Heterogeneous catalysis

Highly Active Supported Pt Nanocatalysts Synthesized by Alcohol Reduction towards Hydrogenation of Cinnamaldehyde: Synergy of Metal Valence and Hydroxyl Groups

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Abstract: The hydrogenation of α , β -unsaturated aldehydes to allylic alcohols or saturated aldehydes provides a typical example to study the catalytic effect on structure-sensitive reactions. In this work, supported platinum nanocatalysts over hydrotalcite were synthesized by an alcohol reduction method. The Pt catalyst prepared by the reduction with a polyol (ethylene glycol) outperforms those prepared with ethanol and methanol in the hydrogenation of cinnamaldehyde. The selectivity towards the C=O bond is the highest

Introduction

The selective hydrogenation of α , β -unsaturated aldehydes to allylic alcohols and/or saturated aldehydes is of scientific importance and industrial relevance. For instance, the unsaturated alcohol products are highly sought for in syntheses of numerous fine chemicals such as fragrances, pharmaceuticals, flavorings and so on. From the academic viewpoint, this reaction provides a good example of catalytic impact on chemoselective reactions.^[1] Among the competing attack on either the conjugated C=C double bond or the carbonyl group (C=O), the former is thermodynamically favored over most of metals (Pd, Rh, Pt) due to a lower free reaction enthalpy of 35 kJ mol⁻¹ than the latter. To overcome the thermodynamic limitation, great efforts have been made to develop catalysts that are able to selectively hydrogenate the C=O bond.

Supported metal catalysts have attracted much attention in the selective hydrogenation owing to the flexible combination

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over the former, although its mean size of Pt particles is the smallest. The hydroxyl groups on hydrotalcite could act as an internally accessible promoter to enhance the selectivity towards the C=O bond. The optimal Pt catalyst showed a high activity with an initial turnover frequency (TOF) of 2.314 s^{-1} . This work unveils the synergic effect of metal valence and in situ promoter on the chemoselective hydrogenation, which could open up a new direction in designing hydrogenation catalysts.

of the metals and supports, their high chemical and structural stability, and excellent recyclability, although their activity may be inferior compared to their homogeneous counterpart.^[2] The supported noble metals like Pt,^[3] Ru,^[4] and Ir^[5] have been proved to be excellent heterogeneous catalysts. Many factors affect the catalytic activity and selectivity including the size^[3c, 6] and shape^[7] of metal particles, a second metal,^[8] the types of supports,^[9] and even the preparation methods.^[10] Until now, it is challenging to achieve high selectivity towards C=O bond hydrogenation under a high substrate conversion, although numerous catalysts have been explored.

Recent studies reported on the synthesis of Pt-based monometallic or bimetallic catalysts over carbon materials by a polyol reduction for cinnamaldehyde hydrogenation. $^{\left[9a,\,10b\right] }$ The relatively mild reduction process is favorable in controlling the sizes and exposed planes of Pt particles. Furthermore, it was reported that the cationic Pt^{δ_+} species could exist after the reduction. However, the role of Pt^{δ_+} has not been associated with the hydrogenation performance of catalysts.^[9a] Xu et al. found Au³⁺ species in the Au/ZrO₂ catalyst and confirmed that isolated surface Au³⁺ ions were active sites for the selective hydrogenation of 1, 3-butadiene.^[11] This suggests that cationic species in the supported catalyst could play a unique role in selective hydrogenation. Furthermore, it was found that an alkali promoter like KOH or NaOH can facilitate C=O hydrogenation.^[3c, 12] Whether the support can act as a native promoter instead of a externally added one is a question that still needs to be addressed. The remaining issues inspired us to design the structure and examine the characteristics of catalysts by controlling the metal valence and surface properties of the support, and finally tune the catalytic performance.

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The hydrotalcites, known as MgAl-layered double hydroxides (LDHs), are a class of anionic clays with a layered structure that involve positively charged brucite-like layers together with charge-balancing anions and water molecules in the interlayer galleries. The cations are surrounded octahedrally by hydroxide ions. These octahedral units form infinite layers by edge-sharing, with the hydroxide ions perpendicular to the layers.^[13] LDHs have been employed as supports to load a variety of catalytically active metals.^[14] The outward hydroxyl groups on the layers could be ideal as "internally accessible promoter", analog to a foreign alkali, to tune the selectivity of hydrogenation products.

Herein, we explored a mild reduction method to load Pt nanoparticles on a pre-synthesized LDH support. The findings showed that the Pt^{2+} species exist in the catalysts after reduction. High activity and selectivity of hydrogenation towards the C=O bond were achieved on the small-sized Pt nanoparticles. Thus, we prove, for the first time, that the synergy of Pt valence and in situ alkali promoter contributes to the high selectivity towards the C=O bond.

Results and Discussion

Characterization of the catalysts

The phase structure of the catalysts was studied by XRD. The XRD patterns of the as-prepared samples are shown in Figure 1. The patterns display characteristic (00*l*) diffractions and (110), (113) ones, which can be well indexed to hydrotalcite-like LDH materials. The d_{003} basal spacing is 7.68 Å, in good agreement with the carbonate-intercalated LDH reported in the literature.^[13] The diffractions and the d_{003} basal spacing of the LDH support (Figure 1a) are almost the same with those of the loaded Pt nanoparticles (Figure 1b–e). This result suggested that the CO_3^{2-} anions in the interlayer galleries of LDH are more stable and could not be easily replaced by the reactant PtCl₆²⁻ anions. Thus, after the reaction, the reduced Pt nanoparticles are mainly located on the surface of two-dimensional layers or the edge sites of LDH rather than within the interlayer space.^[15] It is noted that the diffractions associated



Figure 1. XRD patterns of the LDH support and supported Pt catalysts: (a) LDH, (b) Pt/LDH, (c) Pt/LDH-EG, (d) Pt/LDH-EA, (e) Pt/LDH-MA. The Miller indices are indicated in the patterns.

with metallic Pt or other Pt species cannot be detected within the XRD detection limit in all Pt catalysts. This could be due to the relatively low Pt loading (~2.4 wt%) and/or high dispersion of the tiny Pt nanoparticles anchored onto the support. The characteristics of high dispersion and small size of metal particles are critical to the enhancement in the catalytic activity. In addition, the specific surface areas were measured. Before the loading of Pt, the hydrotalcite has a specific surface area of 91.9 m²g⁻¹, and the supported catalysts Pt/LDH-EG, Pt/LDH-EA, and Pt/LDH-MA have values of 87.8, 88.2, and 87.4 m²g⁻¹, respectively. Accordingly, there is little difference among the Ptsupported catalysts.

Tetradecyl trimethyl ammonium bromide (TTAB) has been reported to act as a stabilizing and structure-directing agent during the synthesis of metal nanocrystals.^[16] The addition of TTAB can mediate the reduction and growth rate of the crystallographic planes with distinct lattice energy, leading to a controlled morphology of the reduced metal nanocrystals. The sizes and morphology of Pt nanoparticles were observed by transmission electron microscopy (TEM) in order to determine the effects of TTAB and various reducing agents. Firstly, the effect of TTAB was studied using ethylene glycol (EG) as a reducing agent. Pt/LDH-EG shows a slightly smaller Pt mean size (2.1 nm, Figure 2b) than that of Pt/LDH (2.5 nm, Figure 2a). However, the former has a narrower size distribution. More than 30% of Pt particles are at or above 3 nm in the latter. No obvious aggregates were observed in the Pt/LDH-EG, thus suggesting excellent dispersion of reduced Pt nanoparticles on the LDH support. It is known that EG, as a mild reducing agent, could mediate the reduction rate and growth kinetics of metal nanocrystals, thus resulting in narrow size distribution.^[17] Besides, TTAB can also tune the reduction kinetics of Pt particles, mainly by the stabilizing effect of bromine ions on the exposed crystal planes of metal.^[18] Consequently, the difference between Pt/LDH and Pt/LDH-EG in the size distribution could be ascribed to the cooperation effect of EG and TTAB.

Secondly, we examined the Pt catalysts obtained using various alcohols under the same reduction conditions. Compared to Pt/LDH-EG, Pt/LDH-EA and Pt/LDH-MA reduced by ethanol and methanol, respectively, have a larger Pt mean size of 3.6 and 2.8 nm (Figure 2 c and 2 d), and broader size distribution as well. A small amount of aggregates was observed in both catalysts. The findings reveal that EG, as a polyol, is superior to the mono-hydroxyl alcohols for mono-dispersed Pt particles. Furthermore, the EDS mappings show that the Pt nanoparticles are highly dispersed on the support in Pt/LDH-EG (Figure S1, Supporting Information). The size and monodispersity of metal particles are critical factors for the catalytic performance. The polyol (EG) reduction is a more favorable way to achieve Pt nanoparticles with a smaller size and narrower size distribution.

To further reveal the microstructure of the Pt NPs, HRTEM observations were carried out. The Pt NPs in Pt/LDH have a quasi-cuboctahedral shape (Figure 2e). The interplanar spacing was measured to be 0.227 nm, suggesting that (111) is the plane perpendicular to the surface. As to Pt/LDH-EG, the Pt NPs present an ellipsoidal appearance with smaller sizes (Fig-

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35 30 25 requency 20 15 5 0 0 2 3 4 5 6 10<u>n</u>m Pt size (nm) f 50 % 40 requency 30 20 10 0∔ 0 3 4 5 6 7 2 3 4 5 Pt size (nm) 40 g (%) 30 30 30 30 30 Frequency 20 15 10 5 0 2 3 4 5 6 Pt size (nm) 5 nm 40 h 35 30 % Frequency (5 0 0+ 0 2 3 4 5 Pt size (nm) 6 10 nm 5 nm

Figure 2. TEM images of the supported Pt catalysts: (a) Pt/LDH, (b) Pt/LDH-EG, (c) Pt/LDH-EA, (d) Pt/LDH-MA. The corresponding size distribution of Pt nanoparticles is shown in the middle column. HRTEM lattice images of Pt catalysts: (e) Pt/LDH, (f) Pt/LDH-EG, (g) Pt/LDH-EA, (h) Pt/LDH-MA. The interplanar spacings are indicated.

ure 2 f). Besides the (111) observed, a fraction of particles exhibited a d-spacing of 0.195 nm, which is indicative of the presence of (200). A previous work demonstrated the shapecontrolled synthesis of free-standing Pt NPs via a bromine-directed way;^[19] however, no significant differences in the morphology between Pt NPs synthesized with and without addition of TTAB were observed. These data indicate that the morphology evolution of the supported Pt NPs differs from that of the free-standing ones in the presence of a directing or stabilizing agent. The Pt NPs reduced by ethanol and methanol show a d-spacing of about 0.225 nm (Figure 2g and 2h). It is known that the catalytic hydrogenation is a reaction that usually depends on the size and/or shape of catalyst.^[20] One can therefore assume that the differences in the sizes and size distributions of the catalysts obtained in our study may lead to a distinct activity and selectivity.

The chemical valence of catalytically active species is a critical factor for the catalytic performance. Therefore, we carried out XPS characterization to study the valence of Pt. For all catalysts, a constant contribution with a maximum at 74.8 ± 0.1 eV is due to the Al 2p core level, coming from LDH support. The Pt 4f core level spectra consist of the spin-orbit components Pt $4f_{7/2}$ and Pt $4f_{5/2r}$ which can be fitted with four components (Figure 3). The peaks at 70.7 ± 0.2 eV and 74.1 ± 0.2 eV can be assigned to metallic Pt⁰ species.^[8b,12] The spin-orbital splitting



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Figure 3. XPS spectra of the Pt 4f core level of the supported catalysts: (A) Pt/LDH, (B) Pt/LDH-EG, (C) Pt/LDH-EA, (D) Pt/LDH-MA.

has a value of about 3.4 eV, which is in agreement with the reported value.^[21] The other two components with maxima at 73.1 ± 0.2 eV and 76.5 ± 0.2 eV are assigned to divalent Pt²⁺ species. The binding energy of Pt 4f_{7/2} and Pt 4f_{5/2} has almost the same values, indicating that the electronic structures of both Pt²⁺ and Pt⁰ are less affected by other species in all Pt catalysts. Furthermore, the ratio of Pt²⁺/Pt⁰ was estimated by the integral peak area of fitted Pt²⁺ and Pt⁰ components. The Pt samples reduced by EG (Pt/LDH and Pt/LDH-EG) have higher Pt²⁺/Pt⁰ ratios (1.21 and 1.28, respectively, Table 1) than those reduced by ethanol and methanol (Pt/LDH-EA = 1.01, Pt/ LDH-MA = 0.99). This interesting finding reveals that more Pt^{2+} species exist in the Pt catalysts synthesized by a polyol reduction. Moreover, the reduction of initial Pt⁴⁺ ions can be mediated by changing the types of alcohols. It has been reported that cationic species of active metals exhibit a unique activity or selectivity in hydrogenation reactions.[11] Therefore, we expect that the Pt²⁺ species in the Pt catalysts may have a cationic effect on the cinnamaldehyde hydrogenation, which will be discussed in the following subsection.

The O 1s spectra were further investigated to gain insight into the oxygen-associated species. For all four Pt catalysts, the

Table 1. XPS binding energy of Pt 4f core levels in the supported catalysts.							
Catalysts	4f _{7/2} [e Pt ⁰	V] Pt ²⁺	4f _{5/2} [e ^v Pt ⁰	V] Pt ²⁺	Ratio (Pt ²⁺ /Pt ⁰) ^[a]		
Pt/LDH Pt/LDH-EG Pt/LDH-EA	70.7 70.9 70.7	73.1 73.1 73.1	74.2 74.4 74.1	76.6 76.6 76.3	1.21 1.28 1.01		
Pt/LDH-MA	70.9 as calcula	73.3 ated by th	74.1 e integral	76.6 peak area	0.99		

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spectra were deconvoluted into two components with a maximum at a binding energy (BE) of 531.9 ± 0.2 eV and 532.8 ± 0.2 eV (Figure 4 and Table 2), which is assigned to a hydroxyl group (OH⁻) and H₂O absorbed on the surface.^[22] Little differ-



Figure 4. XPS spectra of the O 1s core level of the supported catalysts: (A) Pt/LDH, (B) Pt/LDH-EG, (C) Pt/LDH-EA, (D) Pt/LDH-MA.

Table 2. XPS binding energy of the O 1s core level in the supported catalysts.						
Catalysts	O 1s		Ratio ^[a]			
	OH	H₂O				
Pt/LDH	531.9	532.8	1.31			
Pt/LDH-EG	531.9	532.9	1.27			
Pt/LDH-EA	531.9	532.9	1.06			
Pt/LDH-MA	531.8	532.5	1.07			
[a] The ratio of integral peak areas of oxygen species from OH and $\mathrm{H_2O}.$						

ence in the binding energies of both components was observed for all samples. The XPS O 1s analyses verify the hydroxide nature of the LDH support and the presence of a considerable amount of absorbed water. The ratio of hydroxyl to H_2O was estimated by the integral peak area. It was found that the Pt catalysts (Pt/LDH and Pt/LDH-EG) synthesized by EG reduction have higher ratios (1.31 and 1.27) than ethanol- and methanol-reduced Pt catalysts (Pt/LDH-EA and Pt/LDH-MA) with a ratio about 1.07 (Table 2). This reveals that EG-reduced Pt catalysts possess more surface hydroxyl species. Previous studies reported that alkali (KOH or NaOH) could act as a promoter to tune the selectivity of cinnamaldehyde hydrogenation.^[23] Consequently, it is expected that the native hydroxyl-rich characteristic of the LDH support could enhance the selectivity towards C=O hydrogenation without the need of external alkali addition.

Supported metal catalysts are usually studied using a probe molecule, for example, CO by IR spectroscopy, which is able to



Figure 5. FTIR spectra of CO molecules adsorbed on the supported Pt catalysts (A) Pt/LDH-EG, (B) Pt/LDH-EA, (C) Pt/LDH-MA. The time refers to the purging time using a nitrogen gas flow in the stage of gas purge after the CO adsorption.

provide powerful surface-related information. The FTIR spectra of catalysts reduced by alcohols are shown and compared in Figure 5. For the three Pt catalysts, the spectra display three main vibration absorption bands of CO molecules ($v_{C=O}$). The band ranging from 2010-2050 cm⁻¹ can be assigned to the linear adsorption mode of CO onto an individual Pt site.^[24] This band consists of a main peak at about 2020 cm⁻¹ and a shoulder at about 2040 cm⁻¹. It was reported that different Pt species may cause a shift in the linearly adsorbed vibration $v_{C=0}$.^[25] Compared to Pt/LDH-EG (Figure 5A) and Pt/LDH-EA (Figure 5 B), the shoulder in the FTIR spectrum of Pt/LDH-MA is too weak to be observed (Figure 5C). The other two absorptions at approximately 1861 and 1918 cm⁻¹ are attributable to the bridging CO on two or more Pt sites.^[26] Also, the band at 1918 cm⁻¹ could be due to multiple CO adsorption at low-coordinated sites of small-sized Pt particles (e.g., corners, steps or defect sites).^[27] It is observed that the peak positions hardly shift with the purging time of nitrogen, thus indicating stable adsorption of CO in both linear and bridging modes. Furthermore, it is found that the bridging adsorption and multiple CO adsorption are very similar among the catalysts. Pt/LDH-EG

shows a relatively stronger linearly adsorbed vibration band $(2010-2050 \text{ cm}^{-1})$. This indicates that the linear adsorption of CO on Pt species of this catalyst may be the dominant mode.

Catalytic evaluation in cinnamaldehyde hydrogenation

It is known that the competing reactions of C=C and C=O hydrogenation in cinnamaldehyde (CMA) lead to selective products, that is, hydrocinnamaldehyde (HCMA) and cinnamyl alcohol (CMO), respectively (Scheme 1), in which the former is



Scheme 1. The reaction pathway and main products for hydrogenation of cinnamaldehyde. Path A shows selective hydrogenation of the C=C bond to afford HCMA (hydrocinnamaldehyde). Path B shows selective hydrogenation of the C=O bond to afford CMO (cinnamyl alcohol). The complete hydrogenation yields HCMO (phenyl propanol).

a thermodynamically favorable one. Furthermore, it is favorable over the complete hydrogenation product, that is, HCMO. Consequently, it is a great challenge to improve the selectivity towards C=O hydrogenation to obtain the desired CMO product while keeping a high conversion. It was reported that the selectivity of Pt catalysts towards either the C=C or C=O bond is dependent on many factors such as the preparation method, the types of supports, and the metal/support interaction.^[9a, 10b, 28] Here, the cinnamaldehyde hydrogenation was achieved over the Pt catalysts under mild conditions (1 MPa H₂, 60 °C).

For all catalysts, the Pt loading was close to about 2.4 wt% (Table 3). This verifies that the different reducing agents have little impact on the metal loading. The metal dispersion was estimated based on the mean size of Pt particles assuming a cuboctahedral shape of the metal particles.^[29] Pt/LDH-EG has

Table 3. The characteristics of different catalysts and their catalytic performance for hydrogenation of cinnamaldehyde.									
Catalysts Pt loading Pt size Dispersion Conv. $TOF^{[c]}$ Yield Selectivity $[\%]^{[e]}$ [wt $\%]^{[a]}$ [nm] $[\%]^{[b]}$ [%] $[\%]$ $[\%]$ $[\%]^{[d]}$							[e]		
							СМО	HCMA	НСМО
Pt/LDH	2.39	2.5	45.2	72.5	0.894	59.1	81.5	10.5	6.7
Pt/LDH-EG	2.41	2.1	53.8	93.6	2.314	73.7	78.8	9.1	11.2
Pt/LDH-EA	2.43	3.6	31.4	62.5	0.947	39.7	63.5	23.2	12.2
Pt/LDH-MA	2.37	2.8	40.4	50.0	0.603	28.5	57.0	29.8	12.1
[a] As determined by ICP-AES. [b] Estimated from the mean particle size of Pt. [c] Cal- culated at CMA conversion of approximately 10%. [d] Yield of CMO. [e] Selectivity is reported at the level of conversion in the table. Beaction conditions: catalyst: 0.05 g									

reported at the level of conversion in the table. Reaction conditions: catalyst: 0.05 g; substrate: 5 mmol CMA; solvent: 12.5 mL ethanol; H_2 pressure: 1.0 MPa; temperature: 60 °C; reaction time: 30 min.

the highest dispersion (53.8%) due to the smallest metal particle size. It is seen that Pt/LDH-EG results in the highest conversion value of 93.6% under the same catalytic conditions and in a relatively high C=O selectivity towards CMO (78.8%), which is slightly lower than that over Pt/LDH catalyst (81.5%). The high conversion and C=O selectivity lead to a comparably high yield of CMO (73.7%), a desired and thermodynamically unfavorable product. In previous studies, it was usually believed that the selectivity towards CMO decreases with a reduction in Pt particle sizes, but results in higher activity;^[6a, 27] that is, smallsized Pt facilitates the adsorption of the C=C bond owing to a large amount of low-coordinated surface sites. However, in this work, it is found that Pt/LDH-EG (Pt size of 2.1 nm) and Pt/ LDH (Pt size of 2.5 nm) have a higher selectivity towards C=O hydrogenation (78.8% and 81.5%, respectively), although they have smaller Pt particle sizes than Pt/LDH-EA (Pt size of 3.6 nm) and Pt/LDH-MA (Pt size of 2.8 nm). This finding is inconsistent with the usual claim of a metal size effect on the selectivity. It could be explained by both the valence of Pt and the surface hydroxyl species on the LDH support. The Pt could form stable species with the surface oxygenated groups and remain partially reduced species in the final catalysts.^[8b,12] It was convincingly shown herein that the Pt²⁺ species exist in all catalysts and that Pt/LDH-EG and Pt/LDH have a higher Pt²⁺/ Pt⁰ ratio (1.28 and 1.21) than the other two catalysts (Table 1).

On the other hand, Pt/LDH-EG and Pt/LDH possess higher ratios of OH/H₂O species (1.27 and 1.31) than Pt/LDH-EA and Pt/LDH-MA (~1.07) according to the XPS results (Table 2). It suggests that the former two have a larger fraction of hydroxyl groups among the oxygen-containing species. It was reported that the addition of alkali promoters could change the adsorption mode of cinnamaldehyde. For instance, the addition of KOH elevates the selectivity to CMO product in the cinnamaldehyde hydrogenation.^[23a] Concerning the Pt nanocatalysts described in this work, the hydroxyl groups bonded onto LDH layers may act as in situ alkali promoters. The hydroxyl groups on the support could reduce or suppress the adsorption of the C=C bond by electrostatic repulsion of the phenyl ring in cinnamaldehyde. As a result, the synergy of cationic Pt²⁺ and the hydroxyl species outperforms the size effect, leading to a superior CMO selectivity over the small-sized Pt particles. In com-

parison, Pt/LDH-EA and Pt/LDH-MA, despite having larger Pt sizes, possess a moderate selectivity toward CMO (63.5% and 57%) and a considerable selectivity toward the undesired HCMA (23.2% and 29.8%, respectively). These results further support the assumption that the synergic effect of metal valence and hydroxyl of the LDH plays a dominant role rather than the size effect.

The initial turnover frequency (TOF), calculated at a CMA conversion of about 10%, was utilized to evaluate the intrinsic kinetics of hydrogenation reactions.^[30] Among all Pt catalysts, Pt/LDH-EG has the highest TOF value of 2.314 s⁻¹, indicative of its high initial activity. It is interesting that the TOF of Pt/LDH-EG is twice higher than that of Pt/LDH (0.894 s⁻¹), although they were synthesized by using the same re-

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ducing agent. The only difference is that TTAB was added while preparing Pt/LDH-EG. From the TEM analyses one can see that Pt/LDH-EG has a narrower size distribution and a smaller mean size than Pt/LDH (Figure 2). Besides, it has been reported that the reactivity of monovalent or mixed-valence metastable Pd species (Pd^{δ +}) is higher than that of conventional Pd⁰.^[31] In this study, Pt²⁺ species exist in the supported catalysts synthesized by a mild alcohol reduction method. In analogy to Pd catalysis, the metastable Pt²⁺ could be partly responsible for the high TOF value of Pt/LDH-EG because of the largest ratio of Pt²⁺/Pt and the smallest size of Pt in this catalyst.

The TOF values of the synthesized Pt catalysts were compared with those of previously reported Pt-based and Pdbased ones for cinnamaldehyde hydrogenation (Table 4). For a better comparison, the reaction conditions were also listed. It is clearly seen that Pt/LDH-EG has a higher TOF value (2.314 s⁻¹) than almost all Pt catalysts over various supports except Pt(1%)/CA-LiS973 (4.4 s⁻¹).^[32] Nevertheless, the CMO selectivity on Pt(1%)/CA-LiS973 is only 21%, much lower than that on Pt/LDH-EG (78.8%). The Pt(10.7%)/UiO-66-NH₂ catalyst has a very high CMO selectivity of 91.7%.^[10c] However, the TOF value is as low as 0.069 s⁻¹ and the Pt loading is relatively high (10.7%). In addition, the TOF value of Pt/LDH-EG is almost 5 times higher than that of Pt(1.96%)/MA with the same LDH support.^[3c] In this work the Pt nanoparticles were reduced and loaded on pre-synthesized LDH, different from the "one-pot" synthetic method used previously.[3c] As a result, the present approach allows sufficient exposure of active Pt sites, leading to higher activity.

It is known that Pd is a highly active catalyst for hydrogenation of unsaturated aldehydes, with a preference toward the C=C bond with regard to the selectivity.^[8e, 33] We found that the Pt/LDH-EG catalyst has a comparable activity with those Pd catalysts over carbon supports.^[33,34] Consequently, the Pt catalyst prepared by a polyol method possesses a high selectivity to the CMO product while maintaining a high activity that is even comparable to that of Pd catalysts in the cinnamaldehyde hydrogenation.

Next, the evolution of CMA conversion and product selectivity with the reaction time was explored over the Pt/LDH-EG catalyst (Figure 6). The CMA conversion reaches approximately 90% after a short period of 10 min and continues to increase to 93% at 30 min. The CMO selectivity remains at about 80% until a reaction time of 30 min, showing a preferable C=O bond hydrogenation. After a reaction time of 60 min, CMA is almost completely converted (>99%). The CMO selectivity rapidly drops to 67.8% and the HCMO increases to 25.6%. This clearly indicates that CMO is a thermodynamically unstable product and tends to convert into the undesired HCMO via deep hydrogenation, which increases the difficulty in structure-



Figure 6. Variation of conversion and selectivity as a function of reaction time over Pt/LDH-EG. CMA conversion (squares), CMO selectivity (circles), HCMA selectivity (triangles), HCMO selectivity (upside down triangles). Reaction conditions: catalyst: 0.05 g, substrate: 5 mmol CMA, solvent: 12.5 mL ethanol, H₂ pressure: 1.0 MPa, temperature: 60 °C.

Catalyst	Reaction conditions ^[a]	TOF [s ⁻¹]	CMA Conversion [%]	CMO Selectivity [%]	Reference
Pt(1%)/SiO ₂ -NH ₃	0.05 g, 150 $^\circ$ C, 1 MPa, toluene	0.03	15	12	[2a]
Pt(1.96 %)/MA	0.05 g, 60 $^\circ$ C, 1 MPa, 2 h, water	0.488	79.7	85.4	[3c]
Pt(4%)/CNTs	0.02 g, 40 °C, 2 MPa, 2.5 h, isopropanol	0.089	87.2	48.3	[9a]
Pt(2.9%)/RGO	0.02 g, 40 °C, 2 MPa, 2.5 h, isopropanol	0.127	89.6	69.6	[9a]
Pt(5%)/CNT-973 K	0.01 g, 60 °C, 1 MPa, 1 h, ethanol	0.819	64.9	47.6	[10b]
Pt(10.7%)/UiO-66-NH ₂	0.005 g, 25 °C, 4 MPa, 44 h, methanol	0.069	98.7	91.7	[10c]
Pt(5%)/CeO2-ZrO2	0.05 g, 75 °C, 2 MPa, 2 h, isopropanol	0.352	43.5	66.9	[12]
Pt(1%)/CA-LiS973	0.2 g, 90 °C, 1 MPa, 19.5 min, heptane	4.4	50	21	[32]
Pt(0.18%)/ZrO2	0.6 g, 70 °C, 2 MPa, 6 h, ethanol	0.018	49.9	42.2	[35]
Pt(0.5 %)/Graphite	0.36 g, 70 °C, 2 MPa, 1.5 h, ethanol	0.030	83.6	28	[36]
Pd(0.5 mol %)/BP	0.0244 g, 25 °C, 0.1 MPa, 4 h, methanol	0.014	90	(92) ^[b]	[37]
Pd(0.2 %)/OMC	0.1 g, 40 °C, 0.1 MPa, 2 h, isopropyl alcohol	0.0125	4.5	(60.2)	[38]
Pd(4.8 %)/AC-E	0.05 g, 60 °C, 1 MPa, cyclohexane	4.1	90	(91)	[33]
Pd(10%)/C	0.01 g, 50 °C, 4 MPa, 1 h, 1-propanol	2.3	75	(71)	[34]
Pt(2.41 %)/LDH-EG	0.05 g, 60 °C, 1 MPa, 30 min, ethanol	2.314	93.6	78.8	This work

sensitive hydrogenation reactions.

It is usually believed that the reaction temperature has a critical effect on the activity as well as the selectivity. It was found that the CMA conversion increases from 50.7% to 93.6% when the temperature was increased from 30 to $60^{\circ}C$ (Table 5). This is in agreement with previous data on the temperature impact.[3c] Furthermore, the effect of pressure was studied with the reaction pressure of H₂ ranging from 0.5 to 1.5 MPa (Table S1, Supporting Information). The conversion of CMA increases (from 81.7% to 98.3%) with increased pressure 30 min.

Table 5. The effect of reaction temperature on the catalytic performance. ^[a]						
T [°C]	Conversion [%]	Selectivit CMO	y [%] ^[b] HCMA	НСМО		
60	93.6	78.8	9.1	11.2		
40	71.1	80.4	10.6	8.2		
30	50.7	82.9	12.3	4.1		
[a] Catalyst: Pt/LDH-EG. [b] Selectivity is reported at the level of conver- sion in the table. Reaction conditions: catalyst: 0.05 g; substrate: 5 mmol CMA: solvent: 12.5 mL ethanol: H ₂ pressure: 1.0 MPa: reaction time:						

whereas the selectivity to CMO (C=O hydrogenation) decreases (from 79.9% to 69.4%). The yield of CMO reaches a maximum (73.7%) at the pressure of 1 MPa.

The CMO selectivity decreases from 82.9% to 78.8% with increasing temperature. Correspondingly, the selectivity of HCMO product increases from 4.1% to 11.2%. This finding verifies that a higher temperature is favorable for complete hydrogenation. Consequently, the development of active catalysts that work at lower temperatures is beneficial to improve the selectivity towards CMO.

The recyclability of the Pt/LDH-EG catalyst was also investigated (Figure 7). Elemental analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) shows that the Pt loading is 2.25 wt% after four cycles, a value slightly lower than that of the catalyst used initially (2.41 wt%). The CMA conversion was decreased from 93.6% to 86% upon the fourth run, possibly due to small leaching of the Pt species. The CMO selectivity remaines still at 73% after the third cycle. The HCMA selectivity remained almost unchanged. However, the selectivity of HCMO product increases with each cycle. This indicates that the main obstacle to achieve highly selective C= O hydrogenation is the thermodynamically favorable conversion from CMO into HCMO.

The basicity of the catalyst (Pt/LDH-EG) before and after use was studied by FTIR measurements of adsorbed CO_2 probe molecules (Figure S2, Supporting Information). The CO_2 mole-



Figure 7. Recycling of Pt/LDH-EG for cinnamaldehyde hydrogenation. Reaction conditions: catalyst: 0.05 g; substrate: 5 mmol CMA; solvent: 12.5 mL ethanol; H_2 pressure: 1.0 MPa; temperature: 60 °C; reaction time: 30 min.

cules can interact with two types of basic sites on the surface of catalysts. The basic hydroxyl groups form hydrogen carbonate species with CO₂ and basic oxygen atoms form surface carbonate species.^[39,40] It is found that the FTIR spectra of catalyst before and after reactions show two absorption bands. One has a maximum at about 1205 cm⁻¹, which is assigned to the δ (OH) of hydrogen carbonate species from the reaction of CO₂ with basic OH groups. The other at about 1698 cm⁻¹ is assigned to bridged carbonate species or to a bent form of strongly adsorbed carbon dioxide.^[41] The intensity of the band at 1205 cm⁻¹ decreases after catalytic reactions based on the comparison of peak areas. It suggests that the amount of hydrogen carbonate species diminishes, possibly due to the leaching of OH groups on the surface, that is, the decreasing basicity.

In addition, we analyzed the O 1s XPS spectrum of the catalyst (Pt/LDH-EG) after the fourth use (Figure S3, Supporting Information). The ratio of hydroxyl species to water is 1.19, a value smaller than that of the fresh catalyst (1.27). It is an indication that the decrease of conversion and selectivity could be caused by the leaching of basic hydroxyl species.

The structure of the Pt/LDH-EG catalyst after use was characterized by XRD, TEM and XPS. The XRD patterns show no structural change compared to that of the fresh catalyst (Figure S4, Supporting Information). TEM imaging reveals highly dispersed particles and a narrow size distribution, indicating that no obvious agglomeration occurs during the catalytic reactions (Figure S5, Supporting Information). The XPS spectra show the same peaks assigned to Pt^{2+} and Pt^0 species (Figure S6, Supporting Information) with a ratio of $Pt^{2+}/Pt^0=1.23$. The recycling data and structural studies confirm that the Pt catalyst is considerably stable with no significant activity and selectivity loss.

Conclusions

Hydrotalcite-supported Pt nanocatalysts were prepared by a mild alcohol reduction approach. The types of alcohols used and the addition of stabilizing agent have a major effect on the sizes and size distribution of reduced Pt particles. The Pt catalyst prepared by reduction with EG possesses the smallest mean size (2.1 nm) and the narrowest size distribution. Pt²⁺ and Pt⁰ species co-exist in the catalysts, and the ratio of Pt²⁺/ Pt⁰ varies with the types of alcohols. The catalyst prepared by reduction with EG has a higher ratio than those reduced by ethanol and methanol. Besides, the former possesses a larger amount of hydroxyl species than the latter two. The smallsized Pt catalyst (Pt/LDH-EG) shows an unusual selectivity towards the C=O bond and the highest activity (TOF of 2.314 s⁻¹), which is higher than that of most Pt catalysts and comparable to Pd catalysts reported previously. It is attributed to the synergy of cationic species and the hydroxyl moieties on the support. Analogous to alkali (KOH or NaOH), the support provides an in situ promoter (hydroxyl) for improving the selectivity towards C=O hydrogenation. The present study provides new insights to further understand the synergic contribu-

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tions of metal valence and native promoter to the catalytic activity and selectivity of hydrogenation reactions.

Experimental Section

Materials

Hexachloroplatinic acid (H₂PtCl₆·6 H₂O, 99.9%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). *Trans* cinnamaldehyde (98.0%), received from J&K Chemical Co. Ltd., was used without further purification. Tetradecyl trimethyl ammonium bromide (TTAB) was obtained from Aladdin reagent Co. Ltd. Ethylene glycol and NaBH₄ were purchased from Kermel Chemical Reagent Co. Ltd (Tianjin, China). Other chemicals and regents were all analytical reagent grade and used as received without further purification. The purity of hydrogen was 99.999%. Deionized water was used throughout the process.

Preparation of the support (LDH)

The synthesis of hydrotalcite (LDH) was carried out in a procedure similar to that reported previously.^[42] An aqueous solution of $Mg(NO_3)_2$ ·6H₂O and Al(NO₃)₃·9H₂O ([Mg²⁺]=0.3 M, [Al³⁺]=0.1 M) and a mixed alkali solution of NaOH and Na₂CO₃ ([OH⁻]=1.6(Al³⁺ + Mg²⁺), CO₃²⁻=2[Al³⁺]) were rapidly mixed under high-speed stirring within several tens of seconds. Subsequently, the resulting suspension was centrifuged once (4000 rpm, 10 min) and then the wet solid was transferred to a round-bottom flask with 50 mL distilled water. The suspension was then heated to 80 °C for 6 h under vigorous stirring. After cooling to room temperature, the products were centrifuged, washed with deionized water three times until the pH reached 7, and then dried at 80 °C for 12 h to obtain a white solid powder.

Loading of Pt onto the support

The Pt nanoparticles supported on LDH were produced by an alcohol reduction approach. In a typical run, 15 mL ethylene glycol (or ethanol or methanol) was mixed with 60 mL deionized water. Then 0.2 g LDH powder, 0.8 mL H_2PtCl_6 (0.0382 M) and TTAB (tetradecyl trimethyl ammonium bromide, TTAB:Pt=50:1 in molar equiv.) were added to the mixed solution above. The solution was stirred vigorously for 2 h at room temperature. Afterwards, the solution was transferred into a 100 mL stainless steel autoclave with a Teflon liner, which was kept at 120 °C for 4 h. The precipitates were separated by centrifugation (8000 rpm, 5 min) and washed with ethanol and deionized water three times, respectively. Finally, the solid was dried at 50 °C in air for 14 h. The catalysts were denoted as Pt/LDH-EG, Pt/LDH-EA and Pt/LDH-MA, respectively. The catalyst prepared without the addition of TTAB during the EG reduction was labeled Pt/LDH.

Sample Characterization

X-ray diffraction (XRD) measurements. The X-ray diffraction (XRD) analyses of the catalysts were done on a D8ADVANCE instrument with a scan range between 3° and 70° .

High-resolution transmission electron microscopy (HRTEM) analyses. TEM measurements were taken on a JEOL JEM-2100 microscope. The catalyst samples were ultrasonically dispersed in ethanol and a drop of the suspension was added onto a carbon-coated Cu grid followed by the evaporation of solvent in air. X-ray photoelectron spectra (XPS) measurements. The X-ray photoelectron spectroscopy (XPS) spectra of catalysts were acquired using a Thermo VG ESCALAB250 X-ray photoelectron spectrometer using Al_{ka} X-ray source (1486.6 eV) at a pressure of about 2× 10⁻⁹ Pa. The shifts of all binding energies were calibrated using the C 1s core level at 284.6 eV.

Elemental analyses. Elemental analyses for compositions were measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500).

CO-adsorption Fourier-transform infrared (FTIR) measurements. FTIR spectra of CO adsorption were obtained on a PC-controlled FTIR spectrophotometer (PWP 110-40). A sample of 30 mg was pressed into a self-standing pellet and placed in a sealed chamber. The chamber was firstly purged with a flow of high-purity N₂ and heated to 70 °C, and maintained for 1 h. After the pretreatment, the chamber was cooled down to room temperature under a N₂ atmosphere. Subsequently, high-purity CO gas was introduced to carry out the adsorption of CO molecules onto the samples. Afterwards, the chamber was re-purged with N₂ to drive the CO into the gas phase and the weakly adsorbed CO away. The IR spectra were recorded with a resolution of 2 cm⁻¹.

FTIR measurements of adsorbed CO₂ probe molecules. FTIR spectra of CO₂ adsorption on the catalysts were obtained on a FTIR spectrophotometer (PWP 110-40) to study the basicity of the catalysts. The catalyst (~30 mg) was pressed into a self-standing pellet and placed in a sealed chamber. The chamber was purged with high-purity N₂ and heated to 100 °C, and kept for 1 h. Subsequently, the chamber was cooled to room temperature under a flow of N₂. High-purity CO₂ (99.99%) was introduced to achieve the adsorption of CO₂ onto the catalysts. Afterwards, the chamber was purged by N₂ again for 1 h to drive the CO₂ into the gas phase and the weakly adsorbed CO₂ away. The spectral resolution is 2 cm⁻¹.

Catalytic Evaluation

The cinnamaldehyde hydrogenation was carried out in a pressurecontrolled, stainless steel autoclave with a Teflon liner (100 mL) under magnetic stirring. The autoclave was put in a water bath of constant temperature. For each run, 50 mg catalyst, 5 mmol CMA and 12.5 mL ethanol were added into the autoclave. The autoclave was sealed and flushed with 2 MPa H₂ for 10 consecutive cycles of H₂/vacuum to thoroughly remove any residue air. The autoclave was preheated to 60 °C. Then the reaction was started at 60 °C under 1 MPa H₂ for 30 min. In order to maximize the external mass transfer, the stirring speed was sufficiently high during the reaction. After the reaction, the reactor was cooled to room temperature and depressurized to atmospheric pressure slowly and carefully. The products were separated from the catalyst powder by centrifugation. The liquid substances were analyzed by using a gas chromatograph (GC-9800) equipped with a flame ionization detector (FID) and an Agilent DB-624 capillary column.

For recycling use, the catalyst was collected by centrifugation and washed with ethanol and distilled water several times after each run. The catalyst was dried at $50\,^{\circ}$ C for more than 10 h before being used in the next run.

Kinetic studies during the initial hydrogenation of CMA were carried out over all Pt catalysts. Since the initial H_2 amount was high enough and the reaction rate was independent of H_2 , the hydrogenation at the initial stage can be assumed to follow pseudo-firstorder kinetics, that is

$$= \ln(C_0/C) = kt$$

where C_0 and C are the concentrations of CMA at the beginning and at a certain time (*t*), respectively. The initial concentration (C_0) was known, and the concentration (*C*) was measured every 20 s. Plotting $\ln(C_0/C)$ versus *t*, a linear curve was derived before t_e (the end point of the first-order reaction) for each catalyst.

Turnover Frequency (TOF) Calculations

The initial turnover frequency (TOF) for the catalysts was calculated to compare the activity. It was calculated by using Equation (1) at a CMA conversion of approximately 10%.^[32]

$$\mathsf{TOF} = \frac{n_{\mathsf{CMA}} \times conv.\%}{(m_{\mathsf{cat}} y_{\mathsf{Pt}} / M_{\mathsf{Pt}}) \times D_{\mathsf{Pt}} \times t} \tag{1}$$

where n_{CMA} , m_{cat} , y_{Pt} and M_{Pt} represent the mole of CMA, the catalyst weight, Pt loading level, and molar mass, respectively, while *conv*% and *t* are the initial conversion of CMA and the reaction time, respectively. D_{Pt} is the dispersion of surface Pt sites and is estimated from the mean particle size of Pt (equal to 1.13/mean size).^[28]

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- a) K. Q. Sun, Y. C. Hong, G. R. Zhang, B. Q. Xu, ACS Catal. 2011, 1, 1336;
 b) W. W. Lin, H. Y. Cheng, L. M. He, Y. C. Yu, F. Y. Zhao, J. Catal. 2013, 303, 110;
 c) Y. C. Hong, K. Q. Sun, G. R. Zhang, R. Y. Zhong, B. Q. Xu, Chem. Commun. 2011, 47, 1300;
 d) R. V. Meidanshahi, M. Tasviri, M. Khodadai-Moghaddam, M. R. Gholami, Catal. Sci. Technol. 2014, 4, 447.
- [2] a) M. S. Ide, B. Hao, M. Neurock, R. J. Davis, ACS Catal. 2012, 2, 671; b) B. H. Wu, H. Q. Huang, J. Yang, N. F. Zheng, G. Fu, Angew. Chem. Int. Ed. 2012, 51, 3440; Angew. Chem. 2012, 124, 3496; c) S. Handjani, E. Marceau, J. Blanchard, J.-M. Krafft, M. Che, P. Mäki-Arvela, N. Kumar, J. Wärnå, D. Y. Murzin, J. Catal. 2011, 282, 228; d) S. Mukherjee, M. A. Vannice, J. Catal. 2006, 243, 108.
- [3] a) B. H. Zhao, J. G. Chen, X. Liu, Z. W. Liu, Z. Hao, J. Xiao, Z. T. Liu, Ind. Eng. Chem. Res. 2012, 51, 11112; b) S. Laref, F. Delbecq, D. Loffreda, J. Catal. 2009, 265, 35; c) X. Xiang, W. H. He, L. S. Xie, F. Li, Catal. Sci. Technol. 2013, 3, 2819.
- [4] a) J. Hajek, N. Kumar, P. Mäki-Arvela, T. Salmi, D. Y. Murzin, I. Paseka, T. Heikkilä, E. Laine, P. Laukkanen, J. Väyrynen, *Appl. Catal. A* **2003**, *251*, 385; b) P. Gao, A. Q. Wang, X. D. Wang, T. Zhang, *Catal. Lett.* **2008**, *125*, 289.
- [5] a) M. Tamura, K. Tokonami, Y. Nakagawa, K. Tomishige, *Chem. Commun.* 2013, 49, 7034; b) J. P. Breen, R. Burch, J. Gomez-Lopez, K. Griffin, M. Hayes, *Appl. Catal. A* 2004, 268, 267.
- [6] a) A. K. Prashar, S. Mayadevi, R. Nandini Devi, Catal. Commun. 2012, 28, 42: b) Y. J. Zhu, F. Zaera, Catal. Sci. Technol. 2014, 4, 955.

- [7] a) J. C. Serranoruiz, A. Lopez-Cudero, J. Solla-Gullon, A. Sepulveda-Escribano, A. Aldaz, F. Rodriguez-Reinoso, J. Catal. 2008, 253, 159; b) E. V. Ramos-Fernández, J. M. Ramos-Fernández, M. Martínez-Escandell, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, Catal. Lett. 2009, 133, 267.
- [8] a) E. Galloway, M. Armbruster, K. Kovnir, M. S. Tikhov, R. M. Lambert, J. Catal. 2009, 261, 60; b) J. P. Stassi, P. D. Zgolicz, S. R. de Miguel, O. A. Scelza, J. Catal. 2013, 306, 11; c) Y. Li, Z. G. Li, R. X. Zhou, J. Mol. Catal. A 2008, 279, 140; d) R. Y. Zheng, M. D. Porosoff, J. L. Weiner, S. L. Lu, Y. X. Zhu, J. G. Chen, Appl. Catal. A 2012, 419–420, 126; e) X. Yang, D. Chen, S. J. Liao, H. Y. Song, Y. W. Li, Z. Y. Fu, Y. L. Su, J. Catal. 2012, 291, 36.
- [9] a) Z. H. Sun, Z. M. Rong, Y. Wang, Y. Xia, W. Q. Du, Y. Wang, RSC Adv. 2014, 4, 1874; b) Z. M. Tian, X. Xiang, L. S. Xie, F. Li, Ind. Eng. Chem. Res. 2013, 52, 288.
- [10] a) P. D. Zgolicz, J. P. Stassi, M. J. Yañez, O. A. Scelza, S. R. de Miguel, J. Catal. 2012, 290, 37; b) Z. Guo, Y. T. Chen, L. Li, X. M. Wang, G. L. Haller, Y. H. Yang, J. Catal. 2010, 276, 314; c) Z. Y. Guo, C. X. Xiao, R. V. Maligal-Ganesh, L. Zhou, T. W. Goh, X. L. Li, D. Tesfagaber, A. Thiel, W. Y. Huang, ACS Catal. 2014, 4, 1340.
- [11] X. Zhang, H. Shi, B. Q. Xu, Angew. Chem. Int. Ed. 2005, 44, 7132; Angew. Chem. 2005, 117, 7294.
- [12] S. Bhogeswararao, D. Srinivas, J. Catal. 2012, 285, 31.
- [13] M. A. Aramendia, V. Borau, C. Jimenez, J. M. Marinas, J. R. Ruiz, F. J. Urbano, Appl. Catal. A 2001, 206, 95.
- [14] a) F. Z. Zhang, X. Xiang, F. Li, X. Duan, *Catal. Surv. Asia* 2008, *12*, 253;
 b) D. Tongsakul, S. Nishimura, K. Ebitani, *ACS Catal.* 2013, *3*, 2199.
- [15] F. Z. Zhang, X. F. Zhao, C. H. Feng, B. Li, T. Chen, W. Lu, X. D. Lei, S. Xu, ACS Catal. 2011, 1, 232.
- [16] Y. Zhang, M. E. Grass, J. N. Kuhn, F. Tao, S. E. Habas, W. Huang, P. Yang, G. A. Somorjai, J. Am. Chem. Soc. 2008, 130, 5868.
- [17] H. Chen, Q. H. Tang, Y. T. Chen, Y. B. Yan, C. M. Zhou, Z. Guo, X. L. Jia, Y. H. Yang, *Catal. Sci. Technol.* **2013**, *3*, 328.
- [18] J. N. Kuhn, C.-K. Tsung, W. Y. Huang, G. A. Somorjai, J. Catal. 2009, 265, 209.
- [19] K. M. Bratlie, H. Lee, K. Komvopoulos, P. Yang, G. A. Somorjai, *Nano Lett.* 2007, 7, 3097.
- [20] C.-K. Tsung, J. N. Kuhn, W. Y. Huang, C. Aliaga, L.-I. Hung, G. A. Somorjai, P. D. Yang, J. Am. Chem. Soc. 2009, 131, 5816.
- [21] P. Bera, K. R. Priolkar, A. Gayen, Chem. Mater. 2003, 15, 2049.
- [22] K. M. H. Young, T. W. Hamann, Chem. Commun. 2014, 50, 8727.
- [23] a) C.-Y. Hsu, T.-C. Chiu, M.-H. Shih, W.-J. Tsai, W.-Y. Chen, C.-H. Lin, J. Phys. Chem. C 2010, 114, 4502; b) W. Y. Yu, H. F. Liu, M. H. Liu, Q. Tao, J. Mol. Catal. A 1999, 138, 273.
- [24] a) G. S. Lane, J. T. Miller, F. S. Modica, M. K. Barr, J. Catal. 1993, 141, 465;
 b) R. K. Brandt, R. S. Sorbello, R. G. Greenler, Surf. Sci. 1992, 271, 605;
 c) R. K. Brandt, M. R. Hughes, L. P. Bourget, K. Truszkowska, R. G. Greenler, Surf. Sci. 1993, 286, 15.
- [25] a) R. J. Mukerji, A. S. Bolina, W. A. Brown, *Surf. Sci.* 2003, *527*, 198;
 b) R. M. Watwe, B. E. Spiewak, R. D. Cortright, J. A. Dumesic, *Catal. Lett.* 1998, *51*, 139; c) G. Schulze Icking-Konert, H. Handschuh, G. Gantefor, W. Eberhardt, *Phys. Rev. Lett.* 1996, *76*, 1047.
- [26] a) H. Härle, U. Metka, H. R. Volpp, J. Wolfrum, *Phys. Chem. Chem. Phys.* **1999**, *1*, 5059; b) P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, J. Dumesic, *J. Phys. Chem. B* **2001**, *105*, 4018.
- [27] S. C. Tsang, N. Cailuo, W. Oduro, A. T. S. Kong, L. Clifton, K. M. K. Yu, B. Thiebaut, J. Cookson, P. Bishop, ACS Nano 2008, 2, 2547.
- [28] X. H. Li, W. L. Zheng, H. Y. Pan, Y. Yu, L. Chen, P. Wu, J. Catal. 2013, 300, 9.
- [29] B. C. Campo, M. A. Volpe, C. E. Gigola, Ind. Eng. Chem. Res. 2009, 48, 10234.
- [30] J. Zhu, Y. Jia, M. Li, M. Lu, J. Zhu, Ind. Eng. Chem. Res. 2013, 52, 1224.
- [31] C. M. Marrodan, D. Berti, F. Liguori, P. Barbaro, Catal. Sci. Technol. 2012, 2, 2279.
- [32] B. F. Machado, S. Morales-Torres, A. F. Pérez-Cadenas, F. J. Maldonado-Hódar, F. Carrasco-Marín, A. M. T. Silva, J. L. Figueiredo, J. L. Faria, *Appl. Catal. A* 2012, 425–426, 161.
- [33] A. Cabiac, T. Cacciaguerra, P. Trens, R. Durand, G. Delahay, A. Medevielle, D. Plée, B. Coq, Appl. Catal. A 2008, 340, 229.
- [34] F. Y. Zhao, Y. Ikushima, M. Chatterjee, M. Shirai, M. Arai, Green Chem. 2003, 5, 76.
- [35] X. X. Han, R. X. Zhou, B. H. Yue, X. M. Zheng, Catal. Lett. 2006, 109, 157.

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- [36] Y. Li, P. F. Zhu, R. X. Zhou, Appl. Surf. Sci. 2008, 254, 2609.
- [37] S. Fujiwara, N. Takanashi, R. Nishiyabu, Y. Kubo, Green Chem. 2014, 16,
- 3230. [38] H. Z. Gu, X. S. Xu, A. Chen, P. Ao, X. H. Yan, *Catal. Commun.* **2013**, *41*, 65.
- [39] J. C. Lavalley, Catal. Today 1996, 27, 377.
- [40] D. Stošic, S. Bennici, S. Sirotin, P. Stelmachowski, J.-L. Couturier, J.-L. Dubois, A. Travert, A. Auroux, *Catal. Today* 2014, 226, 167.
- [41] M. Daturi, C. Binet, C. J. Lavalley, A. Galtayries, A. Sporken, Phys. Chem. Chem. Phys. 1999, 1, 5717.

[42] X. Xiang, H. I. Hima, H. Wang, F. Li, Chem. Mater. 2008, 20, 1173.

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