Dispersing Metallic Platinum on Green Rust Enables Effective and Selective Hydrogenation of Carbonyl Group in Cinnamaldehyde

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ABSTRACT: Layered double hydroxides (LDHs), a category of two-dimensional nanostructured layered materials, can be employed widely as supports, catalyst precursors, and actual catalysts in a variety of heterogeneous catalytic reactions. In this work, we reported a series of Fe-containing LDHs-supported Pt-based catalysts for base-free selective hydrogenation of cinnamaldehyde into cinnamyl alcohol. It was revealed that their catalytic performances were closely correlated to the compositions of LDH supports. Especially, highly selective hydrogenation of cinnamaldehyde could be achieved over the Fe(II)‒Fe(III)-LDH (green rust, FeFe-LDH) supported Pt catalyst, with a high cinnamyl alcohol selectivity of about 92% at a conversion of 90% after a reaction of 2 h, superior to other Fe(III)-containing LDHs (e.g., NiFe-LDH, CoFe-LDH, and ZnFe-LDH) supported Pt ones. It was demonstrated that the high catalytic efficiency of Pt/FeFe-LDH mainly originated from highly electron-rich character of metallic Pt species and the presence of surface reductive Fe2+ species, thereby being helpful for the chemisorption and activation of carbonyl group in cinnamaldehyde. Moreover, strong interactions between green rust matrix and metallic Pt species could stabilize the surface Pt nanoparticles, thereby inhibiting the metal leaching during the above reaction. The present study illustrates the validity of support control in supported Pt catalysts via tuning the compositions of LDHs, and thus the electronic structure of active metal sites and catalytic performance in the selective hydrogenation of cinnamaldehyde.

INTRODUCTION

As we know, layered double hydroxides (LDHs, \([M_{1-x}M_x]^{n+} (A^{n-})_{x/2}nH_2O\)), a family of two-dimensional (2D) layered anionic materials,1,2 are composed of brucite-type octahedral hydroxide layers and various interlayer charge-balancing anions.3 In the structure of LDHs, divalent and trivalent metal cations uniformly distribute on the brucite-like layers at an atomic level. Of late, this kind of low-cost LDH materials have gained more and more attention because their diverse compositions and flexible microstructures can make them suitable catalyst precursors and actual catalysts in a wide range of heterogeneous catalytic processes.4–10 At present, there is increasing interest in developing NiFe-, CoFe-, and NiCo-LDHs as high-performing electrocatalysts for water oxidation,11–15 thanks to unique redox properties of metal cations within the brucite-like layers. More importantly, 2D LDH materials possess promising potentials as excellent catalyst supports for the stabilization of metal nanoparticles (NPs) by the virtue of several advantages of easy synthesis, favorable surface basicity, high specific areas, and large adsorption capacity,13,14 as well as surface confinement effects of LDHs-derived catalysts.15,16 Correspondingly, via smart design of LDH supports in terms of compositions, surface properties and structures, as well as the control over the size of metal particles, resultant supported metal catalysts could exhibit significantly enhanced catalytic performances.17–20 Furthermore, transition metal cations (e.g., Ni, Cr) on the brucite-like layers are believed to be able to enhance the metal–support synergy.21,22

Presently, as one of the most important chemical processes, selective hydrogenations of \(\alpha,\beta\)-unsaturated aldehydes have attracted tremendous concern because corresponding unsaturated allylic alcohols (UAAs) can be widely utilized as valuable perfumes, pharmaceuticals, food additives, and so on.23–25 Due to the higher activation barrier for the reduction of C≡O bond than that for the reduction of conjugated C‒C bond,26–28 the production of UAAs still is challenging from the point of view of thermodynamics. Therefore, various attempts have been made to enhance both activity and selectivity toward the C≡O bond reduction. So far, numerous explorations have manifested that noble-metal catalysts (i.e., Pd, Pt, Ru, and Au) presented certain potential in the above reactions. Especially, noble metal Pt27,29–35 and bimetallic Pt–M (M = Cu, Co, Fe, or Sn)36–39 catalysts remarkably outperform the others, in some cases with the aid of excess amounts of additional bases.
like NaOH, because Pt has large d-band with repulsive electrons, which results in strong interaction with the C═O bond rather than the C═C bond. In most cases, the simultaneous achievement of both high activity and high selectivity to UAAs still is not satisfactory. Thus, more and more researchers are focusing on the development of high-performing selective catalysts in terms of activity and selectivity to UAAs.

On the other hand, as we know, catalyst support also can greatly affect the electronic and geometric structures of the surface active sites and thus the catalytic performances of the catalysts, in addition to catalytically active compositions. Recently, we and other research group have found that for LDHs-supported Pt catalysts, delicately turning metal particle sizes or adjusting compositions of LDH supports could improve the selectivity toward UAAs in the hydrogenation of cinnamaldehyde (CAL) with the carbonyl group and conjugated C═C double bonds into cinnamyl alcohol (COL), despite moderate catalytic activities. Nevertheless, fundamental insight and knowledge of the effect of metal species in LDHs on the catalytic performance of the catalysts is not clear, which greatly restricts the design and development of more highly active and selective metal catalysts.

Herein, by combining the structural features of Fe-containing LDHs and favorable interactions of metallic Pt species and LDH supports, a new Fe(II)−Fe(III)-LDH (namely green rust, FeFe-LDH) supported Pt catalyst was synthesized and successfully employed in the base-free highly selective CAL hydrogenation into COL. For comparison, several other Fe(III)-containing LDHs (i.e., CoFe-LDH, ZnFe-LDH, and NiFe-LDH) supported Pt ones also were synthesized and the related reactions were examined. It was found that the as-formed Pt/FeFe-LDH was superior to other Pt catalysts in terms of the selectivity to the C═O reduction and afforded a high cinnamyl alcohol selectivity of about 92% at a conversion of 90.0% after a reaction of 2 h. Furthermore, the effect of support compositions on the electronic state of Pt species and the catalytic behaviors of catalysts were clearly demonstrated. In the present work, the use of green rust as catalyst support was shown to be crucial for the realization of high catalytic efficiency of Pt-based catalysts in the CAL hydrogenation to produce COL. To the best of our knowledge, the present effective and selective Pt/FeFe-LDH catalyst has not yet been reported for the above reaction.

RESULTS AND DISCUSSION

Structural Analysis of Samples. Figure 1 presents the X-ray diffraction (XRD) patterns of different LDHs-supported Pt-based samples. In all the cases, typical characteristic (003), (006), (110), and/or (113) planes of hydrotalcite-like phase can be found. Noticeably, for Pt/FeFe-LDH and Pt/ZnFe-LDH samples, two diffractions appearing at lower 2θ angles of about 8.1 and 10.0° correspond to the basal spacings of about 1.0 and 0.88 nm, respectively, reflecting the presence of interlayer sulfate anions. Compared to that for Pt/FeFe-LDH, the decreased basal spacing for Pt/ZnFe-LDH demonstrate that less crystal water may coexist in the interlayer domains. However, the diffraction at about 11.5° for Pt/NiFe-LDH and Pt/CoFe-LDH illustrates the formation of carbonate-intercalated LDH phases. Interestingly, we do not find any diffractions belonging to metallic platinum phase in all cases, owing to the low content of small-sized and highly dispersive Pt particles on the surface of the LDH supports.

As illustrated in Figure 2, the SEM observations reveal a similar platelet-like morphology of four supported Pt samples. In two cases of Pt/FeFe-LDH and Pt/ZnFe-LDH samples, especially, uniform and large LDH nanosheets with thickness of about 20 nm interlace each other to generate a three-dimensional honeycomb-like morphology, and no collapse and agglomeration of nanosheets are observed. By contrast, both Pt/NiFe-LDH and Pt/CoFe-LDH are composed of smaller hexagonal nanoplatelets, and the obvious agglomeration of LDH platelets can be observed. N$_2$ adsorption−desorption experiments demonstrate that Pt/FeFe-LDH possesses a larger specific surface area of 72 m$^2$/g than other supported samples (Table 1) as the result of its regular and small nanosheet-like structure without agglomeration.

The TEM and high-resolution TEM (HRTEM) images of the supported Pt samples are presented in Figure 3. It may be clearly noted that large quantities of tiny Pt NPs with the diameter size of about 3−4 nm are highly dispersed on the surface of Pt/FeFe-LDH without any aggregates of large particles. Further, a HRTEM image of single Pt particle over the Pt/FeFe-LDH validates the clear lattice fringes, which correspond to the interplanar spacing of about 0.226 nm for the (111) plane of metallic Pt$^0$ phase. Based on more than 200 NPs over the Pt/FeFe-LDH, the average size of Pt NPs is measured to be about 3.4 nm (Table 1). However, a few aggregates of large black NPs can be found in the cases of Pt/NiFe-LDH and Pt/CoFe-LDH samples, probably implying the weakened interaction between Pt species and LDH supports.

As summarized in Table 1, the high proportions of metallic Pt$^0$ species always plays an important role in governing the catalytic performances of the catalysts. As shown in Figure 4, in the fine Pt 4f spectra, there are two spin−orbit components of Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ core levels located in the ranges of about 69.8−70.6 and 73.0−73.6 eV, respectively, indicative of the presence of metallic Pt$^0$ species. Except for Pt/CoFe-LDH, other supported Pt samples present another two pairs of doublets at 71.3−71.7 and 74.5−74.9 eV, respectively, indicative of the presence of Pt(II) species. As summarized in Table 1, the high proportions of metallic Pt$^0$ species on samples illustrate the reduction of most Pt(IV)
species, and a small part of Pt\textsuperscript{2+} species probably anchor with surface oxygen of LDH supports through surface hydrogen vacancies on the brucite-like layers to form M\textsuperscript{−}\textsuperscript{−}O\textsuperscript{−}\textsuperscript{−}Pt\textsuperscript{2+} like structure (M = Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Ni\textsuperscript{2+}, or Zn\textsuperscript{2+}), thereby forming stable Pt(II) species.\textsuperscript{43} More interestingly, a gradual shift in Pt 4f peaks for Pt\textsuperscript{0} species to lower binding energies from Pt/CoFe-LDH to Pt/NiFe-LDH, Pt/ZnFe-LDH, and Pt/FeFe-LDH is observed, indicative of enhanced electronic interactions between Pt\textsuperscript{0} species and LDH supports. Correspondingly, the strongest metal–support interaction in the Pt/FeFe-LDH can result in the generation of highly electron-rich Pt\textsuperscript{0} species.

Catalytic Performance of Different Pt Catalysts. It is well known that during the liquid-phase selective CAL hydrogenation, several products can be generated. The single hydrogenation of the C\-=O group can produce COL, whereas the single reduction of the C\-=C group generates hydrocinnamaldehyde (HCAL). Further, COL or HCAL is hydrogenated to form the final hydrocinnamyl alcohol (HCOL) product. In addition, small amounts of acetals may be produced through the aldol condensation in some cases. Here, we studied the effect of the nature of LDH supports on the reactivity of Pt NPs on different Fe-containing LDH supports in selective CAL hydrogenation.

Liquid-phase CAL hydrogenations were conducted over different LDHs-supported Pt catalysts at 110 °C and 1.0 MPa hydrogen pressure. And, blank reactions were performed to evaluate the performance of four pure LDH supports. It is found that all supports are inactive for the present reactions under the same reaction condition as that for Pt-based catalysts. As presented in Figure S, the nature of LDH supports plays a significant role in governing CAL conversions and product selectivities. In our case, acetals and other byproducts derived from decarbonylation or cracking cannot be detected. It is noteworthy that Pt/FeFe-LDH catalyst affords a high COL selectivity of 92% at a CAL conversion of 90% after a reaction of 2 h, indicative of a preferential reduction of the C\-=O bond in CAL. When other LDHs-supported Pt catalysts are employed, the COL selectivity is found to decrease progressively to 75% for Pt/ZnFe-LDH, 32% for Pt/NiFe-LDH, and only about 1% for Pt/CoFe-LDH after 2 h, accompanied by greatly increased HCOL selectivities. Especially, over the Pt/CoFe-LDH, a 99% yield of HCOL is achieved after 2 h, accompanied by greatly increased HCOL selectivities.

Table 1. Compositions, Textural, and Structural Properties of the Samples

| samples         | Pt\textsuperscript{0} (wt %) | D\textsubscript{TEM} (nm) | S\textsubscript{BET} (m\textsuperscript{2}/g) | Dis\textsuperscript{d} (%) | Pt\textsuperscript{0} 4f\textsubscript{7/2} (eV) | Pt\textsuperscript{2+} 4f\textsubscript{7/2} (eV) | Pt\textsuperscript{0}/(Pt\textsuperscript{0} + Pt\textsuperscript{2+}) ratio\textsuperscript{e} |
|-----------------|-------------------------------|---------------------------|---------------------------------------------|-----------------------------|---------------------------------------------|---------------------------------------------|------------------------------------------------|
| Pt/FeFe-LDH     | 2.8                           | 3.4                       | 72                                          | 39.9                        | 69.8                                        | 71.3                                        | 0.78                                           |
| Pt/ZnFe-LDH     | 2.7                           | 3.6                       | 44                                          | 37.6                        | 70.3                                        | 71.6                                        | 0.72                                           |
| Pt/NiFe-LDH     | 2.8                           | 3.5                       | 50                                          | 38.7                        | 70.4                                        | 71.7                                        | 0.89                                           |
| Pt/CoFe-LDH     | 2.9                           | 3.6                       | 53                                          | 37.6                        | 70.6                                        | 1.0                                         | 1.0                                            |

\textsuperscript{a}Determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) results. \textsuperscript{b}Average size of Pt NPs obtained from transmission electron microscopy (TEM) analysis based on more than 200 NPs. \textsuperscript{c}Brunauer–Emmett–Teller (BET) specific surface area. \textsuperscript{d}Pt dispersion degree determined by the particle size obtained from TEM (Dis = 1.133/D\textsubscript{TEM}). \textsuperscript{e}Determined by X-ray photoelectron spectroscopy (XPS) of Pt 4f region.
Figure 6A presents the effect of reaction temperature on the CAL hydrogenation over the Pt/FeFe-LDH after a reaction of 2 h. It is found that the conversion rapidly raises from 12 to 90% when the reaction temperature is elevated from 90 to 110 °C, along with a slightly increased COL selectivity. However, further increase in the reaction temperature causes a decline in the COL selectivity. Noticeably, the hydrogen partial pressure also can affect the CAL hydrogenation (Figure 6B). With the hydrogen pressure raising from 0.5 to 1.0 MPa, the conversion dramatically increases from 46 to 90% with the slightly increased COL selectivity by about 2%. The higher hydrogen pressure can facilitate the hydrogen solubility, making more hydrogen molecules accessible in the reaction medium. Correspondingly, more hydrogen molecules can get access to active metal sites and thus are dissociated into more active hydrogen species, thereby accelerating the rate of the hydrogenation of the C=O bond in CAL and HCAL intermediates. Further increase in the hydrogen pressure results in a slight decrease in the COL selectivity, besides a slightly increased conversion, mainly due to the nearly saturated solubility of hydrogen.

Further, the stability and reusability of Pt/FeFe-LDH was evaluated through five successive cycles. After the reaction, the catalyst could be recovered by centrifugation, washing with ethanol, and drying under vacuum at room temperature. As illustrated in Figure 7, the CAL conversion is only decreased by about 4% after five consecutive runs, along with almost unchanged COL selectivity, indicative of no significant loss in the catalytic performance. Further, the reaction filtrate was analyzed by ICP-AES after five cycles. It is revealed that no obvious leaching of active Pt species can be observed. In addition, TEM image of the used Pt/FeFe-LDH catalyst (not shown) reveals that the size of Pt NPs does not change significantly after five runs. However, the relatively weak interactions between Pt species and ZnFe-LDH matrix is conductive to a rapid decline in the catalytic performance after three runs in terms to both the conversion and the COL selectivity (Figure 7) due to the Pt leaching during the reaction. It is speculated that in the case of Pt/FeFe-LDH, surface reductive Fe^{2+} species as electron donors may enhance
the interactions between Fe$^{2+}$ cations and Pt$^{0}$ species through the Pt$^{0}$−O−Fe$^{2+}$ structures, thereby stabilizing the surface Pt species on the FeFe-LDH to a large extent and preventing Pt NPs from aggregating and inhibiting the metal leaching during the above reaction, in comparison with metallic Pt NPs on other Fe(II)-free LDH supports. This is our hypothesis for the main origin of enhanced stability of Pt/FeFe-LDH. Nevertheless, further investigation of the improved stability of Pt/FeFe-LDH needs to be explored through experimental or theoretical methods in the future. It is expected that green rust material would be a promising catalyst support for immobilizing other metallic nanoparticles to enhance the metal−support interactions.

**Catalytic Mechanism for the CAL Hydrogenation.**

Previously, it was reported that the particle size of active metals could affect their catalytic performance of catalysts in the hydrogenations of α,β-unsaturated aldehydes.$^{47,48}$ That is to say, the smaller the metal particle size, the higher the activity and lower the UAAs selectivity. This is because small metal particles possess more active sites and stronger adsorption for the C≡C group than the C═O one. The average size of Pt NPs in the present LDHs-supported Pt catalysts is almost equal, suggesting that surface electronic structure of catalysts should be a key factor in controlling the catalytic performances of the catalysts.

To gain insights into the catalytic mechanism on the CAL hydrogenation, in situ IR spectra of CO adsorption over LDHs-supported Pt catalysts were analyzed (Figure 8). It is noted that there is a broad absorption in the range of 2075−1975 cm$^{-1}$ in each case, which is attributable to the C═O bond vibration originating from a linearly bound CO to a metallic Pt atom.$^{49}$ No significant adsorption for CO bridging on several Pt atoms can be detected in the range 1900−1780 cm$^{-1}$. Especially, for Pt/FeFe-LDH, there are two splitting peaks in the range 2075−1975 cm$^{-1}$, probably originating from different surface adsorption of CO on two kinds of surface Pt$^{0}$ species. The above results illustrate that CO molecule mainly

### Table 2. Reaction Results of CAL Hydrogenation over Different Supported Pt Catalysts$^{a}$

| Catalysts     | TOF$^{b}$ (s$^{-1}$) | Conversion (%) | Selectivity (%) |
|---------------|----------------------|----------------|-----------------|
|               |                      |                | COL  | HCAL | HCOL |                  |
| Pt/FeFe-LDH   | 0.285                | 78             | 91   | 5    | 4    |
| Pt/ZnFe-LDH   | 0.172                | 48             | 74   | 18   | 8    |
| Pt/NiFe-LDH   | 0.493                | 87             | 33   | 14   | 53   |
| Pt/CoFe-LDH   | 0.728                | 96             | 2    | 3    | 95   |

$^{a}$Reaction conditions: temperature, 110 °C; hydrogen pressure, 1.0 MPa; reaction time, 1.5 h. $^{b}$Turnover frequency (TOF) of CAL conversion calculated based on the rate of CAL conversion per surface active metallic Pt site after a reaction of 30 min.

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Figure 5. Conversions and product selectivities with the reaction time in the CAL hydrogenation over Pt/FeFe-LDH (a), Pt/ZnFe-LDH (b), Pt/NiFe-LDH (c), and Pt/CoFe-LDH (d) catalysts. Reaction conditions: 110 °C and 1.0 MPa hydrogen pressure.
shows a preferential linear adsorption on the Pt$^0$ sites. Compared with those over other supported samples, the absorption intensity of C$=$O vibration over Pt/FeFe-LDH and Pt/ZnFe-LDH samples is significantly enhanced. Moreover, it is worth noting that the C$=$O absorption gradually shifts to lower wavenumbers from Pt/CoFe-LDH to Pt/NiFe-LDH, Pt/ZnFe-LDH, and Pt/FeFe-LDH. Such a vibration frequency shift behavior can be attributed to the fact that the electron-rich Pt$^0$ species are more helpful for the enhancement of back-bonding formed between the $\pi^*$-orbital in the CO molecule and the Pt$^0$ sites.

Additionally, the IR spectra of CAL adsorption on different LDHs-supported Pt samples were recorded to understand the adsorption behavior of CAL (Figure 9), although measurement conditions are different from the actual reaction conditions. In the case of Pt/CoFe-LDH, two broad absorption bands appear at about 1681 and 1631 cm$^{-1}$, respectively, which are ascribed to the asymmetric C$=$O and C$=$C stretching vibrations for adsorbed CAL molecule. Interestingly, with the change in LDH supports from CoFe-LDH to NiFe-LDH, ZnFe-LDH, and FeFe-LDH, the C$=$O vibration gradually shifts to higher
The enhanced catalytic performance of Pt/FeFe-LDH high-light the importance of precise design of LDH supports with desirable compositions. It is expected that such an effect of green rust support may be a promising approach for designing catalysts with superior catalytic performance.

In summary, a new green-rust-supported Pt catalyst was synthesized for the selective hydrogenation of CAL into COL. It was found that as-formed Pt catalyst afforded a higher COL selectivity of 91% at 90% CAL conversion, in comparison with other Fe-containing LDHs-supported Pt ones. In situ IR spectra of the CO adsorption results confirmed the difference in surface electronic structure of active Pt species in different LDHs-supported Pt samples, whereas the IR spectra of CAL adsorption results showed that Pt/FeFe-LDH could more easily activate the carbonyl group in CAL and reduce the probability of C==C bond coordinated to active metal sites, which should be favorable for the selective reduction of carbonyl group during the CAL hydrogenation.

The above results also demonstrate that the distinctive catalytic activity of Pt/CoFe-LDH and Pt/CoFe-LDH catalysts based on the TOF values are higher than that of Pt/FeFe-LDH (Table 2), but the COL selectivities obtained is much smaller than that over the Pt/FeFe-LDH. This is primarily due to the relatively higher proportions of Pt0 species in total Pt species on Pt/CoFe-LDH and Pt/CoFe-LDH, which are favorable for the hydrogen dissociation into active hydrogen species. In addition, compared with other Pt-based samples, the greatly enhanced CAL adsorption on the Pt/CoFe-LDH can further promote the CAL hydrogenation, in good agreement with the reactivity evaluation results.

Based on the above structural characterization and catalytic results, the following factors can account for its superior catalytic performance of Pt/FeFe-LDH in terms of the COL selectivity to other supported Pt ones.

First, the XPS analysis reveals that Pt 4f7/2 and Pt 4f5/2 peaks of Pt NPs shift to lower binding energies after immobilizing on the FeFe-LDH support, indicative of negatively charged nature of Pt0 NPs. It is generally believed that CAL may absorb on the catalyst surface via two paths, the planar geometry through the C==C bond and the vertical C==O atop geometry, thereby producing COL and HCAL, respectively. In the case of the present Pt/FeFe-LDH, according to in situ IR of CO adsorption and IR for CAL adsorption results, the absorbed CAL should preferentially exist in the form of the vertical C==O atop geometry through the interaction of the back-bonding of \( \pi^*_{C==O} \) with negatively charged Pt0 species, which is different from the interaction between the carbonyl group and surface Al\(^{3+} \) sites in the previously reported Pt/CoAl mixed metal oxide catalyst system, and thus the carbonyl group can be more easily activated in the selective hydrogenation of CAL compared in comparison with the C==C double bond.

Second, surface reductive Fe2+ species as electron donors can interact with the oxygen atom of the C==O group in CAL to weaken the C==O bond to a large extent. Correspondingly, it can be speculated that Fe2+ species are most likely to be oxidized to form Fe3+ species, whereas the C==O bond can convert into a C==O \( \sigma \)-bond. Such configurations between CAL and electron-rich Pt0 or Fe2+ species significantly enhance the selective chemisorption of CAL, thereby spatially constructing an electron-transfer channel for activating the C==O bond and the dramatical decrease in the barrier for the reduction of carbonyl group by dissociative hydrogen on Pt0 species.

Third, negatively charged Pt0 NPs also can promote the desorption of electron-rich olefin group in COL. As a result, for Pt/FeFe-LDH catalyst, both electron-rich Pt0 species and surface reductive Fe2+ species can greatly enhance the carbonyl group activation, resulting in an impressive catalytic efficiency in the CAL hydrogenation into COL.

**CONCLUSIONS**

In summary, a new green-rust-supported Pt catalyst was synthesized for the selective hydrogenation of CAL into COL. It was found that as-formed Pt catalyst afforded a higher COL selectivity of 91% at 90% CAL conversion, in comparison with other Fe-containing LDHs-supported Pt ones. In situ IR spectra of the CO adsorption results confirmed the difference in surface electronic structure of active Pt species in different LDHs-supported Pt samples, whereas the IR spectra of CAL adsorption results showed that Pt/FeFe-LDH could more easily activate the carbonyl group in CAL and reduce the probability of C==C bond coordinated to active metal sites, which should be favorable for the selective reduction of carbonyl group during the CAL hydrogenation.
other highly active supported metal catalysts applied in various heterogeneous catalytic processes.

**EXPERIMENTAL SECTION**

**Preparation of Samples. FeFe-LDH.** A salt solution containing FeSO₄·7H₂O (0.08 mol) and Fe₂(SO₄)₃·(0.04 mol) in 100 mL of deionized deionized water was prepared. Then, a base solution of NaOH (2.0 M) was slowly dropped into the above salt solution at 40 °C under nitrogen until pH = 7.0. Subsequently, the resulting suspension was aged for 2 h, and the reaction solution was cooled in ice water. The filtered precipitate was washed with deionized ice water and ethanol for three times. Finally, the obtained FeFe-LDH sample was dried under vacuum.

CoFe-LDH and NiFe-LDH. A salt solution containing Co(NO₃)₂·6H₂O (0.08 mol) and Fe₂(SO₄)₃·(0.04 mol) in 100 mL of deionized water was prepared. Then, a base solution containing NaOH and Na₂CO₃ ([OH⁻] = 1.6[M²⁺] + [Fe³⁺] and [CO₃²⁻] = 2[Fe³⁺]) was slowly dropped into above salt solution at 40 °C until pH = 10.0. Subsequently, the resulting suspension was aged for 12 h, and the precipitate was filtered, washed with deionized water, and finally dried at 70 °C overnight to obtain NiFe-LDH or CoFe-LDH support.

**ZnFe-LDH.** ZnFe-LDH was synthesized according to our developed method. A salt solution containing ZnSO₄·7H₂O (0.08 mol) and FeSO₄·7H₂O (0.04 mol) in 100 mL of deionized water was prepared. Then, a base solution of NaOH and Na₂CO₃ ([OH⁻] = 1.6[M²⁺] + [Fe³⁺] and [CO₃²⁻] = 2[Fe³⁺]) was slowly dropped into above salt solution at 40 °C under a flow of air until pH = 7.0. Subsequently, the resulting suspension was aged for 24 h, filtered, washed, and dried at 70 °C for 12 h to obtain a pale-yellow ZnFe-LDH solid.

**Supported Pt Catalysts.** All supported Pt samples were prepared by a sol-immobilization method. First, a solution containing poly (N-vinyl-2-pyrrolidione) (0.02 g) and H₃PtCl₆·6H₂O (0.04 g) dissolved in 25 mL of deionized water was vigorously stirred for 20 min. Subsequently, 25 mL of NaBH₄ aqueous solution (NaBH₄/Pt molar ratio = 20:1) was dropped rapidly into the above solution at room temperature. The obtained suspension was stirred for 7 h to obtain solid particles of Pt. Afterward, the LDH support (0.5 g) was added into the suspension and stirred for 2 h. Finally, the obtained solid was washed with deionized water and dried under vacuum.

**Characterization.** Shimadzu XRD-6000 diffractometer was employed to gain X-ray powder diffraction (XRD) data at a Cu Kα radiation (λ = 0.15418 nm). The content of Pt in samples was determined using Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscopy (ICP-AES). Scanning electron microscopy (SEM) measurements were carried out on a Supra 55 electron microscopy, whereas transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-2010 electron microscope. Nitrogen adsorption–desorption isotherms of the samples were collected using a Micromeritics ASAP 2020 sorptometer apparatus. X-ray photoelectron spectra (XPS) analysis was carried out on VG ESCALAB 2201 XL spectrometer with an Al Kα X-ray radiation of 1486.6 eV. The C 1s core level (284.6 eV) was utilized to calibrate the binding energy. In situ Fourier transform infrared (FT-IR) of CO adsorbed on samples was characterized on a FT-IR instrument spectrophotometer (Thermo Nicolet 380). First, a self-supporting sample wafer (100 mg) was put into an IR cell and heated to 70 °C under N₂ and held for 1 h. Afterward, pure CO (10 mL/min) was switched into the cell at room temperature. Finally, IR spectra of CO adsorption were obtained under vacuum. IR spectra of CAL adsorption were collected on the identical FT-IR instrument. The self-supporting sample wafer (50 mg) was first dried at 70 °C under vacuum for 12 h, soaked in CAL for 24 h, and then dried at 25 °C overnight under vacuum. After the wafer was purged with He for 4 h, IR spectra of CAL adsorption were recorded.

**Selective Hydrogenation Tests.** Liquid-phase CAL hydrogenation of CAL was performed in a stainless-steel autoclave reactor (50 mL), where the catalyst (0.03 g), CAL (4.0 mmol), and isopropanol (10 mL) were charged. In a magnified experiment, the catalyst (0.3 g), CAL (5 mL), and isopropanol (100 mL) were charged into an autoclave reactor (150 mL). After that, the reactor was charged with nitrogen for three times and then the reactor was heated to a certain temperature in an oil bath under atmospheric pressure. Subsequently, the reactor was purged with H₂ and pressurized to 1.0 MPa. Finally, the hydrogenation was initiated when the stirring began at a speed of 900 rpm. In the above process, the external mass transfer limitation was negligible. The final liquid products were analyzed on an Agilent GC7890B gas chromatograph equipped with HP-5 capillary column and flame ionization detector. The internal standard was benzyl alcohol.

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The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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