	10	227	1.8
Pt/ Al_2O_3 - SiO_2	4.7	10	123	4.3
Pt/ Al_2O_3 - SiO_2	4.7	22.5	136	5.5
Pt/ Al_2O_3 (ref)	5	0	n.d.	6.5

Where n.d. – not determined.

30 min, followed by a reduction in hydrogen for 60 min at the same temperature, and finally cooled down in hydrogen in 30 min.

The catalytic hydrogenations were carried out at 90 bar (constant pressure regulator valve) in either a 25-ml stainless steel Parr autoclave (20 °C) equipped with a 16-ml glass liner and a PTFE cover or in a 50-ml stainless steel reactor and glass liner (−10 °C). Both reactors were magnetically stirred (750 rpm) and equipped with a valve for sample collection. The reaction mixture contained 4 mg (13.6 μ mol) CD, 42 mg of catalyst in 5 ml (20 °C), or 10 ml (−10 °C) of toluene. Samples were taken regularly from the reaction mixture to follow the conversion and selectivity with time.

The samples were at first washed with 0.5 M HCl in water. The pH of the separated aqueous phase was set to 12 with 0.5 M NaOH, before repeated extraction with toluene. The combined organic phases were washed with 0.1 M NaOH saturated with NaCl. Finally, the samples were filtered and analyzed by gas-chromatography (Thermo Quest Trace 2000, HP-5 capillary column, FID). Details on the preparation and characterization of the hydrogenated CD derivatives are given in the supporting information of our former report [17].

3. Results and discussion

The flame-made Pt/ Al_2O_3 , Pt/ Al_2O_3 - SiO_2 and Pt/ Al_2O_3 - Cs_2O catalysts have been characterized by N_2 -adsorption, CO chemisorption, X-ray diffraction, and electron microscopy [22,23]. The highest acidity was determined by TPD of NH_3 for catalysts containing 22.5 wt.% SiO_2 , while the addition of 10 wt.% Cs_2O maximized the basicity as shown by TPD of CO_2 [22]. Promotion with silica barely affected the BET surface area but increased the average Pt particle size (Table 1). The undoped and Cs_2O -doped samples on the other hand exhibited similar Pt particle size. All materials contained more or less spherical-shaped Pt particles, and no significant difference in the surface morphology could be detected by HRTEM and DRIFTS studies of CO adsorption [22,23]. Thus, we suggest that the observed changes in the catalytic performance originate

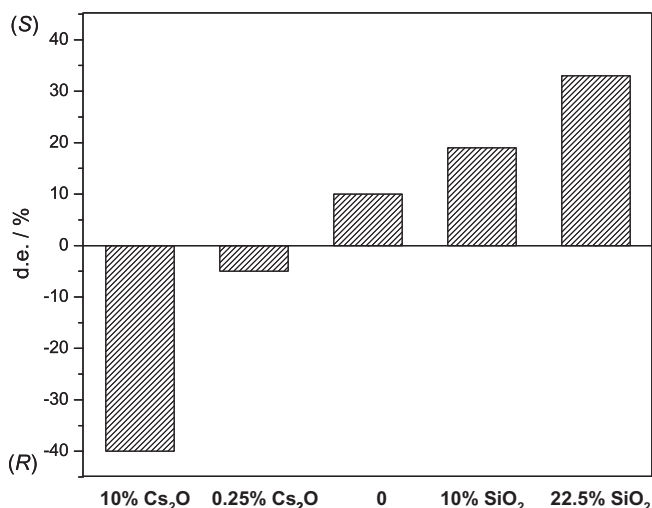


Fig. 1. Diastereomeric excess (d.e.) in the hydrogenation of CDH₂ to CDH₆-A as a function of the promoter content in the alumina support.

mainly from changes in the electronic properties of Pt. The self-prepared catalysts were compared to a commercially available reference catalyst (Pt/Al₂O₃ (ref)), which is widely used in Pt-catalyzed enantioselective hydrogenations. The textural properties and catalytic performance of Pt/Al₂O₃ (ref) in the hydrogenation of CD are also known [17,18].

The orientation of CD was determined by following the diastereoselectivity in the hydrogenation of its quinoline unit. The initial

saturation of the vinyl-group of CD (at C(10)–C(11)) to dihydrocinchonidine (CDH₂, Scheme 1) is very fast compared to the saturation of the quinoline ring and was not followed in detail. The subsequent chemo- and diastereoselective hydrogenation of the quinoline moiety of CDH₂ to the different hexahydrocinchonidines (CDH₆, Scheme 1) is the key reaction step, as it allows getting insight into the conformation of the molecule adsorbed on the Pt surface. The selectivity was determined at 25 ± 5% conversion of CDH₂. This value was sufficient to ensure the complete conversion of CD by hydrogenation of its vinyl-group. On the other hand, the selectivity to the fully hydrogenated CDH₁₂ could be kept below 10% on all catalysts.

The support effect on the diastereomeric excess (d.e.) is shown in Fig. 1, and details including also the kinetic data and the effect of reaction temperature are summarized in Table 2. Both unpromoted catalysts (Pt/Al₂O₃ and Pt/Al₂O₃ (ref)) gave a rather small excess of (S)-CDH₆ (10–15% d.e.), indicating that the impact of their different mean Pt particle size (1.9 vs. 6.5 nm) is minor.

Doping the alumina support with SiO₂ increased the d.e. to (S)-CDH₆-A, and the diastereoselectivity of Pt supported on the most acidic-mixed oxide (22.5 wt.% SiO₂) tripled at –10 °C (Fig. 1). The really surprising observation was that the diastereoselectivity inverted in a considerable extent by doping alumina with 10 wt.% Cs₂O. Already, the addition of only 0.25 wt.% of Cs₂O was sufficient to switch the d.e. from (S)-CDH₆-A to (R)-CDH₆-A. Due to the almost identical Pt particle size of the Cs₂O-doped and undoped Pt/Al₂O₃ (1.9 ± 0.1 nm, Table 1), the observed switch in the preferred diastereomer can unambiguously be attributed to the different electronic properties of Pt [7].

The support effect on the orientation of the alkaloid on Pt during hydrogenation of its heteroaromatic ring is shown in Fig. 2,

Table 2
Reaction rates (TOFs) and selectivities in the hydrogenation of CDH₂.

catalyst	Promoter (wt.%)	Temperature (°C)	TOF (h ⁻¹)	A/B	d.e. (%)
Pt/Al ₂ O ₃	0	–10	0.43	16	10 (S)
		20	5.2	12	11 (S)
Pt/Al ₂ O ₃ -Cs ₂ O	0.25	–10	0.35	20	5 (R)
		20	0.61	39	40 (R)
Pt/Al ₂ O ₃ -SiO ₂	10	–10	0.86	12	19 (S)
		20	6.3	24	19 (R)
Pt/Al ₂ O ₃ -SiO ₂	22.5	–10	0.70	13	33 (S)
		20	7.1	12	21 (S)
Pt/Al ₂ O ₃ (ref)	0	–10	0.66	14	15 (S)

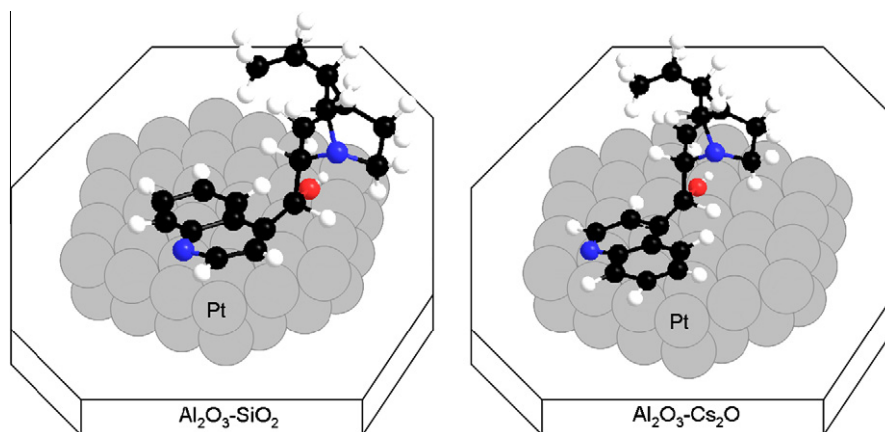


Fig. 2. Schematic drawing of the probable adsorption geometry of CDH₂ on a Pt(1 1 1) model surface located on acidic and basic supports. H – white, C – black, N – blue (gray), O – red (gray). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

using the example of the stable “Surface Open” conformations for illustration. The observation of an excess of (*R*)-CDH₆-A over the Cs₂O-doped catalysts indicates a higher surface coverage of C(4′)-pro(*R*) species (such as the SO(3), SC(2), and SQB(2) conformers [21]), assuming hydrogen uptake from the surface [17,18]. The opposite diastereomer (*S*)-CDH₆-A is formed in excess over the acidic catalysts (Fig. 2), which indicates a preferred C(4′)-pro(*S*) adsorption geometry (SO(4), SC(1), SQB(1) conformers [21]).

The support effect is also observed in the chemoselectivity of the hydrogenation of CDH₂. The A/B ratio given in Table 2 describes the relative amount of homoaromatic hexahydrocinchonidines (CDH₆-A) to the heteroaromatic CDH₆-B (Scheme 1). Moderate selectivities (A/B = 12–16) were found for all Pt/Al₂O₃ and Pt/Al₂O₃-SiO₂ catalysts, but promotion with Cs₂O led to a remarkably bigger difference in the rate of hydrogenation of the aromatic and heteroaromatic rings (A/B = 20–39).

On the other hand, no clear trend was observed regarding the effect of the acid/base properties of the support on the overall rate of CDH₂ conversion. The TOFs given in Table 2 are determined from the slope of the linear part of the conversion vs. time plots and related to the fraction of Pt surface atoms. The estimated error of determination was ±10%. The significant activity differences of the investigated catalysts probably originate from the structure-sensitivity of this reaction [17,24]. The use of SiO₂-supported Pt particles of similar size but different shape proved that the Pt surface morphology affects the reactivity of CD, but does not change the preferred diastereomer, i.e., no switch from an excess of (*S*)- to (*R*)-CDH₆-A was observed [17].

Finally, we want to emphasize the dramatic difference between the effects of an acidic support and an acidic solvent or additive. We have shown recently that replacement of toluene by acetic acid changed the preferred diastereomer of CDH₂ hydrogenation from (*S*)- to (*R*)-CDH₆-A [17]. The probable explanation is that acetic acid not only protonates the basic quinuclidine nitrogen of the alkaloid, but it forms various cyclic complexes with 1:1 and 2:1 acid:alkaloid molar ratios which alter the adsorption mode on Pt [25]. On the contrary, increasing the support acidity enhances the dominance of the (*S*)-CDH₆-A diastereomer that is formed on the undoped Pt/Al₂O₃ in small excess (Fig. 1). In other words, carboxylic acid type solvents or additives change the adsorption mode of CD (and CDH₂) via H-bonding interactions, while the acidic and basic supports influence the adsorption mode via changing the electronic properties of the surface Pt atoms.

4. Conclusions

The critical importance of metal–support interactions belongs to the key concepts in heterogeneous catalysis. There are numer-

ous examples on the possibility of tuning the rate and selectivity of various metal-catalyzed reactions by variation of the catalyst support. Here, we present a novel observation, the control of the diastereoselectivity of cinchonidine hydrogenation by tuning the acid–base properties of the alumina support. In addition, analysis of the product composition allows us to determine the switch in the adsorption mode of the alkaloid on the Pt surface during hydrogenation of its heteroaromatic ring. This type of truly in situ information is not available using any known surface science technique.

Acknowledgments

Financial support of this work by the Swiss National Science Foundation and ETH Research Grants TH-09 06-2 is kindly acknowledged. We also thank B. Schimmoeller and S.E. Pratsinis for the synthesis and characterization of the flame-made catalysts.

References

- [1] G.L. Haller, *J. Catal.* 216 (2003) 12.
- [2] K. Hayek, R. Kramer, Z. Paal, *Appl. Catal. A: Gen.* 162 (1997) 1.
- [3] A.Y. Stakheev, L.M. Kustov, *Appl. Catal. A: Gen.* 188 (1999) 3.
- [4] M.K. Oudenhuijzen, J.A.v. Bokhoven, D.E. Ramaker, D.C. Koningsberger, *J. Phys. Chem. B* 108 (2004) 20247.
- [5] D.C. Koningsberger, M.K. Oudenhuijzen, J.d. Graaf, J.A.v. Bokhoven, D.E. Ramaker, *J. Catal.* 216 (2003) 178.
- [6] Y. Ji, A.M.J.v.d. Eerden, V. Koot, P.J. Kooyman, J.D. Meeldijk, B.M. Weckhuysen, D.C. Koningsberger, *J. Catal.* 234 (2005) 376.
- [7] A.Y. Stakheev, Y. Zhang, A.V. Ivanov, G.N. Baeva, D.E. Ramaker, D.C. Koningsberger, *J. Phys. Chem. C* 111 (2007) 3938.
- [8] M. Besson, C. Pinel, *Top. Catal.* 25 (2003) 43.
- [9] P. Kukula, R. Prins, *Top. Catal.* 25 (2003) 29.
- [10] T. Mallat, E. Orglmeister, A. Baiker, *Chem. Rev.* 107 (2007) 4863.
- [11] D. Ferri, T. Bürgi, *J. Am. Chem. Soc.* 123 (2001) 12074.
- [12] K.A. Avery, R. Mann, M. Norton, D.J. Willock, *Top. Catal.* 25 (2003) 89.
- [13] R.J. LeBlanc, W. Chu, C.T. Williams, *J. Mol. Catal. A: Chem.* 212 (2004) 277.
- [14] F. Zaera, *Acc. Chem. Res.* 42 (2009) 1152.
- [15] D. Wang, H.-J. Yan, Q.-M. Xu, M.-J. Han, L.-J. Wan, *Top. Catal.* 35 (2005) 131.
- [16] S. Lavoie, M.-A. Laliberté, P.H. McBreen, *J. Am. Chem. Soc.* 125 (2003) 15756.
- [17] E. Schmidt, W. Kleist, F. Krumeich, T. Mallat, A. Baiker, *Chem. Eur. J.* 16 (2010) 2181.
- [18] E. Schmidt, T. Mallat, A. Baiker, *J. Catal.* 272 (2010) 140.
- [19] G. Szöllösi, P. Forgó, M. Bartók, *Chirality* 15 (2003) S82.
- [20] H.-U. Blaser, H.P. Jalett, W. Lottenbach, M. Studer, *J. Am. Chem. Soc.* 122 (2000) 12675.
- [21] A. Vargas, A. Baiker, *J. Catal.* 239 (2006) 220.
- [22] B. Schimmoeller, F. Hoxha, T. Mallat, F. Krumeich, S.E. Pratsinis, A. Baiker, *Appl. Catal. A: Gen.* 374 (2010) 48.
- [23] F. Hoxha, B. Schimmoeller, Z. Cakl, A. Urakawa, T. Mallat, S.E. Pratsinis, A. Baiker, *J. Catal.* 271 (2010) 115.
- [24] E. Schmidt, A. Vargas, T. Mallat, A. Baiker, *J. Am. Chem. Soc.* 131 (2009) 12358.
- [25] M. von Arx, T. Bürgi, T. Mallat, A. Baiker, *Chem. Eur. J.* 8 (2002) 1430.