Pt/TiO₂ Catalyzed Hydrogenation of Benzoic Acid with Unprecedented High Activity

Miao Guo

Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Xiangtao Kong

Anyang Normal University

Chunzhi Li

Dalian Institute of Chemical Physics

Qihua Yang (✉ yangqh@dicp.ac.cn)

Dalian Institute of Chemical Physics <https://orcid.org/0000-0002-1118-3397>

Article

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Abstract

The hydrogenation of benzoic acid (BA) to corresponding cyclohexanecarboxylic acid has important industry and academia significance, however, the electron deficient aromatic ring and the catalyst “poison” by carboxyl group make BA hydrogenation as one of the most challenging transformations. Herein, we found that Pt NPs deposited on TiO_2 were very effective for BA hydrogenation with a record TOF of 4490 h^{-1} under 80°C and 50 bar H_2 in hexane, one order higher than the reported results. DFT calculation showed that Pt NPs had a weaker interaction with BA than Ru and Pd NPs commonly used for BA hydrogenation, which improved the toxicity resistance of catalyst to BA. Pt/ TiO_2 catalysts with electron deficient and electron enriched Pt sites were successfully synthesized by modifying the electron transfer direction between Pt and TiO_2 . Isotopic experiments suggested the participation of dissociated H from carboxyl group in BA hydrogenation. Consequently, the electron deficient Pt sites with stronger adsorption of BA were more active than electron rich Pt sites in BA hydrogenation. In addition to BA, terephthalic acid, iso-phthalic acid, trimesic acid and other BA derivatives could also be efficiently converted to corresponding aromatic saturated products, demonstrating the wide substrate scope of Pt/ TiO_2 .

Introduction

The selective hydrogenation of benzoic acid (BA) or its derivatives has been widely used for the production of fine chemicals, intermediates and industrial raw materials [1-3]. For example, BA hydrogenation to cyclohexanecarboxylic acid (CCA) is an important step in the production of nylon-6 in industry [4-5]. However, the need to overcome the high resonance energy of the electron deficient aromatic ring [6] and the catalyst “poison” by carboxyl group [7,8] make BA hydrogenation as one of the most challenging transformations. Harsh conditions ($100\sim 250^\circ\text{C}$, $50\sim 150$ bar H_2) are typically required in order to obtain high BA conversion, which inevitably causes the decrease in selectivity due to the side reactions of decarboxylation and over hydrogenation [9,10]. Up to now, various supported metal catalysts (e.g. Pd, Ru, Rh, and Ni) have been used for BA hydrogenation under relatively mild conditions, but the activity is still relatively low [11,12].

Previous results demonstrated that most of the supported metal catalysts were active only with water as solvent under mild condition and showed low or no activity in organic solvents for BA hydrogenation [13]. The typical solvation effect is possibly related with the preferential adsorption of aromatic ring on metal surface induced by the interaction of carboxyl group with H_2O molecules [13,14] and the participation of H^* from the dissociated H_2O molecules in the reaction [2,15]. Though water could modify the adsorption mode of substrates, it may also block the surface active sites [16,17]. Taken together the low H_2 solubility in water (e.g. $0.792 \text{ mmol L}^{-1}$, 298.15 K , 1 atm H_2) [18], water is not a good choice for efficient BA hydrogenation under mild conditions.

Carboxylates tend to strongly adsorb on metal surface, which significantly deteriorates the catalytic activity through so-called “poison effects” [19]. In contrast, the adsorption of aromatic ring of BA on metal surface is weak considering that the electron deficient phenyl ring does not easily bind to the surface unoccupied *d*-metal orbitals via π -bonds [20,21]. This may be the reason that most metal NPs showed relatively low activity in BA hydrogenation. Recently, our group reported that the activity of Ru NPs was greatly enhanced in BA hydrogenation by tuning the adsorption mode of BA on metal surface with phosphine ligands [2]. Therefore, to realize the efficient BA hydrogenation, the supported metal NPs with appropriate adsorption strength towards carboxyl group and aromatic ring may be the good choice.

Herein, we reported that Pt/TiO₂ is a highly active and selective catalyst for BA hydrogenation under mild conditions in either organic solvents or water by screening a series of supported metal NPs. Pt/TiO₂ gives a record activity with apparent TOF up to 4490 h⁻¹ under 80 °C and 50 bar H₂ in hexane. The studies indicated that electron deficient Pt sites were more active than electron rich Pt sites, possibly due to the facilitated participation of H from carboxyl group in BA hydrogenation on electron deficient Pt sites.

Results And Discussion

Screening the Supported Metal NPs for BA Hydrogenation

Firstly, commercially available carbon supported metal NPs were tested in BA hydrogenation (**Figure 1a**). Pd/C (5 wt%) and Ru/C (5 wt%) were almost inactive in hexane at 40 °C and 10 bar H₂, similar to previous report [13, 22]. To our delight, Pt/C (5 wt%) afforded 51% conversion with > 99% selectivity to CCA under identical conditions. Inspired by this result, different types of supported Pt catalysts with Pt loading of 2 wt% were screened in BA hydrogenation (**Figure 1a**) considering that the support with different acid/base or redox properties may influence the catalytic performance of supported metal NPs [23,24]. Pt/MgO, Pt/CeO₂, Pt/CN and Pt/ γ -Al₂O₃ afforded less than 20% BA conversion. Pt/SiO₂ and Pt/ZrO₂ gave moderate BA conversion respectively of 65% and 35%. Pt/TiO₂ afforded high BA conversion of 96% with > 99% selectivity to CCA. The catalyst screen results suggest that the base and acid support respectively deteriorate [25] and promote [26] the aromatic hydrogenation activity of Pt in BA hydrogenation. Even at 25 °C and 1 bar H₂, Pt/TiO₂ could still afforded > 99% BA conversion and CCA selectivity (**Table 1**). The apparent TOF of Pt/TiO₂ was calculated to be 115 h⁻¹ at 25 °C, 1 bar H₂ and 638 h⁻¹ at 40 °C, 10 bar H₂. To increase S/C ratio is very important for practical applications. Thus, the BA hydrogenation was performed at S/C as high as 1200 over Pt/TiO₂ in the presence of acetic acid to facilitate the dissolution of BA in hexane. Under such harsh conditions, Pt/TiO₂ could still afford 90% conversion with the apparent TOF of 4490 h⁻¹ at 80 °C and 50 bar H₂, an order of magnitude higher than the supported metal NPs ever reported (**Table S1**).

Table 1. The catalytic performance of Pt/TiO₂ catalysts in the hydrogenation of BA.^a

Cat.	Solvent	S/C	Conv. (%)	Sel. (%) ^b	TOF (h ⁻¹) ^c
Pt/TiO ₂	hexane	250	> 99	> 99	638 (2200)
	water	250	84	> 99	266 (917)
	acetic acid	250	68	96	177 (610)
Pt/TiO ₂ ^d	hexane	100	> 99	> 99	115 (397)
Pt/TiO ₂ ^e	hexane/acetic acid	1200	90	99	4490 (15480)
Pt/TiO ₂ -200	hexane	250	59	> 99	171 (757)
Pt/TiO ₂ -450	hexane	250	10	98	25 (103)

^aReaction conditions: 40 °C, 10 bar H₂, 1 h. ^bSelectivity to CCA. Only less than 5% cyclohexenecarboxylic acid (CEA) was detected as the intermediate during the reaction process. ^cApparent TOF is calculated as moles of converted BA per mole of Pt per hour with the conversion less than 30%. The values in parentheses were the TOF calculated based on Pt dispersion. ^d25 °C, 1 bar H₂, 3 h. ^e80 °C, 50 bar H₂, 1.5 h.

The catalyst screen results suggest that Pt NPs are active for BA hydrogenation in hexane irrespective of the supports, different from Pd and Ru NPs. Density functional theory (DFT) calculation showed that the adsorption energies of BA on Pt (111), Pd (111) and Ru (1000) is respectively of -1.53 eV, -2.87 eV and -2.95 eV, showing the stronger adsorption of BA on Ru and Pd than on Pt and the adsorption energies of acetic acid on Pt (111), Pd (111) and Ru (1000) gave similar tendency (**Figure 1b**). This suggests that the relative weak adsorption strength of BA on Pt may contribute to the high activity of Pt NPs in BA hydrogenation.

Pt/TiO₂ was active in hexane, H₂O, cyclohexane, isopropyl alcohol and EtOH (**Tables 1 and S2**), showing the wide solvent tolerance. Even using acetic acid as the solvent, 68% conversion could still be obtained, showing the high anti-carboxyl poisoning ability of Pt NPs. The product selectivity to CCA is > 93% for all the solvents investigated with cyclohexenecarboxylic acid as the side product. BA conversion in aprotic and oxygenate free solvents (e.g. n-hexane) is much higher than that in protic and oxygenate solvents. The decreased hydrogenation rate may be related to the hydrogen bonding of protic solvent and BA, which may hinder the BA adsorption on Pt surface [27]. It is noteworthy to mention that the activity of Pt/TiO₂ was much lower in water than in hexane, which is possibly related with the active sites blocking and low solubility of H₂ in water [16, 18, 28].

The Influence of Electronic and Geometric Structures of Pt on BA Hydrogenation

Pt/TiO₂-200 and Pt/TiO₂-450 were prepared by treatment of Pt/TiO₂ under H₂ atmosphere at 200 and 450 °C, respectively. The TEM, HRSEM and HAADF-STEM images of Pt/TiO₂, Pt/TiO₂-200 and Pt/TiO₂-

450 showed the uniform distribution of Pt with particle size of 2.9 nm, showing that no aggregation of Pt NPs occurred during the H₂ treatment process (**Figures 2, S1-S3**). The CO chemisorption results showed that Pt dispersion for Pt/TiO₂, Pt/TiO₂-200 and Pt/TiO₂-450 was respectively of 29.0, 22.6 and 24.2 (**Table 2**). The Pt dispersion of Pt/TiO₂-200 and Pt/TiO₂-450 slightly decreased, which may be caused by the weak adsorption ability of CO at the interface of Pt and TiO₂ after H₂ treatment [29]. The Pt dispersion obtained by H₂ molecules was almost the same for Pt/TiO₂, Pt/TiO₂-200 and Pt/TiO₂-450 (**Table 2**). It should be noted that the Pt dispersion of Pt/TiO₂ before and after H₂ treatment was comparable, showing that the H₂ treatment of Pt/TiO₂ did not induce the severe coverage of Pt surface by TiO_x, which may be due to pre-nucleation reduction method for the synthesis of the parent Pt/TiO₂ [30,31].

The reaction profiles for BA hydrogenation displayed that more BA was converted to CCA with Pt/TiO₂ than with Pt/TiO₂-450 within the same reaction time (**Figure S4**). Under similar conditions, Pt/TiO₂ with > 99% conversion was more active than Pt/TiO₂-200 and Pt/TiO₂-450 with conversion respectively of 59% and 10% (**Table 1**). To make reasonable comparisons, the TOF of Pt/TiO₂ catalysts was normalized to Pt dispersion obtained with CO chemisorption. Pt/TiO₂, Pt/TiO₂-200 and Pt/TiO₂-450 respectively afforded TOF of 2200 h⁻¹, 757 h⁻¹ and 103 h⁻¹, further confirming that Pt/TiO₂ is more active than Pt/TiO₂-200 and Pt/TiO₂-450.

Generally, the H₂ treatment of Pt/TiO₂ at high temperature would induce the change in electronic and geometric structure of Pt due to the strong metal-support interaction (SMSI) [32]. In order to understand the different catalytic properties of Pt/TiO₂ catalysts, the electronic structure of Pt was firstly characterized by X-ray photoelectron spectroscopy (XPS) (**Figure 2c, Table 2**). Compared with Pt/TiO₂, Pt 4f binding energies (BEs) of Pt/TiO₂-200 and Pt/TiO₂-450 showed an obvious downward shift respectively by 0.3 eV and 0.4 eV, suggesting that Pt/TiO₂ had more electron deficient Pt sites than Pt/TiO₂-200 and Pt/TiO₂-450. The decrease in Pt 4f BEs indicates the charge transfer from Ti cations to Pt NPs induced by SMSI [33], which was further confirmed by the higher Ti 2p_{3/2} BEs of Pt/TiO₂ than those of Pt/TiO₂-200 and Pt/TiO₂-450 (**Figure S5**). It should be noted that Ti 2p_{3/2} BEs of Pt/TiO₂ were lower than those of TiO₂, implying the electron transfer from Pt to Ti cations. The Pt⁰/Pt^{δ+} ratio of Pt/TiO₂ increased from 68/32 to 74/26 after heat treatment in H₂, showing that the reduction degree of Pt increased at high temperature (**Table 2**). The electronic structure of Pt/TiO₂ catalysts could be facilely modified due to the electron-withdrawing ability of acidic TiO₂ support [34] and the SMSI effect of Pt-TiO₂ system [35].

The electronic and geometric structures of Pt NPs were further characterized with in situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) of CO chemisorption (**Figure 2d**). DRIFTS of adsorbed CO for Pt/TiO₂ showed four distinct ν_{CO} bands in the linear carbonyl region located at approximately 2115, 2096, 2079 and 2062 cm⁻¹. The band at 2115 cm⁻¹ can be assigned to Pt^{δ+} [36]. The lower frequency vibrational stretch at 2062 cm⁻¹ was assigned to CO molecules adsorbed on low-

coordination Pt-edge and -corner sites. The higher frequency vibrational stretch at 2096 and 2079 cm^{-1} can be assigned to CO molecules that are adsorbed on the Pt (111) terrace sites (the coordination number of 9) and Pt (110) (the coordination number of 8), respectively [37-42]. The DRIFTS of adsorbed CO for Pt/TiO₂-200 was similar to that of Pt/TiO₂ with the exception that the red shift of the vibration peaks was observed, showing the electron donation from Ti cations to Pt due to SMSI effect. The lower activity of Pt/TiO₂-200 than Pt/TiO₂ suggested that Pt with electron deficient surface was favorable for the BA hydrogenation considering that the two catalysts had similar geometric surface structure of Pt.

Table 2. Pt dispersion measured with H₂/CO chemisorption, Pt 4f and Ti 2p binding energies by XPS of Pt catalysts.

Cat.	Pt dispersion (%) a	Pt dispersion (%) b	Ti 2p _{3/2} (eV) c	Pt 4f _{7/2} (eV) c	Pt ⁰ /Pt ⁺ (%) c
Pt/TiO ₂	29.0	48.4	458.4	71.1	68/32
Pt/TiO ₂ -200	22.6	49.6	458.6	70.8	70/30
Pt/TiO ₂ -450	24.2	44.6	458.6	70.7	74/26
TiO ₂	–	–	458.5	–	–

^aData calculated from CO chemisorption results. ^bData calculated from H₂ chemisorption results. ^cData obtained from XPS results.

The DRIFTS of adsorbed CO for Pt/TiO₂-450 is quite different from those of Pt/TiO₂ and Pt/TiO₂-200. The obvious change in peak intensities of Pt/TiO₂-450 suggested the reconstruction of surface Pt atoms under high temperature H₂ treatment [39]. The relatively high peak intensity at 2083 cm^{-1} indicated that Pt surface had more well-ordered Pt surface (111). The peak assigned to Pt (111) gradually red shifted with H₂ treatment temperature increasing, implying the TiO₂ donates more electrons to Pt at higher temperature [43]. In comparison with Pt/TiO₂ and Pt/TiO₂-200, the much lower activity of Pt/TiO₂-450 indicated that the electron deficient and low coordination Pt sites may be active for BA hydrogenation.

The reaction order of BA and H₂ was investigated with Pt/TiO₂ and Pt/TiO₂-450 as representative catalysts considering that the reaction kinetics are particularly sensitive to the active Pt structure (**Figures 3a, 3b**) [44,45]. The order of BA hydrogenation with respect to BA is respectively of -0.29, and 0.45 for Pt/TiO₂, and Pt/TiO₂-450, implying the stronger adsorption of BA on Pt/TiO₂ than on Pt/TiO₂-450. The reaction rate of Pt/TiO₂ increased along with the H₂ pressure and no plateau was observed with H₂ pressure range of 6 to 40 bar, which was possibly related with the strong adsorption of BA. The reaction order with respect to H₂ for Pt/TiO₂ and Pt/TiO₂-450 is +0.50 and ~0, respectively. The positive order in

hydrogen for the BA hydrogenation is a logical consequence of hydrogenation being involved in rate-determining step. The kinetic results showed that the overall reaction order of BA hydrogenation on Pt/TiO₂-450 is much larger than that on Pt/TiO₂ (+0.46 vs. +0.25, **Table S3**), indicating different reaction mechanism for the two catalysts. Temperature dependent reactivity measurements were taken to obtain apparent activation barriers with Pt/TiO₂ and Pt/TiO₂-450 as representative (**Figure 3c**). The activation energies for Pt/TiO₂ and Pt/TiO₂-450 were respectively of ~38 kJ mol⁻¹ and ~56 kJ mol⁻¹, showing the two catalysts have different catalytic sites for BA hydrogenation [46-48]. The higher energy barriers of Pt/TiO₂-450 explains its low activity in BA hydrogenation.

The characterization data showed that the electron density of Pt NPs followed the order of Pt/TiO₂ < Pt/TiO₂-200 < Pt/TiO₂-450. In combination with the catalytic activity, we can infer that the electronic deficient Pt may favor the high BA hydrogenation. From kinetic data, Pt/TiO₂ and Pt/TiO₂-450 had strong and weak adsorption towards BA, implying that electron rich Pt had weaker adsorption for BA. According to the Sabatier rule, too strong or too weak adsorption of reactants on catalysts does not favor high activity. The minus reaction order of BA over Pt/TiO₂ means that BA (or CCA) in fact is “a poison” for the catalyst, which blocked the active sites.⁴⁹ The higher reaction order of H₂ over Pt/TiO₂ than over Pt/TiO₂-450 indicated that H₂ adsorption is relative more difficult for the former sample due to the strong BA adsorption. But Pt/TiO₂ still showed much higher activity than Pt/TiO₂-450, suggesting that the H₂ activation played an important role in BA hydrogenation. The H₂ activation ability of the catalysts was measured using H₂-D₂ exchange experiments (**Figure 3d, Table S4**). The normalized HD formation rate of Pt/TiO₂ is more than 10 fold that of Pt/TiO₂-450, showing that Pt/TiO₂ with electronic deficient Pt surface is more active for H₂ activation than Pt/TiO₂-450 with electronic rich Pt surface. This result suggests that the high activity of Pt/TiO₂ is partly attributed to the high H₂ activation ability.

The Role of the Carboxyl Group

Generally, the deficient phenyl ring does not easily bond on metal surface [20], which always results in low catalytic activity [50]. However, the high activity of Pt/TiO₂ in BA hydrogenation suggests that carboxyl group may affect the hydrogenation activity. To identify the role of carboxyl group in BA hydrogenation, hydrogenation of benzo-trifluoride and toluene were conducted (**Figure 4a**). Pt/TiO₂ could efficiently catalyze the hydrogenation of the above substrates to the corresponding aromatic ring hydrogenated products. The activity followed the order of BA > toluene > benzo-trifluoride under similar reaction conditions. The unusual high activity of BA hydrogenation was in contrast to the previous findings that the deficient phenyl ring was difficult to be hydrogenated. This suggests that the carboxyl group may be involved in the whole reaction process although it cannot easily be hydrogenated at mild reaction conditions [10].

DFT calculation results showed that the most favorable adsorption configuration of toluene on Pt(111) was the benzene ring adsorption parallel to the metal plane, and the methyl group was far away from the Pt surface. This mainly due to better superposition of its π -orbitals with the Pt conduction band (**Figure**

4b) [51,52]. Different from toluene, BA molecule adopted a configuration that an O atom of the carboxyl group was co-adsorbed on the Pt surface. The strong adsorption of BA on Pt/TiO₂ as discussed above may be derived from the co-adsorption of carboxyl group on Pt surface [53]. The dissociated hydrogen stems from the carboxyl group may act as one of the H sources. To confirm this, a control experiment was conducted by using benzoic acid-d⁵ and D₂ as reactants. The MS analysis of the product showed the appearance of molecular ion peaks at m/z of 139.2 and 138.2 with the intensity ratio of 1.9, denoting the presence of 6 deuterated and 5 deuterated CCA in the product (**Figure 4c**). An obvious sharp peak at 1.255 was observed in the ¹H-NMR spectrum of the product assigned to the H on the m- or p-position of cyclohexane ring (**Figure 4c**), further confirming the results of MS analysis. The above results show that the dissociated H from carboxyl group is involved in the hydrogenation process. To this end, the active Pt–H species from homolytic dissociation of hydrogen and dissociated H from carboxyl group attack the activated BA molecule to produce CCA. Besides, the adsorption of carboxyl group on Pt/TiO₂ favored the orientation of the aromatic ring on the Pt surface, which may facilitate the hydrogen transfer from Pt surface to BA molecules [54]. On the basis of this mechanism, the Pt with electron deficient surface favored the adsorption and dissociation of carboxyl group, which could enhance the BA hydrogenation activity.

Substrate scopes of Pt/TiO₂

Pt/TiO₂ was also used for the hydrogenation of BA derivatives at mild conditions (**Table 3**). Firstly, the hydrogenations of methyl-substituted BA (o-, m-, and p-), p-ethyl benzoic acid and p-pentyl benzoic acid were investigated and the full conversion was obtained in 6 h with the kinetically favored cis isomer [55]. The cis/trans ratio varied in the range of 20/30 to 86/14 (**Table 3, entry 1-5**). For p-isopropyl benzoic acid, it needed 10 h to reach full conversion with the cis/trans ratio of 68/32 (**Table 3, entry 6**). Even for p-trifluoromethylbenzoic acid with more electron deficient aromatic ring, full conversion was achieved in 10 h though S/C ratio was decreased to 50/1 (**Table 3, entry 7**), demonstrating the high activity of Pt/TiO₂. p-Hydroxylbenzoic acid, phenyl propionic acid and phenyl pentanoic acid could be efficiently transferred to corresponding products over Pt/TiO₂ (**Table 3, entry 8-10**). The hydrogenation of methyl benzoate, mono-methyl terephthalate and dioctyl phthalate resulted in the formation of the aromatic hydrogenated products using Pt/TiO₂ as catalyst (**Table 3, entry 11-13**). It should be mentioned that Pt/TiO₂ could also catalyze the hydrogenation of terephthalic acid, phthalic acid, iso-phthalic acid and even the challenging trimesic acid and trimethyl trimesate to corresponding aromatic ring saturated product under mild conditions, further demonstrating the high efficiency of Pt/TiO₂ for the hydrogenation of aromatic acids (**Table 3, entry 14-18**). The hydrogenation of dioctyl phthalate/phthalate acid and trimesic acid/trimethyl trimesate respectively produced the trans and cis isomers, and the hydrogenation of the other substrates investigated in this paper resulted in the formation of cis isomer as the main product on the basis of NMR analysis (see **SI**), which may be caused by the steric hindrance effect [56].

Table 3. Hydrogenation of BA derivatives using Pt/TiO₂ as catalyst.^a

Entry	Substrate	Product	Time (h)	Conv. (%)	Sel. (%) ^b
1			6	> 99	99 (cis:trans=70:30)
2			6	> 99	99 (cis:trans=79:21)
3			6	> 99	99 (cis:trans=86:14)
4			6	> 99	99 (cis:trans=72:28)
5			6	> 99	99 (cis:trans=72:28)
6			10	> 99	99 (cis:trans=68:32)
7 ^d			10	> 99	> 99 (cis:trans=64:36)
8 ^e			12	> 99	> 99 (cis:trans=65:35) ^c
9			6	> 99	> 99
10 ^d			6	> 99	> 99
11			6	> 99	> 99
12 ^f			10	> 99	99% (cis:trans=66:34)
13 ^g			3	> 99	99% (cis:trans=0:~100)
14 ^h			2	> 99	99% (cis:trans=0:~100)
15 ⁱ			3	> 99	99% (cis:trans=77:23)
16 ^j			3	> 99	99% (cis:trans=77:23)
17 ⁱ			3	> 99	99% (cis:trans=~100:0)
18 ^g			3	> 99	99% (cis:trans=~100:0)

^aReaction conditions: 40 °C, 10 bar H₂, S/C = 250, 3 mL hexane, ^bSelectivity to ring hydrogenation product; the cis:trans ratio was determined by ¹H-NMR results (See **SI**) [57]; ^cChair conformation. ^dS/C= 50; ^e3mL H₂O; ^f1.5 mL hexane and 1.5 mL acetic acid; ^g60 °C; ^h60 °C, 1.5 mL H₂O and 1.5 mL acetic acid; ⁱ60 °C, 20 bar H₂, 3 mL solvent (10 v/v % H₂O in n-hexane); ^j80 °C, 20 bar H₂, 3 mL hexane (10 v/v % H₂O in n-hexane).

The recycle stability of Pt/TiO₂ was investigated using BA hydrogenation as a model reaction (**Figure 4d**). The recovered Pt/TiO₂ can be repeatedly used in the hydrogenation reactions, for example in 5 runs of our demonstration, without showing discernible decrease in the conversion of BA or the reaction selectivity. The Pt/TiO₂ after five cycles had similar particle size as the fresh one on the basis of TEM characterizations (**Figure S6**), confirming that no aggregation of Pt NPs occurred during recycling process.

Conclusion

In summary, Pt/TiO₂ was found to be a superior catalyst for BA hydrogenation in comparison with Ru/C and Pd/C due to the weak interaction strength between Pt and BA which inhibited the toxic of BA to the catalyst. A record TOF of 4490 h⁻¹ was achieved with Pt/TiO₂ under 80 °C and 50 bar H₂ in hexane, more than 10 times higher than the literature results under similar conditions. Isotopic studies confirmed that the dissociated hydrogen from the carboxyl group was involved in BA hydrogenation which could be facilitated by the strong adsorption of BA on Pt surface. By comparing the activity of Pt/TiO₂ catalysts with different surface electronic and geometric structures, it could be concluded that electron deficient and low coordination Pt sites had higher catalytic activity than electron rich and high coordination Pt sites in BA hydrogenation, possibly due to the combined effect of higher H₂ activation ability and the stronger adsorption of BA by electron deficient Pt sites. The wide substrate scope including e.g. very challenging terephthalic acid, phthalate acid, phthalic acid, iso-phthalic and trimesic acid demonstrates the potential practical applications of Pt/TiO₂ in hydrogenation of BA and its derivatives.

Experimental Section

Chemicals and Materials

The chemicals were purchased from commercial suppliers and used as received with details listed below: 4-methylbenzoic acid (98%, Innochem (Beijing) chemicals), anisic acid (98%), benzamide (98%), cyclohex-1-ene-1-carboxylic acid (97%) were from ARK Chemicals. dioctyl phthalate (99%), phthalic acid (98%), 4-ethylbenzoic acid (98%), 4-isopropylbenzoic acid (98%) and 4-amybenzoic acid (98%) were from Aladdin (Shanghai) chemicals. 4-Hydroxybenzoic acid (99%), 2-methylbenzoic acid (98%) and 3-methylbenzoic acid (98%) were from TCI (Shanghai) chemicals. Benzoic-2, 3, 4, 5, 6-d⁵ acid (≥99 atom % D) was purchased from Macklin Chemicals. Chloroplatinic acid (H₂PtCl₆), toluene and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. TiO₂ (Rutile, 25-30 nm) was bought from Aladdin (Shanghai) chemicals. Fumed silica (SiO₂) and Pt/C (5%) were respectively from Sigma-Aldrich and TCI chemicals.

Catalyst Preparation

Preparation of the Pt/TiO₂ Catalyst

Pt catalysts with Pt loading of 2 wt% were prepared by the deposition precipitation method using NaBH_4 as the reactant [34, 58]. Typically, 200 mg of TiO_2 and the desired amount of H_2PtCl_6 (4 mg Pt) was initially dispersed into 50 mL of aqueous solution. After stirring for 1 h at room temperature, a freshly prepared NaBH_4 aqueous solution (2.3 mg, 0.2 mg mL^{-1}) was added slowly. After stirring for another 1 h, the solid was collected by filtration and washed with water and ethanol for three times. Finally, the obtained powder was dried at room temperature overnight. The catalyst was denoted as Pt/ TiO_2 .

Preparation of the Pt/ TiO_2 -200 and Pt/ TiO_2 -450 Catalyst

Pt/ TiO_2 was treated in a H_2 atmosphere with a flow rate of 20 mL min^{-1} at the desired temperature for 2 h with a heating rate of 1°C min^{-1} . The sample after treatment was denoted as Pt/ TiO_2 -T, where T (200 and 450) refers to the treatment temperature.

Synthesis of Other Oxide Support Loaded Pt Catalyst

Pt/ SiO_2 with Pt loading of 2 wt% was prepared by the wet impregnation method by dispersing SiO_2 (200 mg) in 2 mL of aqueous solution of H_2PtCl_6 (4 mg Pt) for 5 h. Then the solid product after drying by an evaporator and reduced under H_2 atmosphere at 300°C for 2 h to afford Pt/ SiO_2 . Other oxide supported Pt catalysts were prepared with a similar method to Pt/ TiO_2 except that the corresponding oxide was used as supports. Analysis by inductively couple plasma atomic emission analysis (ICP-AES) clearly indicated that the desired amounts of metal species were successfully loaded onto each of the catalysts.

Characterization

Transmission electron microscopy (TEM) image were obtained using a HITACHI HT7700 at an acceleration voltage of 100 kV. High-resolution scanning electron microscopy (HRSEM) was undertaken by using a HITACHI S5500 apparatus operating at an acceleration voltage of 1-30 kV. X-ray photoelectron (XPS) was performed on an ESCALAB 250xi spectrometer using Al K α radiation. All the XPS spectra were calibrated by the C1s peak (284.6 eV) from contamination to compensate the charge effects. N_2 sorption isotherms were carried out on a Micromeritics ASAP2020 volumetric adsorption analyzer. Liquid ^1H and ^{13}C , NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 25°C .

In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) of CO chemisorption was measured on a Thermo Scientific IR spectrometer with a mercury cadmium telluride (MCT) detector, recorded with a resolution of 4 cm^{-1} [59]. Prior to CO adsorption, the samples were treated in situ in the DRIFT cell under a H_2 flow (20 mL min^{-1}) at the desired temperatures for 1 h, followed by purging with a He flow at the same temperature for 30 min. After cooling to room temperature, a background spectrum was collected. Then the He flow was switched to a pure CO flow (20 mL min^{-1}) until saturated adsorption was achieved. CO adsorption experiments were carried out sequentially on a single sample. Gas-phase CO spectra were collected at the same pressure and subtracted from the corresponding sample spectra.

CO/H₂ chemisorption measurement was performed at 50 °C on a Autochem II 2920 chemisorption instrument with a thermal conductivity detector (TCD). The sample (~100 mg) was pretreated with hydrogen at desired temperatures for 1 h, followed by purging with high-purity He (or Ar) for 30 min. After the sample was cooled down to 50 °C, a 5% CO/He (or 10% H₂/Ar) mixture was injected into the reactor repeatedly until CO (or H₂) adsorption was saturated. The dispersion of Pt was calculated from the amount of CO adsorbed by assuming the CO/Pt adsorption stoichiometry to be 1/1.

H₂-D₂ exchange reactions were carried out in a flow quartz reactor at 22 °C [60]. The formation rate of HD was measured by mass signal intensity (ion current). Before the test, the catalysts were heated in H₂ (10 mL min⁻¹) at 200 °C for 20 min. After the sample was cooled down to room temperature, D₂ (10 mL min⁻¹) mixed with H₂ was passed through the sample. The gas hourly space velocity (GHSV) is 2.9×10^7 mL h⁻¹ g_{metal}⁻¹. Under these conditions, the H₂-D₂ exchange conversions were always kept below 15% for calculation of turnover frequency (TOF) [61]. Products (HD, H₂, and D₂) were analysed with an online mass spectrometer (GAM200, InProcess Instruments). The mass/charge ratio (m/z) values used are 2 for H₂, 4 for D₂, and 3 for HD. The background HD exchanges from the corresponding support were deducted from the results.

General Procedure for the Hydrogenation of Benzoic Acid (BA).

The hydrogenation reactions were carried out in a stainless steel autoclave (300 mL) with a thermocouple-probed detector. In a typical process for benzoic acid (BA) hydrogenation, a desired amount of the solid catalyst was placed in an ampule tube, followed by the addition of BA (0.12 mmol) and 3 mL of n-hexane (for reaction performed at S/C of 1200, 0.3 mL of acetic acid was added to assist the dissolution of BA). The ampule tube was loaded into the reactor. After the tube was purged six times with hydrogen, the final pressure was adjusted to 10 bar and the reactor was heated to desired temperature with vigorous stirring. After the reaction, the solid catalyst was separated by centrifugation and the filtrate was collected, diluted with n-hexane, and analyzed by an Agilent 6890N GC instrument equipped with an Agilent J&W GC HP-INNOWax capillary column (30 m × 0.32 mm × 0.25 μm). The diphenyl ether was used as the internal standard to determine the conversion, selectivity and carbon balance. The carbon balance was ~ 100%.

For the recycle experiments, the liquid was decanted after centrifugation of the reaction mixture. The residual catalyst was thoroughly washed with n-hexane, and used directly for the next run.

Computational Setup

All the calculations were performed with density functional theory (DFT) by using the Vienna Ab-initio Simulation Package (VASP) [62,63]. The projector augmented-wave pseudopotential method with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional including zero-damping DFT-D3 of Grimme's correction was employed [64,65]. A plane-wave basis with cutoff energy of 400 eV was adopted. Four-atomic-layer slab models of Pt(111), Pd(111), and Ru(0001) with the bottom two layers

fixed consisting of 144 metal atoms were built. The vacuum spaces were set as 15 Å between the layers. A gamma k-point sampling of 1×1×1 was selected. The convergence energy and force were set to be 1×10^{-5} eV and 0.02 eV/Å, respectively.

The adsorption energy E_{ad} was calculated as:

$$E_{ad} = E_{ad/sub} - E_{mol} - E_{sub}$$

The $E_{ads/sub}$, E_{mol} and E_{sub} are the total energy of the adsorbed molecule, the molecule in the gas phase, and the pure slab, respectively.

Declarations

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AUTHOR CONTRIBUTIONS

Q. H. Y. conceived the idea. Q. H. Y., M. G., X. T. K. and C. Z. L. co-wrote the paper. M. G. synthesized the nanomaterials and carried out the catalysis experiments. X. T. K. carried out the model construction and DFT calculations. C. Z. L. analyzed part of NMR results. All the authors contributed to the overall scientific interpretation and edited the manuscript.

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Figures

Figure 1

(a) The catalytic results of supported metal NPs for BA hydrogenation in hexane (40 oC, 10 bar H₂, S/C of 700, 2 h). (b) Adsorption energies of BA and acetic acid on Pt (111), Pd (111) and Ru (0001) obtained by DFT calculations.

Figure 2

(a) HRSEM image and (b) HAADF-STEM image of Pt/TiO₂ (scale bar 50 nm). (c) Pt 4f XPS core level spectra and (d) CO DRIFTS results for (i) Pt/TiO₂, (ii) Pt/TiO₂-200 and (iii) Pt/TiO₂-450. The inset in panel a shows particle size distribution of Pt/TiO₂.

Figure 3

Reaction orders with respect to (a) BA and (b) H₂, (c) Arrhenius plots showing apparent activation barriers, and (d) H₂-D₂ exchange results of (i) Pt/TiO₂ and (ii) Pt/TiO₂-450. Reaction conditions for (a) and (b): 3 mL n-hexane, H₂ pressure: 1 - 40 bar, BA concentration: ~ 3 - ~ 10 mg/mL, 40 oC for Pt/TiO₂, 60 oC for Pt/TiO₂-450. Reaction conditions for (c): T = 30-70 oC, S/C=250, 3 mL hexane. The BA conversion was maintained ~ 10 - ~ 20 % by adjusting reaction time.

Figure 4

(a) Comparison of the catalytic activity of Pt/TiO₂ in hydrogenation of benzotrifluoride, toluene and BA. (b) The adsorption mode of (i) BA and (ii) toluene on Pt (111). (c) ¹H-NMR (i) and MS analysis (ii) of the product for benzoic-d₅ acid hydrogenation with D₂. (d) Recycling stability of Pt/TiO₂ in the hydrogenation of BA.

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