



Priority Communication

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

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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.

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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

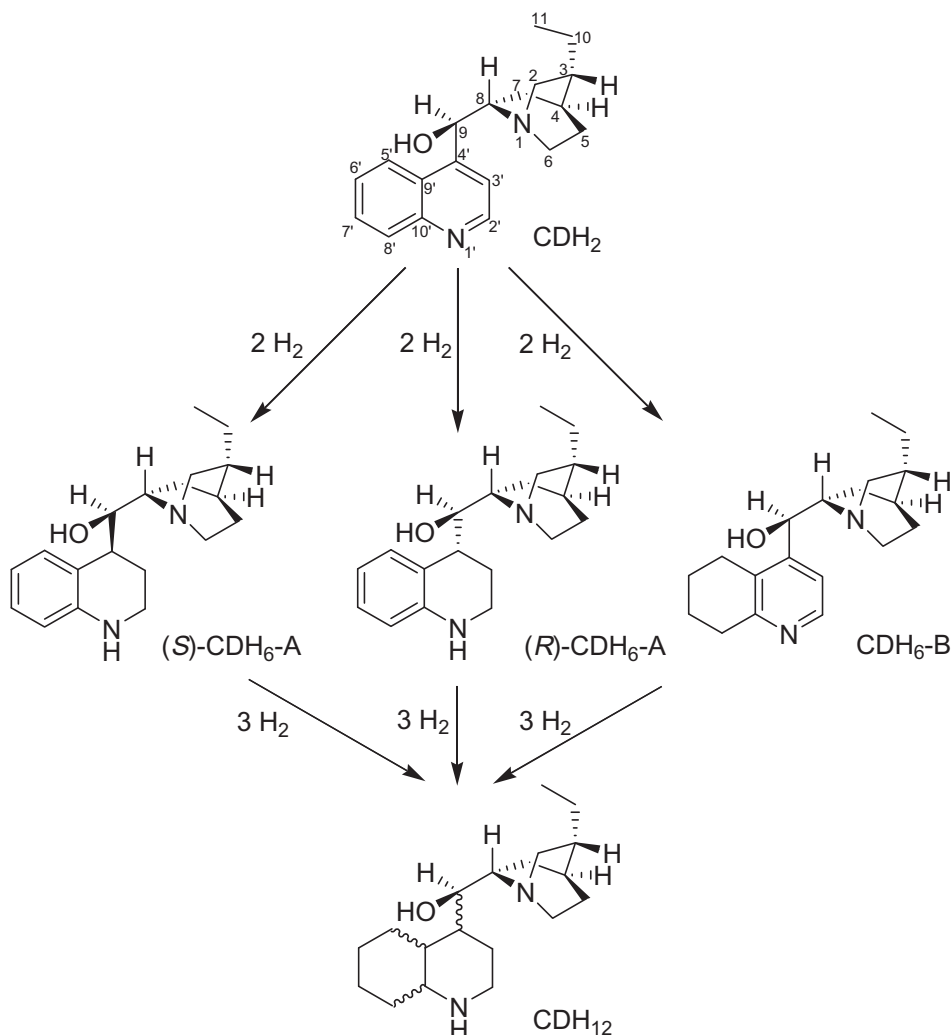
Generally, analytical grade reagents and solvents were used. Toluene (Fluka, >99.7%) was dried over activated molecular sieve 4A; CD (Fluka, >98% alkaloid) was used as received. The 5 wt.% Pt/alumina reference catalyst (Pt/Al₂O₃ (ref)) was purchased from Engelhard (Engelhard 4759).

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

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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

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