



Influence of support acid–base properties on the platinum-catalyzed enantioselective hydrogenation of activated ketones

Fatos Hoxha^a, Bjoern Schimmoeller^b, Zdenek Cakl^a, Atsushi Urakawa^a,
Tamas Mallat^a, Sotiris E. Pratsinis^b, Alfons Baiker^{a,*}

^aInstitute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, CH-8093 Zurich, Switzerland

^bParticle Technology Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, CH-8092 Zurich, Switzerland

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ABSTRACT

The influence of support acidity and basicity was investigated in the enantioselective hydrogenation of methyl benzoylformate and ketopantolactone on cinchonidine-modified Pt/Al₂O₃–SiO₂ and Pt/Al₂O₃–Cs₂O catalysts. Two series of flame-derived 4.7 wt.% Pt/Al₂O₃ catalysts in which the acid–base properties of the support were systematically varied by introducing SiO₂ (5–80 wt.%) or Cs₂O (0.25–10 wt.%) were applied. Addition of SiO₂ improved the enantioselectivity with a maximum at 30 wt.%. Enantioselectivity correlated well with the acidity of the catalysts characterized by TPD of NH₃ and with the selectivity to hydrogenolysis of methyl cyclohexyl ketone to ethylcyclohexane. On the contrary, doping with Cs was detrimental to the formation of the (*R*)-alcohols and the drop in enantioselectivity could unambiguously be attributed to the basicity of the support characterized by TPD of CO₂. The critical impact of support ionicity on the electronic properties of Pt, and thus on the adsorption and interaction of the reaction components on the metal surface, was further proven by the good correlation between the enantioselectivities of all catalysts and the ratio of CO adsorbed in bridged to linear (B/L) geometry. The practical importance of our findings is demonstrated by the best ee (94 ± 0.5%) achieved so far in the industrially relevant hydrogenation of ketopantolactone to (*R*)-pantolactone.

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1. Introduction

The Pt–cinchona system is the most efficient heterogeneous catalyst for the enantioselective hydrogenation of activated ketones, and also the most studied among the chirally modified metal catalysts (for recent reviews, see [1–8]). A major part of the research aimed at finding the appropriate combination of catalyst, modifier, and the reaction conditions to achieve practically useful enantioselectivities and broaden the application range of catalyst system. It has been attempted to improve the enantioselectivity by varying the catalyst synthesis method and the nature of the support. Besides alumina, various other supports have been tested, such as carbon, SiO₂, TiO₂, CaCO₃, zeolites, clays, and organic polymers [9–18], and even unsupported Pt nanoparticles have been explored as an alternative [19,20]. The early activity decayed after the broad recognition that none of the attempts led to a catalyst superior to a commercially available 5 wt.% Pt/Al₂O₃ catalyst (Engelhard 4759). Interestingly, there is no systematic study in the literature regarding the support effect on the enantioselectivity of Pt, and the acidity of the support – for example zeolites – was considered to have only minor impact [15].

On the other hand, the support acid–base properties can control the chemoselectivity in the hydrogenation of ketones on Pt and other noble metal catalysts [21–23]. The hydrogenolysis of the C–O bond can be accelerated or suppressed by increasing the catalyst acidity or basicity, respectively, with inorganic or organic additives and thus, the selectivity toward the alcohol can be tuned [24]. Note that cinchona-modified Pt provides always the alcohol in the hydrogenation of activated ketones, due to the strongly basic quinuclidine N of the alkaloid.

The influence of support ionicity, i.e. the acid–base properties, on the geometric and electronic properties of Pt has been extensively studied by Koningsberger's group in recent years [25–32]. They changed systematically the ionicity of alumina by introducing different dopants (Si, W, F, Cl, K, Rb, and Cs) via the sol–gel method. A broad range of characterization techniques and DFT calculations helped to elucidate the remarkable metal–support interaction. They proved that the Pt–H bond strength is higher on ionic (basic) supports and lower on acidic and more covalent supports, which is the origin of the changes in the reactivity of Pt toward hydrogenation and hydrogenolysis.

Being inspired from the idea of controlling the reactivity of Pt by fine tuning the ionic properties of the support, we aimed at extending this analysis to the enantioselection on Pt in the hydrogenation of activated ketones. We prepared two series of Pt catalysts,

* Corresponding author. Fax: +41 44 632 11 63.

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

supported on Si- and Cs-doped Al_2O_3 , by single-step flame spray pyrolysis [33]. We choose this technique because of its simplicity and exceptional reproducibility in the synthesis of multi-component catalysts [34–36]. The 4.7 wt.% Pt/ Al_2O_3 - SiO_2 and 4.7 wt.% Pt/ Al_2O_3 - Cs_2O catalysts used in the present study contain 0–80 wt.% SiO_2 and 0–10 wt.% Cs_2O , related to the alumina support. The preparation and characterization of the catalysts by N_2 absorption, X-ray diffraction (XRD), CO chemisorption, electron microscopy, and NH_3 and CO_2 temperature-programmed desorption (TPD) has been reported elsewhere [33]. A remarkably good correlation was found between the surface acidity of the Pt/ Al_2O_3 - SiO_2 catalysts and their activity toward hydrogenolysis in the hydrogenation of acetophenone. On the other hand, already 0.25 wt.% Cs_2O hindered the hydrogenolysis of 1-phenylethanol to ethylbenzene [33].

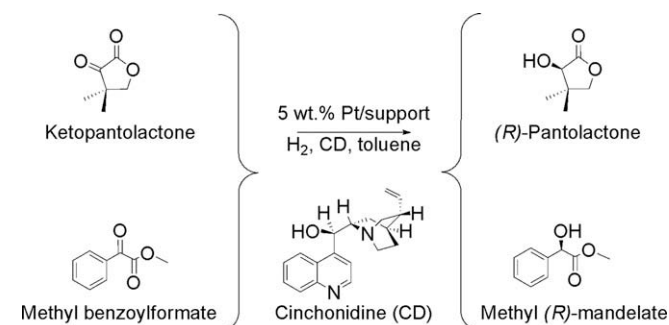
Here, we report the enantioselective hydrogenation of ketopantolactone and methyl benzoylformate in the presence of cinchonidine as chiral modifier of Pt (Scheme 1). The two model substrates were selected based on the absence of an H atom in α -position to the keto-carbonyl group to avoid the aldol condensation and thus minimize the side reactions induced by Pt, alumina, and the basic alkaloid [7,37–39]. In case of ketopantolactone, also decarbonylation by Pt was barely detectable by ATR-IR spectroscopy [40]. To help understanding the origin of changes in enantioselectivity, characterization of the catalysts was completed with the chemoselective hydrogenation of cyclohexyl methyl ketone (Scheme 2) and a DRIFT spectroscopic study of CO adsorption, a proven technique to follow variations in the electronic properties of Pt with the support ionicity [31,41–44].

2. Experimental

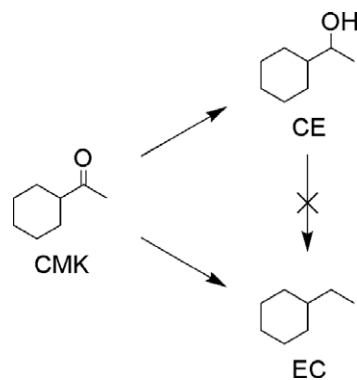
2.1. Materials

The anhydrous solution of ketopantolactone **1a** (Roche AG, 99%) in toluene was prepared by azeotropic distillation of toluene at reduced pressure. Cyclohexyl methyl ketone (Alfa Aesar, 95%) was carefully distilled in vacuum before use. Other chemicals were used as received: methyl benzoylformate **2a** (Acros, 99%), cinchonidine (CD) (Fluka, $\geq 98\%$ alkaloid), and toluene (Acros, extra dry, water < 30 ppm).

The preparation and structural characterization of the flame-made Pt catalysts has been reported elsewhere [33]. Aluminum sec. butoxide (Aldrich, >98%), hexamethyldisiloxane (Fluka, >98%), and cesium acetylacetonate (Fluka) dissolved in 2-ethylhexanoic acid (Aldrich, >98%, 0.5 M) were used as aluminum, silicon, and cesium precursors, respectively. The chemical and textural properties of the applied catalysts are collected in Table 1. The



Scheme 1. The major enantiomers in the hydrogenation of ketopantolactone and methyl benzoylformate over 4.7 wt.% Pt supported on SiO_2 - or Cs_2O -doped Al_2O_3 modified by cinchonidine (CD).



Scheme 2. Hydrogenation and hydrogenolysis of cyclohexyl methyl ketone.

TOF values were calculated based on the number of surface Pt atoms [33].

2.2. Diffuse reflectance infrared Fourier transform spectroscopy – CO adsorption

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to study CO adsorption on the catalysts. The analysis was carried out at 297 K with an EQUINOX 55 spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled HgCdTe detector. Multiple samples (max. 5), separated by quartz wool, were placed without dilution in a plug-flow DRIFTS cell [45], allowing identical experimental conditions for all samples. The off-gas of the cell was analyzed by a mass spectrometer. Spectra were collected by averaging 200 scans at 4 cm^{-1} resolution. The standard reductive treatment procedure mentioned in the next chapter was used to reduce the catalysts in flowing 20 vol.% H_2/He (40 ml/min). CO adsorption was monitored over 60 min in flowing 10 vol.% CO/He (40 ml/min), followed by flowing He (40 ml/min) for 30 min. The peak areas were determined after deconvolution of the spectra [46]. The spectrum of the reference catalyst E4759 is reported elsewhere [47].

2.3. Catalytic hydrogenation

The catalysts were always reduced at elevated temperature prior to use. According to the standard procedure, the catalyst was heated under flowing nitrogen up to $400\text{ }^\circ\text{C}$ in 30 min, followed by a reduction in flowing hydrogen for 60 min at the same temperature, and finally cooling down in hydrogen in 30 min.

Hydrogenation of methyl benzoylformate at atmospheric pressure was carried out in a 100-ml glass reactor equipped with magnetic stirrer, septum for sample collection or substrate addition, and an inlet and outlet line for gas flowing. The reactor allowed avoiding the contact of the freshly reduced catalyst with air, since the reductive heat treatment and the hydrogenation reaction could be carried out in the same reactor. After introducing the solvent and modifier into the reactor containing the freshly reduced catalyst under hydrogen at room temperature, the mixture was stirred for 1 min. The reaction was started by introducing the substrate and immediately switching on the stirring. Under standard conditions, $16.15\text{ }\mu\text{mol}$ Pt catalyst (63 mg), $20.4\text{ }\mu\text{mol}$ modifier, 4.14 mmol substrate, and 20 ml solvent were stirred magnetically (1000 rpm) at $20\text{ }^\circ\text{C}$ for 4 h. In all experiments, the Pt/modifier/substrate molar ratios were kept constant at 1/1.26/256.

Hydrogenation of ketopantolactone was carried out at elevated pressure in a 25-ml stainless steel Parr autoclave equipped with a 16-ml glass liner and a PTFE cover, and a magnetic stirrer. The autoclave was equipped also with a valve for sample collection

Table 1

Chemical and textural properties of Pt/Al₂O₃–SiO₂ and Pt/Al₂O₃–Cs₂O catalysts containing 4.7 wt.% Pt. Catalysts are designated as Pt/Al–xSi and Pt/Al–xCs, respectively, where x is the content of the dopant in wt.%.

Catalyst	SiO ₂ in the support (wt.%)	Cs ₂ O in the support, (wt.%)	Al ₂ O ₃ in the support (wt.%)	BET surface area (m ² g ⁻¹)	Average Pt particle size (nm)	Pt dispersion (%)
Pt/Al	–	–	100	138	1.9	60.3
Pt/Al–5Si	5	–	95	128	3.2	35.8
Pt/Al–10Si	10	–	90	123	4.3	26.1
Pt/Al–15Si	15	–	85	126	4.0	28.5
Pt/Al–22.5Si	22.5	–	77.5	136	5.5	20.6
Pt/Al–30Si	30	–	70	139	4.3	26.6
Pt/Al–50Si	50	–	50	157	7.8	14.5
Pt/Al–80Si	80	–	20	211	13.5	8.4
Pt/Al–0.25Cs	–	0.25	99.75	208	2.0	56.2
Pt/Al–0.5Cs	–	0.5	99.5	234	2.2	51.9
Pt/Al–3Cs	–	3	97	257	2.1	55.1
Pt/Al–5Cs	–	5	95	243	1.6	69.0
Pt/Al–10Cs	–	10	90	227	1.8	61.5

or substrate addition. The treatment of the catalyst was carried out in a fixed-bed reactor following the standard procedure. At the end, the freshly reduced catalyst was purged with nitrogen for 10 min at room temperature to remove the excess of hydrogen and then transferred immediately to the autoclave. During the hydrogenations of ketopantolactone at 100 bar, the proper amount of catalyst containing 1.41 μmol Pt (5.5 mg), 1.7 μmol modifier, 1.61 mmol substrate, and 5 ml solvent were stirred magnetically (1000 rpm) at 18 °C for 30 min. The Pt/modifier/substrate molar ratios were kept constant at 1/1.21/1142. The pressure was held at a constant value with a pressure regulator valve.

The conversion and enantioselectivity (ee) were determined by GC analysis, using an HP 6890 gas chromatograph and a Chirasil-DEX CB (Chrompack 7502 25 m × 0.25 mm × 0.25 μm) capillary column. All experiments were carried out at least twice, and the average values are shown in the figures. Always the (*R*)-enantiomer was formed in excess without any detectable side product. The estimated standard deviation of ee was about ±0.5%.

Hydrogenation of ketopantolactone under optimized conditions was carried out with the CD-modified Pt/Al–22.5Si catalyst (for designation of catalysts see Table 1) at –10 °C and 100 bars in 5 ml toluene. The Pt/modifier/substrate molar ratios were 1/0.03/718.

Hydrogenation of cyclohexyl methyl ketone was investigated at 3 bar in the same 25-ml Parr autoclave as described previously. The Pt/substrate molar ratio was kept constant at 1/101. The proper amount of catalyst containing 4.9 μmol Pt, 0.5 mmol substrate, and 6 ml solvent were stirred magnetically (1000 rpm) at 20 °C for 120 min. The pressure was held at a constant value with a constant pressure regulator valve. The conversion and product composition were determined by GC analysis, using a Termo Quest Trace 2000 gas chromatograph and a HP-FFAP (Agilent HP-FFAP 30 m × 0.32 mm × 0.25 μm) capillary column. Bicyclohexyl was used as internal standard (0.1 mmol).

3. Results and discussion

3.1. Catalyst properties – chemoselective hydrogenation of cyclohexyl methyl ketone

The abbreviation and composition of the catalysts, as well as their BET surface area and mean Pt particle size, are collected in Table 1. A detailed characterization using nitrogen adsorption, XRD, CO chemisorption for Pt particle size determination, temperature-programmed desorption (TPD) of NH₃ and CO₂, and electron microscopy (TEM and STEM) combined with EDX analysis have been reported elsewhere [33]. Summarizing it shortly, incorpora-

tion of 5–80 wt.% SiO₂ into the bulk of the non-porous alumina diminished the crystallinity, and the SiO₂-rich samples were amor-

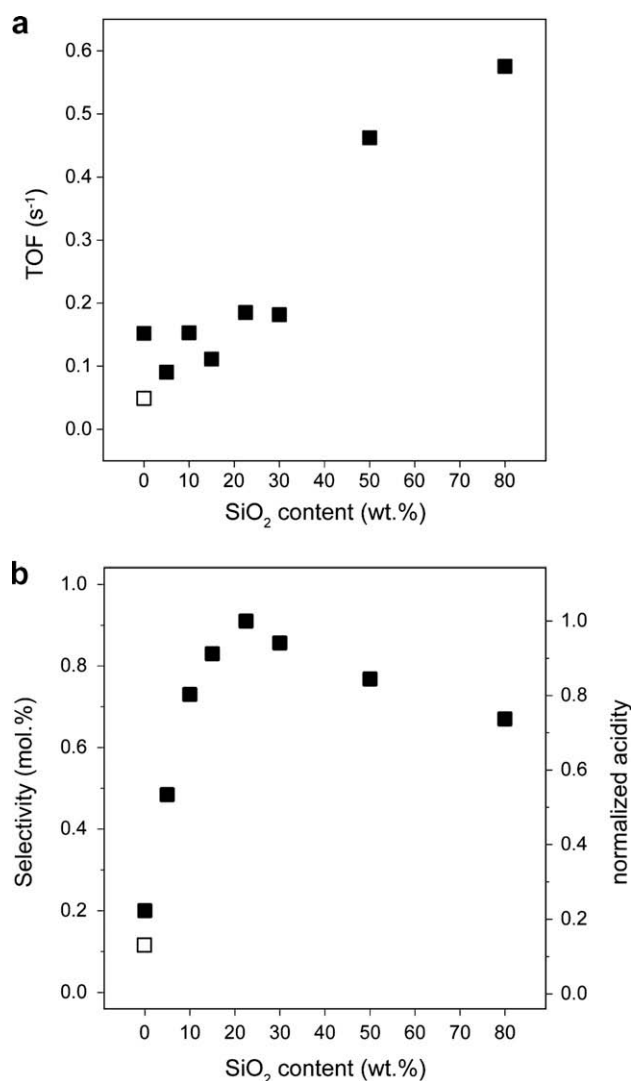


Fig. 1. Influence of the SiO₂ content of the Pt/Al–Si catalysts on the selectivity to C–O bond hydrogenolysis (to ethylcyclohexane, EC, Scheme 2) during the hydrogenation of cyclohexyl methyl ketone (CMK) over the Pt/Al₂O₃–SiO₂ catalysts. Data refer to 50% conversion of CMK, and empty squares represent the reference catalyst E4759.

phous. Temperature-programmed desorption of ammonia revealed a maximum acidity at 22.5–30 wt.% SiO₂ in the support. The support acidity had a strong influence on the properties of the Pt–H system, as evidenced by the hydrogenation of acetophenone. The catalysts were highly active, and at 50% conversion, the selectivity to the hydrogenolysis byproducts ethylbenzene and ethylcyclohexane increased with increasing SiO₂ content by more than 20-fold.

The mean Pt particle size remained in the range 1.6–2.2 nm in the catalysts doped with 0.25–10 wt.% Cs₂O. The basicity increased rapidly with Cs₂O-doping, as confirmed by the temperature-programmed desorption of carbon dioxide. The dopant was probably located in the surface region of the catalyst particles and strongly influenced the chemoselectivity in acetophenone hydrogenation: only 0.25 wt.% Cs₂O ceased the hydrogenolysis of 1-phenylethanol to ethylbenzene, and 5 wt.% Cs₂O blocked the formation of ethylcyclohexane from cyclohexyl methyl ketone.

A limitation of acetophenone hydrogenation as a test reaction is that the competing saturation of the phenyl ring may distort the determination of the relative rates of hydrogenolysis and hydrogenation of the C–O bond. To avoid this effect, we completed the characterization of the Pt/Al₂O₃–SiO₂ catalysts with the hydrogenation of cyclohexyl methyl ketone (CMK, Scheme 2), which reaction is in fact a part of the reaction route in acetophenone hydrogenation. CMK can be hydrogenated to the saturated alcohol 1-cyclohexylethanol (CE) or hydrogenolyzed to ethylcyclohexane (EC). A control experiment showed that hydrogenolysis of the aliphatic alcohol under the reaction conditions was not detectable even after 20 h, in agreement with former reports [48,49]. As illustrated in Fig. 1a, all SiO₂-doped catalysts were more active than the reference Pt/Al₂O₃, which is the mostly used catalyst in the enantioselective hydrogenation of ketones. There is no clear correlation between the TOFs related to the number of surface Pt sites and the SiO₂ content of the mixed oxide support at low SiO₂ content, where the mean Pt particle size varied only in the relatively narrow range 2–5.5 nm (Table 1). There is a maximum in C–O bond hydrogenolysis selectivity at around 20–30 wt.% SiO₂ in the support, and all SiO₂-doped samples were more selective than the undoped Pt/Al and the reference catalyst Pt/Al₂O₃.

3.2. Enantioselective hydrogenation over Pt/Al₂O₃–SiO₂ catalysts

Variation of enantioselectivity with the support composition in the hydrogenation of ketopantolactone over the CD-modified Pt/Al–Si catalyst series is plotted in Fig. 2a. With increasing SiO₂ content in the support up to 30 wt.%, the enantioselectivity to (*R*)-pantolactone increased by 16%. Higher silica content was detrimental but even those catalysts were more enantioselective than the reference Pt/Al₂O₃. A possible explanation for this behavior is that too small Pt particles cannot accommodate the bulky CD–substrate interacting complex and give lower ees [37,50], and doping with Si increases the average Pt size (Table 1). However, literature shows contradictory data on the particle size effect [12,51], and Fig. 2b shows that this explanation might be valid only at low SiO₂ contents. Particularly at around the optimum enantioselectivity, the Pt particle size cannot be the critical parameter.

A better correlation is found when the ee is plotted against the acidity of the catalysts, using the hydrogenolysis selectivity to ethylcyclohexane at 50% conversion of cyclohexyl methyl ketone (Fig. 1b). Already a visual analysis reveals a striking similarity between enantioselectivity and chemoselectivity shown in Figs. 2a and 1b, respectively. To quantify this correlation, we defined the highest hydrogenolysis selectivity of the Pt/Al–22.5Si as unity, and thus arrived at a scale of “normalized acidity” of this catalyst series (Fig. 1b). The enantioselectivity to (*R*)-pantolactone shows a good linear correlation ($R^2 = 0.93$) with the normalized acidity

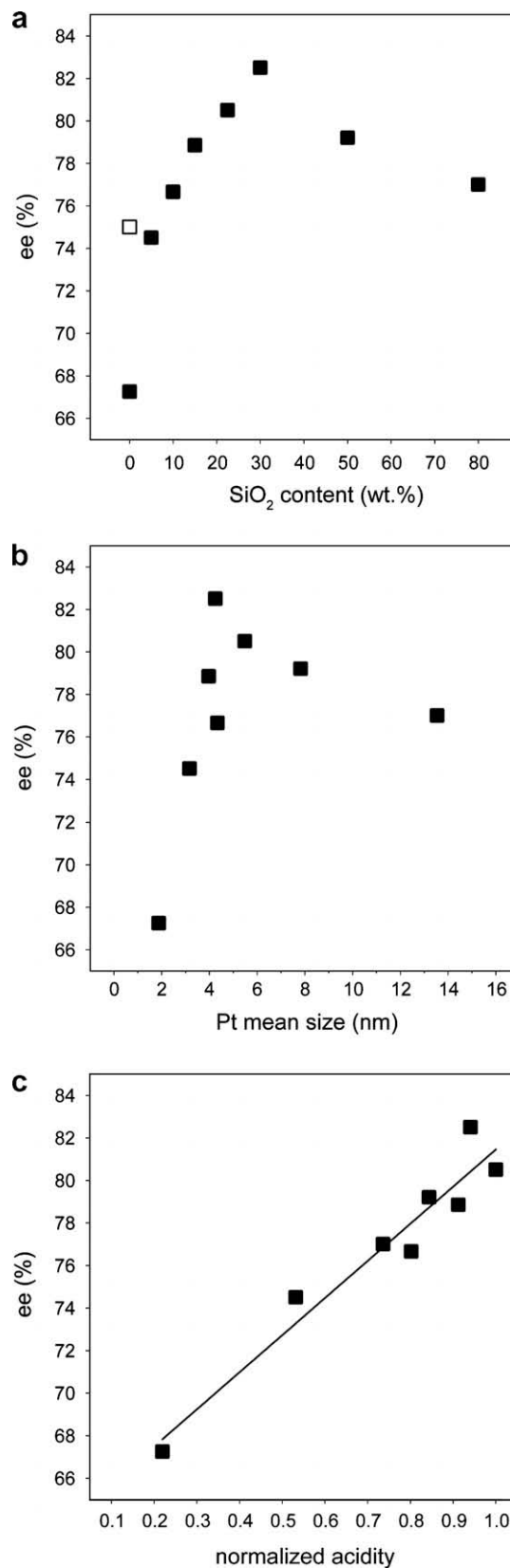


Fig. 2. Hydrogenation of ketopantolactone over CD-modified Pt/Al–Si catalysts. Enantioselectivities determined at full conversion are plotted as a function of SiO₂ content in the support (a), Pt particle size (b), and “normalized acidity” of the catalysts (c). Standard conditions, toluene, 100 bar, 18 °C; open symbols refer to the reference catalyst E4759. The “normalized acidity” is derived from the hydrogenolysis selectivity of the catalysts in the hydrogenation of methyl cyclohexyl ketone (Fig. 1b).

as illustrated in Fig. 2c. This correlation suggests that there is a common origin of the enantioselectivity to (*R*)-pantolactone and the hydrogenolysis selectivity to ethylcyclohexane in the hydrogenation of the two structurally very different ketones: the variation of the support acidity that controls the properties of the Pt–H system via the metal–support interaction [21–23,28,30].

A similar trend was observed in the hydrogenation of methyl benzoylformate over the same catalyst series (Fig. 3a). The improvement in enantioselectivity was smaller in this reaction, probably because the conditions selected are closer to the optimum (92% in the best case of Pt/Al–30Si vs 84% for the Pt/Al catalyst). We arrived at the same interpretation of the data concerning the origin of enhanced enantioselectivity by SiO₂-doping: the increase in particle size can explain only the changes below 4–5 nm (Fig. 3b), while there is a reasonably good correlation between the ee and the normalized acidity of the catalysts (Fig. 3c). This reaction was sufficiently slow to allow determination of the initial reaction rates by GC analysis. The rates of alcohol formation were constant up to high conversion for each catalyst. By increasing the Si content in the support, the hydrogenation rate decreased (Fig. 3d), parallel to the increase of the Pt particle size (Table 1). The TOF values, related to the fraction of surface Pt atoms, varied

in the range 0.15–0.38 s⁻¹, and all catalysts were more active than the reference catalyst E4759 (TOF: 0.13 s⁻¹).

The potential of catalysts synthesized by flame spray pyrolysis is well illustrated by the high activities of the Si-doped catalysts and also by the better enantioselectivity achieved in the hydrogenation of ketopantolactone (above 10 wt.% SiO₂) and methyl benzoylformate (whole series), compared to the enantioselectivity of the commonly used Pt/Al₂O₃ E4759 (Figs. 2a and 3a, open symbols).

3.3. Enantioselective hydrogenation over Pt/Al₂O₃–Cs₂O catalysts

In the hydrogenation of ketopantolactone over Cs-doped Pt/Al₂O₃ catalysts, the enantioselectivity dropped sharply from 67% to 26% ee by increasing the Cs content in the support (Fig. 4). Already very small amounts of Cs in the support (0.25–0.5 wt.% Cs₂O) had a detrimental effect. Since the average Pt particle size in this catalyst series varied in a narrow range 1.6–2.2 nm (Table 1), the potential role of this parameter is negligible. In contrast, the basicity of the catalysts characterized by the maximum temperature of the CO₂ desorption peak (TPD analysis [33]) revealed an inverse correlation: the position of the peak maximum in-

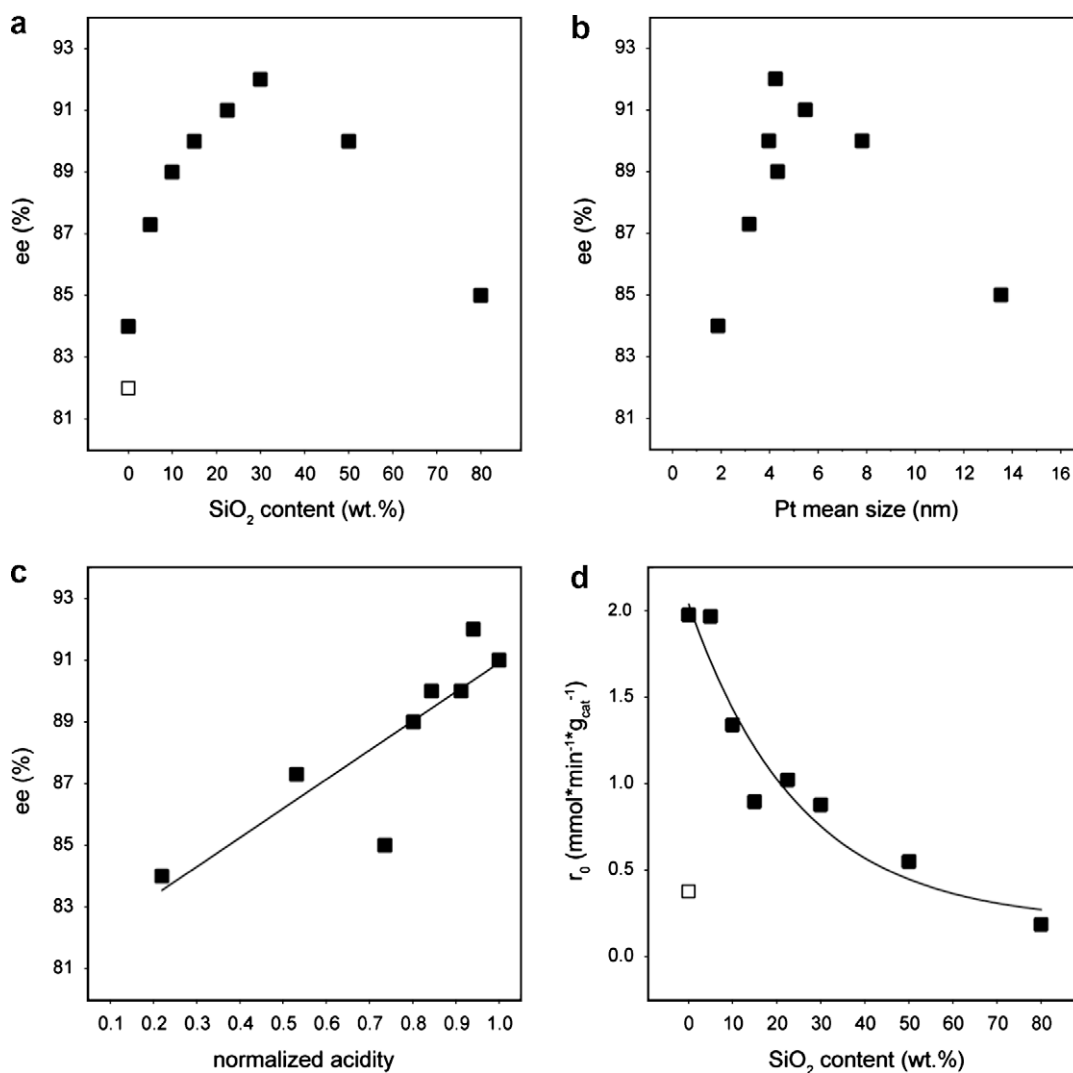


Fig. 3. Hydrogenation of methyl benzoylformate over CD-modified Pt/Al–Si catalysts. Enantioselectivity is plotted as a function of the SiO₂ content in the support (a), the mean Pt particle size (b), and the catalyst acidity (c). The initial reaction rates (d) and the enantioselectivities at full conversion were determined under standard conditions in toluene, at 1 bar and 20 °C. Open symbols refer to the reference catalyst E4759.

creased monotonously in the whole concentration range investigated, particularly below 1 wt.%. In other words, the higher the basicity of the support, the lower is the enantioselectivity in carbonyl hydrogenation, independent of the Pt particle size. A comparison of Figs. 2a and 4 reveals a remarkably higher efficiency of Cs as dopant, which is attributed to its probable location on the support [33]: while Si may enter into the alumina lattice and be well distributed there, Cs₂O is probably enriched in the outer layer of alumina and thus exerts a stronger effect on the Pt particles.

The negative influence of Cs₂O on the enantioselectivity was significant also in the hydrogenation of methyl benzoylformate, as shown in Fig. 5. Only 10 wt.% Cs₂O in the support reduced the enantioselectivity from 84% to 31%. On the other hand, no unambiguous correlation was found between the hydrogenation rate and the Cs₂O content in the support. The rate of alcohol formation remained constant up to high conversion for each catalyst and the TOF, related to the fraction of surface Pt atoms, varied in the range 0.18–0.35 s⁻¹. The higher activity of both Si- and Cs-doped catalyst series, compared to the reference E4759 Pt/Al₂O₃, is attributed to the non-porous structure of flame-made catalysts and the absence of intra-particle mass transfer limitation [33].

3.4. IR study of CO adsorption

The IR spectroscopic study of CO adsorption is the mostly used method to gain insight into the electronic properties and morphology of platinum. In order to help comparing our results to literature data, we extended the characterization of the Pt/Al–Si and Pt/Al–Cs catalyst series with this method. To allow a direct comparison of these data with catalytic results, the samples were pre-reduced in a flowing H₂/He mixture at 400 °C. Mass spectrometric analysis of the exhaust gas indicated that the stabilized reduced state of the catalysts was reached within 30 min (the concentration of the exhaust gas mixture was constant showing low water content). Due to the importance of SiO₂-doped catalysts in enantioselective hydrogenations, the following discussion will focus on the characteristics of this series.

The DRIFT spectra of CO adsorbed on the reduced Pt/Al, Pt/Al–30Si, and on Pt/Al–10Cs samples are shown in Fig. 6 as representative examples. Two modes of CO adsorption were identified from the spectra: the bands around 2080 cm⁻¹ are commonly attributed to a linear, single bonded (on-top) species, and the broad and less intensive signal at ca. 1830 cm⁻¹ is attributed to bridged CO [33].

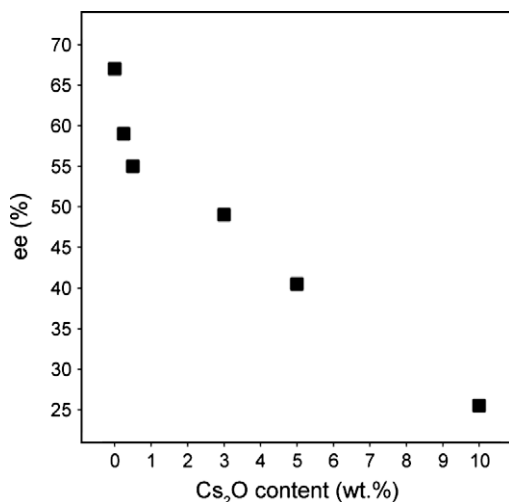


Fig. 4. Enantioselectivities determined at full conversion of ketopantolactone on Cs₂O-doped Pt/Al₂O₃ catalysts; standard conditions, toluene, 100 bar, 18 °C.

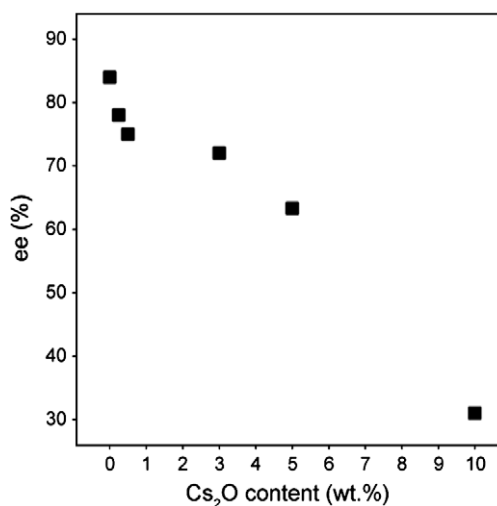


Fig. 5. The influence of Cs₂O-doping on the enantioselectivities determined at full conversion of methyl benzoylformate; standard conditions, toluene, 1 bar, 20 °C.

The high energy signal is split into two narrow intensive signals, at ca. 2085 cm⁻¹ and 2065 cm⁻¹, and a broad band at ca. 2030 cm⁻¹. The first two signals are assigned to CO bound to highly coordinated Pt atoms such as {1 1 1} and {1 0 0} terraces, respectively, whereas the latter signal is attributed to CO adsorbed on low coordinated Pt sites at step-edges, corners, and defects [46,47,52–56].

SiO₂-doping modifies not only the signal intensities but also the band shapes. With increasing SiO₂ content, the bands corresponding to CO linearly bound to highly coordinated Pt{1 1 1} and Pt{1 0 0} terraces are enhanced in relative intensity and shifted to higher wavenumbers in the range 2090–2095 cm⁻¹ and 2067–2080 cm⁻¹, respectively (Fig. 7a and b). The ratio of CO linearly adsorbed on Pt{1 1 1} and Pt{1 0 0} terraces varies in a narrow range for all SiO₂-doped catalysts, almost independent of the SiO₂ content (Fig. 7d). Interesting is the fact that the band intensity corresponding to the CO bound to low coordinated Pt atoms reaches a maximum at around 15–30 wt.% SiO₂ content (not shown). Variation of the band position and the area of bridged CO is also shown in Fig. 7a and c. The wavenumber shifts from 1802 to 1874 cm⁻¹ with increasing the SiO₂ content up to 50 wt.% SiO₂ but the catalyst with the highest SiO₂ content (Pt/Al–80Si) does not follow this trend. In contrast to the changes in linearly bound CO, the band area of bridged CO decreases by increasing the SiO₂ content in the support.

Similar to several other characteristics of the two catalyst series, the CO adsorption spectra on the Cs₂O-doped catalysts displayed the opposite trend compared to those of the SiO₂-doped samples. The intensity of the signals corresponding to linear adsorption decreased, while that of the bridged CO band increased with increasing the Cs content in the support. Parallel to these changes, the signals assigned to CO bound to {1 1 1} and {1 0 0} terraces and to low coordinated Pt atoms were shifted to lower wavenumbers, reaching a minimum at 5 wt.% Cs₂O. To illustrate the opposite effects of doping alumina with Si or Cs, we plotted in Fig. 8 the intensity ratio of bridged (B) to linearly (L) adsorbed CO (B/L) as a function of the dopant content in the support. Despite of some significant fluctuation in the B/L ratio, the inverse trend induced by the basic and acidic additives is clearly discernible. The increasing B/L intensity ratio with increasing Cs₂O content in the support is in agreement with former CO adsorption studies on Pt supported on K-modified Al₂O₃, where K favored the bridged adsorption mode of CO on Pt on the expense of the linear (on-top) CO species [42,46].

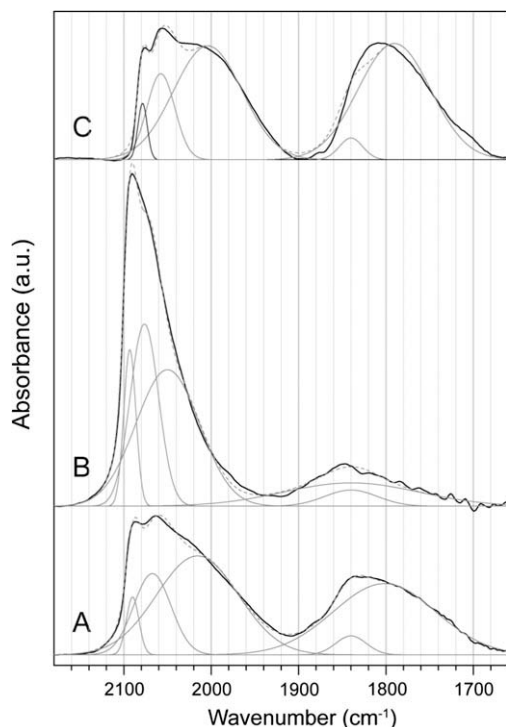


Fig. 6. DRIFT spectra of CO adsorption on (A) Pt/Al and the deconvoluted components of the CO bands, (B) Pt/Al-30Si, and (C) Pt/Al-10Cs samples after prereduction at 400 °C in flowing H₂. The fitted spectrum and the deconvoluted components are represented with dashed and gray lines, respectively.

The shift in the CO band position is often interpreted as evidence of changes in the electronic properties of supported metals [43,57]. The exact position of the absorption bands depends on the particle size [58], surface coverage [59], and electronic changes in the metal structure [57]. Since the particle size of the Pt/Al-Si catalyst series varies with the SiO₂ content (Table 1) and the CO adsorption bands are broad, the shifts in the band position probably reflect both the changes in the electronic properties and in the size of the Pt particles.

In a theoretical analysis of the electronic parameters that determine the coordination of CO to a transition-metal surface, Van Santen [60] demonstrated that the intensity ratio of bridged to linear (B/L) bonded CO is a critical parameter. A growing B/L ratio indicates an increase of the electron density on the supported Pt particles, which phenomenon is typical for Pt on a support doped with a base [43,44]. Opposite is the situation for Pt particles located on an acidic support, where the electron density on Pt is diminished with increasing the support acidity, and this change is reflected by a smaller B/L ratio. The B/L ratio was used in several studies by Koningsberger and coworkers as a key measure for the electronic state of supported Pt [31,41,42]. It was found for all supports that the IR bands of adsorbed CO shifted to higher wavelengths, and the B/L ratio decreased with increasing acidity of the support. Both effects were attributed to a decrease in the electronic charge of the support oxygen atoms and hence to a decrease of the electron density on the supported Pt particles [43,44].

Next we will discuss the application of the B/L ratio as a unique parameter in the interpretation of the enantioselectivity of both SiO₂- and Cs₂O-doped Pt/Al₂O₃ catalysts.

3.5. Origin of the support effect on the enantioselectivity

In Section 3.2, we tried to correlate the enantioselectivities in the hydrogenation of methyl benzoylformate and ketopantolac-

tone with the variations in the particle size and the acid–base properties of the catalysts. By introducing up to 80 wt.% SiO₂ into the support, the mean Pt particle size increased considerably (Table 1). We have discussed previously that the flame spray pyrolysis conditions chosen allowed reasonable Pt particle size only for the synthesis of the catalyst series covering the alumina-rich region [33]. Nevertheless, when considering the range 5–30 wt.% SiO₂, which is the most interesting concerning the catalytic results (Figs. 2 and 3), the mean Pt particle size varied in a relatively narrow range of 4.35 ± 1.05 nm. In both test reactions, the highest ee was obtained at 30 wt.% SiO₂, and the mean Pt size of this catalyst was 4.3 nm. Figs. 2b and 3b illustrate that – considering the whole concentration range – the correlation between enantioselectivity and mean Pt size is poor. It has been shown that the enantioselectivity in the hydrogenation of activated ketones depends on the Pt particle size and the optimum is at or above 3–4 nm [11,61]. Note, however, that the suggested correlation is far not satisfying. For example, tiny Pt nanoparticles of less than 2 nm average diameter [19] provided higher enantioselectivities than those catalysts described in the previously mentioned reports.

The other important feature of the SiO₂-doped catalysts is the support acidity. TPD of ammonia indicated the highest acidity at 22.5 and 30 wt.% SiO₂ contents, and the data correlate well with the hydrogenolysis activity of the Si-doped catalysts during methyl cyclohexyl ketone hydrogenation (Fig. 1b). Figs. 2c and 3c display the good correlation between the enantioselectivity and the normalized acidity, derived from the selectivity to the hydrogenolysis product in methyl cyclohexyl ketone hydrogenation (Fig. 1b).

For the Cs₂O-doped catalysts, the origin of the support effect is clear. In this series of catalysts (0–10 wt.% Cs₂O), the synthesis conditions were ideal, and the average Pt particle size varied in the narrow range 1.9 ± 0.3 nm (Table 1). Hence, the dramatic drops in the enantioselectivity to (R)-alcohols in the two test reactions (Figs. 3 and 4) can be unambiguously related to the increased basicity of the doped catalysts, as determined by TPD of CO₂ [33].

To get further support to our interpretation of the outstanding enantioselectivity of the SiO₂-doped catalysts, we plotted in Fig. 9 the enantioselectivities of both catalyst series (SiO₂- and Cs₂O-doped) as a function of the B/L ratio of CO adsorption. (In order to better illustrate the effect of silica-promotion, the variation of ee with the SiO₂ content is plotted also separately in Fig. 9b.) The unique advantage of the B/L ratio is that it gives a common scale to characterize both the acidic and basic properties of the catalysts. The general trend apparent in both test reactions is the improving enantioselectivity with decreasing B/L ratio. In other words, the acidic support favors and the basic support diminishes the enantioselection on the Pt surface, as compared to the performance of Pt/Al₂O₃ (Pt/Al). The best ees were reached in a relatively narrow range of the B/L ratio at around 0.25 (Fig. 9). Although some scattering is obvious in Fig. 9, these deviations do not detract from the basic correlation. For example, the Pt/Al-80Si catalyst is an outlier with a B/L of ~0.1, but as we discussed previously, the conditions chosen for catalyst synthesis are not optimal for samples of high silica content and these catalysts behave differently, compared to the rest of the series.

In the interpretation of the metal–support interaction, it is commonly assumed that the shift in the electronic properties of Pt with the acid–base properties of the support controls the characteristics of the Pt–H system [31]. Considering the role of the electronic properties of Pt in the enantioselection, we may go a step further and speculate that probably also the adsorption mode and strength of the modifier and the substrate are influenced by the acid–base properties of the support, although this assumption needs confirmation.

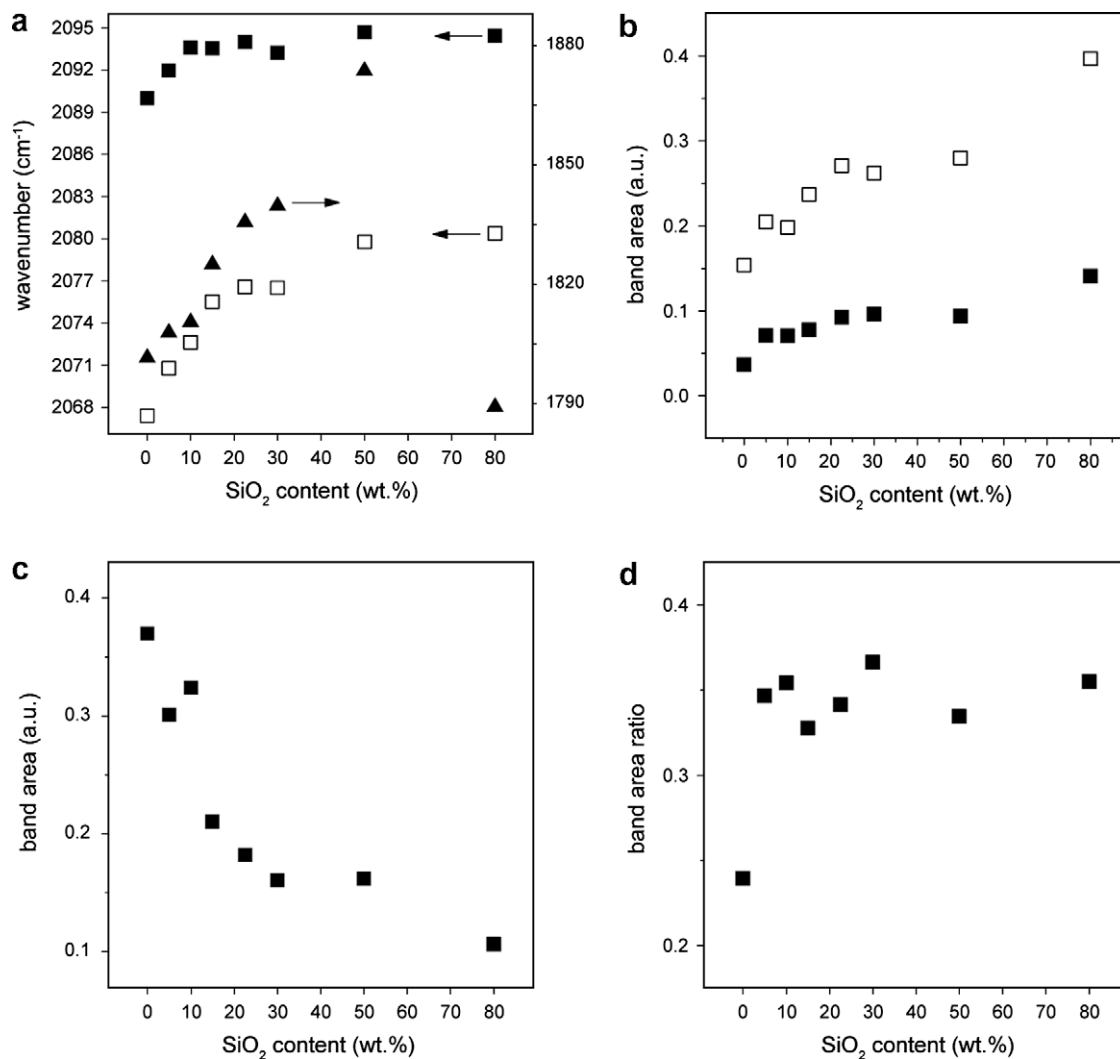


Fig. 7. Influence of SiO₂-doping on the characteristics of CO adsorption on the reduced catalysts, as derived from the deconvoluted IR spectra. (a) Shift of the wavenumber of CO linearly adsorbed on Pt{111} (■) and {100} (□) terraces, and bridged adsorption of CO (▲). (b) Variation of the band area of CO linearly adsorbed on Pt{111} (■) and {100} (□) terraces. (c) Variation of the band area of bridged CO adsorption. (d) The ratio of CO linearly adsorbed on Pt{111} and Pt{100} terraces.

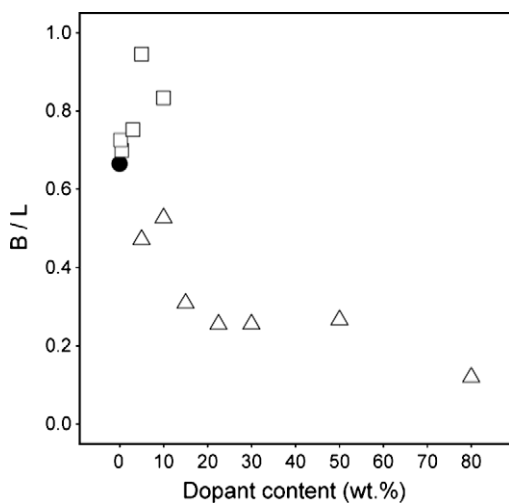


Fig. 8. Intensity ratio of bridged and linearly adsorbed CO (B/L) as a function of dopant content (Cs₂O or SiO₂) in the support; Δ - Pt/Al-Si series, □ - Pt/Al-Cs series, ● - undoped Pt/Al₂O₃. Data are extracted from the deconvoluted IR spectra.

3.6. Ketopantolactone hydrogenation under optimized conditions

An intriguing question is whether the above described correlation between the support acidity/basicity and the enantioselectivity can lead us to practically useful applications. In general, it is not very difficult to find a set of reaction conditions (sometimes far from the optimum), which allows a higher performance of the proposed new catalyst compared to the reference catalyst. The only real test of superiority is the comparison of the performance of the two catalysts under the conditions optimized separately for each of them.

The enantioselective hydrogenation of benzoylformates has been thoroughly investigated in the past decade [62–64]. Years-long optimization of the reaction conditions, catalyst pretreatment, and the modifier structure by Bartók and coworkers allowed 98% ee at 25 bar and 0 °C in the presence of acetic acid, using dihydrocinchonidine as the chiral modifier of Pt/Al₂O₃ and the ethyl ester of the substrate [65–67]. To our knowledge, this is the highest value achieved with a chirally modified metal catalyst, and there are only two more examples to 98% ee using cinchona-modified Pt [19,68]. Hydrogenation of ketopantolactone has also been a popular test reaction for chirally modified Pt [69–72], and the highest ee of

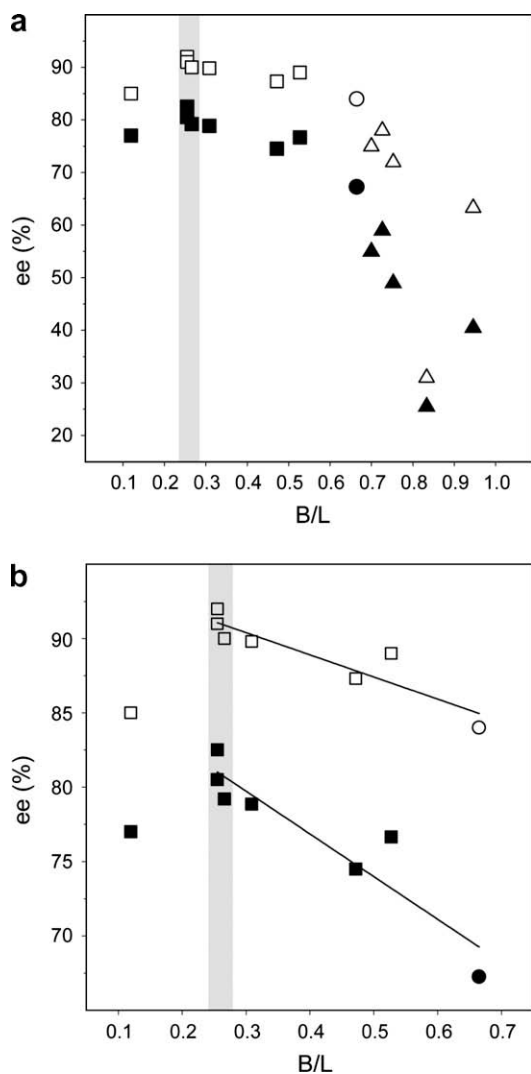


Fig. 9. Variation of the ee with the electronic properties of Pt reflected by the B/L ratio of CO adsorption on the a) Pt/Al, Pt/Al-Si, and Pt/Al-Cs catalyst series and b) Pt/Al and Pt/Al-Si catalyst series. Filled symbols: ketopantolactone hydrogenation, open symbols: methyl benzoylformate hydrogenation. ●○: Pt/Al catalyst; ■□: Pt/Al-Si catalysts, and ▲△: Pt/Al-Cs catalysts.

91.6% was achieved on the Pt/Al₂O₃ – cinchonidine system at 70 bar and –9 °C in toluene [73]. In that study, and also in the hydrogenation of ethyl benzoylformate affording 98% ee, the commercial Pt/Al₂O₃ (E4759) catalyst was applied, which is used as a reference in the present study.

In the following, the hydrogenation of ketopantolactone to (*R*)-pantolactone – an important intermediate in the industrial synthesis of pantothenic acid – was chosen as the test reaction. To prove the superior performance of Si-doped Pt/Al₂O₃ catalysts, the Pt/Al-22.5Si sample was selected for a limited parameter study. This catalyst possessed the highest acidity as indicated by TPD of ammonia and hydrogenolysis of methyl cyclohexyl ketone [33]. A key parameter in the optimization of ketopantolactone hydrogenation was the CD concentration [73]. The optimum in the CD/Pt molar ratio was 0.01 with the E4759 catalyst but using our Si-doped catalyst, the ee could be improved by increasing this ratio by a factor of 3–10, under otherwise identical conditions (Fig. 10). The difference probably arises from the higher amount of CD adsorbed on the more acidic support, leading to a lower actual CD concentration in solution, and thus on the Pt surface. The change can be compensated by increasing the overall CD/Pt molar ratio. Note that the dis-

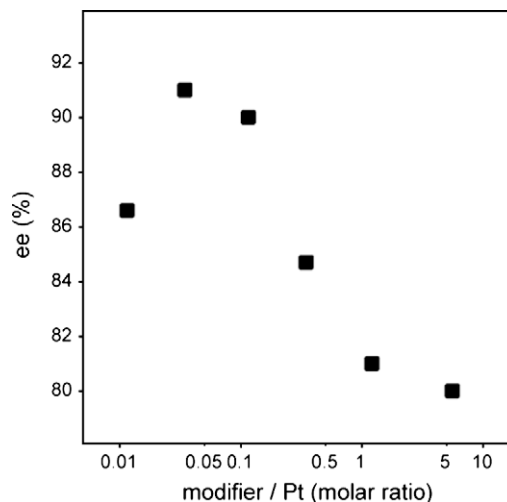


Fig. 10. Influence of the molar ratio of CD to the total amount of Pt on the enantioselectivity in the hydrogenation of ketopantolactone over the Pt/Al-22.5Si catalyst. Standard conditions, toluene, 100 bar, 18 °C.

persion of Pt in the two catalysts is also different, but this effect is relatively small. Repeating the best reaction in Fig. 10 at –10 °C gave $94 \pm 0.5\%$ ee, which value was well reproducible. It is expected that a careful re-optimization including a broader range of reaction parameters can provide even better enantioselectivities.

4. Conclusions

The effect of the support on catalyst performance, or more specifically on the Pt electronic properties in heterogeneous catalysis, is an extensively studied – and debated – field. It is still a challenging task to localize the origin of the phenomenon and separate it from the disturbance caused by, for example, the different impurities in the catalyst systems compared.

In this study, we applied two series of flame-made Pt/Al₂O₃ catalysts, where the acidic or basic properties of the support were varied by the introduction of SiO₂ and Cs₂O, respectively. Changing the acid–base properties of the support allowed to vary systematically the electronic properties of Pt, characterized by the bridged to linear (B/L) ratio of chemisorbed CO. A striking correlation was uncovered between the enantioselectivities achieved in the hydrogenation of ketopantolactone and methyl benzoylformate, and the acid–base properties of the catalysts reflected by the ratio B/L of chemisorbed CO. This correlation indicates that the acid–base properties of the support are a key factor for the optimization of the enantioselectivity in the hydrogenation of activated ketones.

The practical importance of this study was demonstrated by the highest enantioselectivity achieved in the hydrogenation of ketopantolactone. On the other hand, our study indicates that trace amounts of basic impurities originating from the catalyst synthesis may explain the sometimes huge differences in the performance of supported Pt catalysts.

As a final note, there is a fundamental difference between the effect of acidic supports and an acid additive or solvent. The support acidity affects the electronic state of Pt and thus influences the enantioselectivity and reaction rate. In contrast, acid additives protonate the basic N atom of the alkaloid modifier and they can even form various linear or cyclic H-bonded complexes with the alkaloid and the ketone [74], and these chemical changes influence the reaction rate and enantioselectivity. To illustrate the differences, in the hydrogenation of ketopantolactone, acetic acid diminishes the ee [75] while the acidic support improves it.

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