



Differentiation of Pt-Fe and Pt-Ni₃ Surface Catalytic Mechanisms towards Contrasting Products in Chemoselective Hydrogenation of α , β -Unsaturated Aldehydes

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Abstract: Noble-metal catalysts serve as an irreplaceable role in the reported reaction systems are not beneficial for selectiv	

pharmaceutical, perfume and fine chemicals fields. However, there still remains a grand challenge in controlling chemoselectivity. Herein, we have synthesized a bimetallic nanostructure supported on porous metal-organic frameworks (Pt-Fe/UiO-66, Pt-Ni₃/UiO-66), in which Pt nanoparticles was modified with non-noble metal (Fe or Ni) directly. The as-synthesized catalysts can function as a switch for selective hydrogenation of α , β -unsaturated aldehydes to afford the potential products on-demand. In comparison with the conventional Pt-based catalysts, Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66 catalysts exhibit excellently catalytic activity, enhanced selectivity and improved stability for selectivity hydrogenation. The partial charge reconfiguration and electronic coupling effect existing in such distinctive bicomponent nanocatalysts was confirmed by some comprehensive characterization and Density Functional Theory (DFT) calculations. The developed method for precisely modification the composition and interaction between the noble metal and nonnoble metal provides a feasible avenue to design the advanced catalysts.

Introduction

Selective hydrogenation (SH), an important industrial process, are widely used in various chemical industry filed. For example, the main semihydrogenated products such as unsaturated alcohols (by hydrogenation at C=O bond) and saturated aldehydes (by hydrogenation at the conjugated C=C bond) from the α , β -unsaturated aldehydes have been used in pharmaceutical intermediates, fragrances, perfumes and fine chemicals areas.^[1] A. Mulle et al. reported hydrogenation of cinnamaldehyde is an important intermediate in the treatment of HIV.^[2] At present, it is an extremely challenge to develop high efficient catalysts for orientation the corresponding products on-demand, because the thermodynamical and kinetical effects in

the reported reaction systems are not beneficial for selective transformation.^[3] Therefore, improving the efficiency and selectivity with a certain bond (C=C or C=O) in the SH of α , β -unsaturated aldehydes to beam the highly value-added chemicals is challenging and significant.

Platinum (Pt)-based catalysts have been widely employed and demonstrated to be the effective catalysts for SH because of their high activity for H₂ dissociation.^[4] However, it is difficult to achieve the satisfactory catalytic properties upon using unmodified Pt nanoparticles (NPs) as the main active sites. From a mechanistic point of view, the electronic and geometrical structures of the catalytic sites determine the adsorption mode and strength of the substrate.^[5] In the catalytic process, preferentially adsorbing and activating the target functional group on the catalyst surface is promising but challenging. To solve this problem, substantial efforts have been made such as confining Pt NPs in porous materials, downsizing Pt NPs to clusters, even to single atoms, adding secondary metals or metal oxides, etc..^[6]

Bicomponent catalysts usually exhibit superior catalytic properties compared with single-component catalysts thanks to the electronic and geometric modifications.^[7] The introduction of secondary component not only reduces the usage of noble metal Pt in the synthetic procedure, but also could adjust the Pt electronic redistribution (e.g., d-band structure) by the ligand and strain effects.^[8] For instance, Pt-Fe (Co, Sn) based bicomponent catalysts were widely investigated for the SH of α , β -unsaturated aldehydes/ketones. Therein, the secondary component (FeO_x, CoO_x and SnO_x) as a Lewis acid are coordinately unsaturated, which can promote the preferential adsorption and activation of the C=O bonds.^[9] Hosono and coworkers reported the supported

RuFe catalysts showed high catalytic activity and selectivity in cinnamaldehyde hydrogenation, and confirmed the electron transfer happen between Ru and Fe. The negatively charged Ru sites favor the adsorption and polarization of electrophilic C=O bonds.^[10] The aforementioned researches display designing and manipulating the well-defined bimetallic catalysts has become a powerful strategy to reveal the origin of synergistic effect.

Metal-organic frameworks (MOFs), as a special class of porous materials, have been emerging as the attractive materials in the catalytic field owing to their well-defined structure, ultra-high surface area, flexible tailorability and accurate designability, all of which cater to the catalytic requirement well.^[11] Zirconium-organic frameworks (UiO-66) have been widely applied because the textural (Lewis acidity) and structure (high surface area) performance of UiO-66 are beneficial for the interaction between the metal sites and support.^[12] Our group has lately carried out some work to explore the oxidative transformation of furfural over Au NPs supported functionalized UiO-66-X (X = NH₂, COOH, NO₂) and some good results has been obtaied.^[13]

In this work, we used the secondary component (Fe or Ni) to decorate the noble metal Pt and MOFs as supporter to fabricate Pt-Fe/UiO-66 and Pt-Ni₃/UiO-6 catalysts. The SH of cinnamaldehyde (CAL) containing both C=C and C=O bonds was selected as a typical model reaction for investigation the performance of the Pt-Fe(Ni₃)/UiO-66 bi-component structure

with the desire to control chemoselectivity. The surface characterization and Density Functional Theory (DFT) calculations demonstrate that electron injection from non-noble 3d-transition metal (Fe, Ni) to Pt promotes H_2 dissociation on the electron-rich Pt site, and the electron-deficient Fe and Ni preferentially adsorb and active C=O group and C=C group of the CAL, respectively, to obtain the industrially desirable product.

Results and Discussion

A series of UiO-66 anchored Pt-Fe or Pt-Ni bicomponent nanocatalysts with certain atom ratios were prepared by a convenient method using chloroplatinic acid (H₂PtCl₆·6H₂O), nickel(II) chloride hexahydrate (NiCl₂·6H₂O), and iron(III) chloride hexahydrate (FeCl₃·6H₂O) as the metal precursors, sodium (NaBH₄) as borohydride the reducing agent, polv-(vinylpyrrolidone) (PVP) as a stabilizer and deionized water as the component solvent (see the Experimental Section for details). The as-obtained Pt-based (Pt-Fe/UiO-66, Pt-Ni₃/UiO-66) bimetallic catalysts were characterized by High-Resolution Transmission Electron Microscopy (HRTEM) and High-Resolution Scanning Electron Microscopy (HRSEM). As illustrated in Figure 1a and 1d, the prepared Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66 retained the octahedral structure morphology of the original UiO-66. As detected by HRTEM in Figure 1c and 1f,



Figure 1. HRSEM and HRTEM images of as-obtained (a-c) Pt-Fe/UiO-66 and (d-f) Pt-Ni₃/UiO-66 with interplanar distances; HRTEM-EDX images and elemental mapping for (g, h) Pt-Fe/UiO-66 and (i, j) Pt-Ni₃/UiO-66 (Note: The Cu-Kα and Cu-Kβ were come from copper mesh which were used as support in measurement).

the well-resolved lattice fringes with interplanar spacings of 0.223 nm and 0.212 nm can be indexed to the (111) plane of Pt-Fe phases and Pt-Ni₃ phases, respectively.^[7d,14] The resulting HRTEM-EDX mapping images and CO pulse chemisorption clearly indicate that Pt-Fe and Pt-Ni₃ nanostructures should be highly dispersed on the surface of UiO-66 (Figure 1g, 1i and S1). Besides, HRTEM-EDX spectrum of Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66, showed the atomic ratio of about Pt:Fe = 53.8:46.2 (1:1) and Pt:Ni = 23.1:76.9 (1:3), respectively (Figure 1h and 2j).

Moreover, the FT-IR spectra of UiO-66, fresh Pt-Fe(Ni₃)/UiO-66, and used Pt-Fe(Ni₃)/UiO-66 also verified the chemical integrity of zirconium-organic frameworks under the established preparation and catalytic conditions (Figure 2d). In addition, the XRD patterns of the as-obtained catalysts are provided in Figure 2e. The crystal structure of the UiO-66 did not change before and after Pt-Fe and Pt-Ni3 were supported, and the well-defined characteristic peaks attributed to the diffraction patterns of UiO-66 phase. It is worth noting that the characteristic diffraction peaks of platinum species do not appear due to low metal loading (ca. 0.75wt %, measured by ICP-AES). The surface acid sites of the synthesized catalysts were analyzed by in situ pyridine-adsorption DRIFTS (Figure 2a and S2). According to the literature, the bands at about 1439 cm⁻¹ and 1605 cm⁻¹ were assigned to Lewis acid sites, and the band at around 1578 cm⁻¹ was assigned to Brønsted acid sites. Meanwhile, the feature at about 1485 cm⁻¹ was attributed to either or both Lewis and Brønsted acid sites.^[14] The coexistence of Lewis and Brønsted acid can be attributed to MOFs because UiO-66 has abundant metal nodes (Lewis acid sites) and uncoordinated carboxylic ligands (Brønsted acid sites). The Lewis acid sites of the UiO-66 are beneficial for the interaction between the metal species and supports. $\ensuremath{^{[12]}}$

Furthermore, to further identify the surface electronic states Pt-based catalysts, the representative samples were of evaluated by in situ DRIFTS with a CO probe molecule. Figure 2b shows the DRIFTS spectra of CO-adsorbed on catalysts after purging with nitrogen at 25 °C for 10 min. The strong broad COadsorption band at about 2050 cm⁻¹ is assigned to the vibration frequency of CO interacting with Lewis acid sites in the MOFs.^[15] In addition, one stable band (around 2085 cm⁻¹) can be assigned to CO linearly adsorbed on Pt sites were detected on synthesized Pt-based catalysts. The CO band position of Pt-Fe(Ni₃)/UiO-66 is a little lower than that observed on Pt/UiO-66 catalysts, which means that the relatively strong interaction between Pt and Fe or Ni occurred in the synthetic process.^[14,16] The X-ray Photoelectron Spectroscopy (XPS) was employed to investigate the chemical state of the Pt/UiO-66, Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66 (Figure 2c). The binding energy of Pt 4f7/2 peak at 71.86 eV corresponds to Pt⁰ species.^[4] It can be seen that the Pt 4f region of Pt-Ni₃/UiO-66 and Pt-Fe/UiO-66 catalysts show significant shifts to lower binding energies of 0.60 and 0.31 eV, respectively, when compared with single-component Pt/UiO-66 catalyst, indicating that the electron transfer from Fe or Ni to Pt.^[7a] To further reveal the iron and nickel chemical states, the deconvolution results for Fe 2p and Ni 2p were evaluated in Figure S3. The Fe 2p_{3/2} peaks at 710.2 and 711.8 eV can be corresponded to Fe^{2+} and Fe^{3+} species, respectively, and the Ni 2p_{3/2} peaks at 855.6 eV can be attributed to Ni^{2+.[14]} Briefly, the charge accumulation and chemical bonding leads to the obvious shift of characteristic peaks, which indicats that the interaction Pt species between and Fe or Ni species.



Figure 2. In situ DRIFT spectra of (a) pyridine-adsorption and (b) CO-adsorption on UiO-66 and Pt-based catalysts after purging with N₂; (c) XPS Pt 4f spectra of synthesized Pt-based catalysts; (d) FT-IR spectra and (e) XRD patterns of UiO-66, Pt-Fe/UiO-66, used Pt-Fe/UiO-66, used Pt-Ni₃/UiO-66.



Figure 3. (a, b) Crystalline phase structures, (c, d) density of states and (e, f) ELF contour plots on the (111) plane of Pt-Fe and Pt-Ni₃ surfaces.

The different planes of catalysts have a noteworthy influence on the reaction performance.^[14c,e] In this work, we chose the most stable and preferential facets for calculations, i.e., the (111) plane of Pt-Fe and the (111) plane of Pt-Ni₃, based on the results of HRTEM, XPS and previous literatures, [7d,14] which can represent the surface catalytic property. Besides, the calculated charge distribution and reaction routes are consistent with the experimental data, which also further verifies the rationality of the constructed catalyst models. The crystalline phase structure, electronic Density of States (DOS), Electron Localization Function (ELF) and Bader charge analysis of Pt-Fe and Pt-Ni₃ are presented in Figure 3, Figure S4, Figure S5 and Table S1 (DFT models and calculations setup were described in Supporting Information). As shown in Figure 5c and 5d, the Total Densities of States (TDOS) and Partial Density of States (PDOS) indicate that the bonding peaks of the Pt-Fe and Pt-Ni₃ main contribution come from the hybridized d-orbitals of the Pt and Fe, Pt and Ni atoms, respectively. The Bader charge of pure Pt element is 10, which indicate that Pt element gains extra charge from iron and nickel, respectively. Briefly, the Bader charge analysis illustrates that in both cases the electrons transfer from Fe or Ni to Pt lead to the electronegativity difference, which is consistent with that of XPS. The ELF calculation has often been employed as a robust indicator for characterizing the chemical bonding and degree of electron localization.^[18] The ELF=0 represents the delocalized system and ionic bonding between the atoms, however, the ELF=1.0 characterizes the completely electron localization and the covalent bonds between the atoms, besides, ELF=0.5 represents the uniform electron gas and the presence of metal bonds.^[19] Figure 3e and 3f are the 2D ELF map on (111) planes of the Pt-Fe and Pt-Ni₃. Here the blue area indicates the charge depletion and the red area indicates the charge accumulation. Distinctly, after introducing the Fe, the degree of electron localization for Pt atoms is obviously improved, enhancing the chemical bonding strength between the Pt and Fe atoms.^[20]

However, for Pt-Ni₃ phase interface system, the degree of electron localization of Pt atoms changes slightly. Therefore, the degree of electron localization and chemical bonding of Pt atoms also reveal the interaction for Pt-Fe system is stronger than that of the Pt-Ni₃ system.

The catalytic properties of the as-obtained Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66 were evaluated in SH of α , β -unsaturated aldehydes. The hydrogenation scheme of cinnamaldehyde (CAL) is given as Figure 4a, where the generated products include cinnamic alcohol (COL), phenylpropanol (HCOL), phenylpropanal (HCAL) and so on. For the Fe/UiO-66 and Ni/UiO-66 catalytic systems, the main chemoselectivity were COL (85.4%) and HCAL (76.6%), respectively (Figure 4b), however, the original UiO-66 showed lower activity. With the introduction of Pt species, the catalytic activity has been greatly improved, but the selectivity of the product was aimless. Notably, when Pt-Fe/UiO-66 was used as the catalyst, the conversion of CAL and the selectivity of COL were 87.4% and 96.2%, respectively. In addition, a 58.6% conversion of CAL and 86.1% selectivity of COL were obtained when Pt-Ni/UiO-66 was employed. Then, we have prepared Pt-Co/UiO-66, Pt-Co₃/UiO-66, Pt-Sn/UiO-66, and Pt-Sn₃/UiO-66 catalysts for the selective hydrogenation of CAL. As shown in Table S2, the Pt-Co/UiO-66 and Pt-Sn/UiO-66 show high selectivity for COL. It is unsatisfactory that Pt-Co₃/UiO-66 and Pt-Sn₃/UiO-66 do not obtain high HCAL selectivity. These results indicated that the combination of Pt and Fe/Ni is desirable for the chemoselective transformation of CAL to COL or HCAL in the presence of molecular hydrogen on-demand.



Figure 4. (a) Hydrogenation of cinnamaldehyde-reaction pathways; (b) Control and blank experiments of the SH of CAL (Reaction conditions: Catalyst (25 mg), CAL (0.132 g, 1 mmol), ethyl acetate (10 mL), H₂ (2 MPa), 2 h and 100 °C. Other product refers to cinnamaldehyde diethyl acetal).

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Figure 5. Comparison of (a) catalytic selectivity and (b) turnover frequency (TOF) for SH of CAL over Pt-based bimetallic catalysts with different supports (Pink area (left): Selectivity of COL; Cyan area (right): Selectivity of HCAL). Data have been obtained from refs 13-15, 21-23, and this work.

Subsequently, the doping molar ratio of bicomponents was carefully optimized, and the metallic content were measured by ICP-AES (Figure S6, Table S3 and S4). With the increase of Pt content, the conversion of CAL was significantly improved, but the selectivity was scattershot. It is exciting that the presence of Fe can enhance the selectivity of COL (Figure S6a). Simultaneously, the influences of different reduction temperature and time for the SH of CAL were investigated in Figure S7 and S8. When Pt-Fe/UiO-66 was employed as catalyst, we achieved a full conversion (99.9%) and satisfactory selectivity (94.3%) within 4 hours. In addition, in order to adjust the product distribution to obtain HCAL, the molar ratio of Pt-Ni was investigated in Figure S6b. The results showed that the Ni species in Pt-Ni/UiO-66 played a key role in the transformation of CAL to HCAL. When the Pt-Ni molar ratio was 1:3, the conversion of CAL was 99.9% and the selectivity of HCAL was 93.8%.

The recycling experiment of Pt-Fe(Ni₃)/UiO-66 catalysts, as shown in Figure S9a and 9b, were further investigated within short time. The conversion of CAL exhibited a slight decrease but the selectivity of target products kept almost unchanged after being recycled for five times, which indicates that Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66 catalysts possess excellent catalytic durability. Moreover, the recycled catalysts were also characterized by XRD, FT-IR and HRTEM techniques, and the results further demonstrated the Pt-Fe(Ni₃)/UiO-66 catalysts were stable in the suitable catalytic reaction condition (Figure 2d, 2e and S10).

The structure, morphology and composition of the supports have important effects on the catalytic properties. For comparison, ZrO₂/CNT-supported Pt-Fe and Pt-Ni₃ bimetallic catalysts (Pt-Fe/ZrO₂, Pt-Ni₃/ZrO₂, Pt-Fe/CNT, Pt-Ni₃/CNT) were prepared. Figure 5 and Table S5 show the comparison of catalytic selectivity and turnover frequency (TOF) for SH of CAL over Pt-based bimetallic catalysts with different supports. As can be observed, Pt-based bimetals supported on zirconium-organic frameworks (UiO-66) showed higher conversion and selectivity than those supported on conventional carriers. This was

explained by the fact that the Lewis acidity, porosity and high surface area of the UiO-66 are beneficial for the interaction between the metal sites and support. Furthermore, the dispersion of active sites was measured by CO pulse chemisorption, which was employed to calculate turnover frequency (TOF). Figure 5b gives the specific TOFs obtained under similar reaction conditions for describing the intrinsic activity of the Pt-based bimetallic catalysts. As reported in the recent literature, the TOFs of 14753 h⁻¹ for hydrogenating CAL to COL was achieved by $Co_xFe_{1-x}Al_2O_{4+\delta}$.^[21e] Herein, we give the specific TOFs of the recent Pt-based bimetallic catalysts. The TOFs of 1670 h⁻¹ and 3048 h⁻¹ are achieved under Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66, respectively, although the higher TOFs of 5544 h⁻¹ for hydrogenating CAL to COL was achieved by PtFe_{0.25}/Al₂O₃@SBA-15.^[6c] These results indicated the catalytic selectivity and turnover frequency of Pt-Fe(Ni₃)/UiO-66 were higher than the values achieved in other catalysts as summarized in Figure 5b and Table S5.[6,8,9,21]

We were intrigued by the great success in selective cinnamaldehyde hydrogenation towards potential products in a highly on-demand fashion. In order to further explore the general applicability of Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66, a variety of other unsaturated carbonyl compounds were also performed as substrates under the optimized condition, and the performance were shown in Table 1. The results indicated that the conversion of other substrates were up to more than 90%. In the presence of Pt-Fe/UiO-66 catalyst, the selectivity of unsaturated alcohols were over 80%. Naturally, Pt-Ni₃/UiO-66 displays contrasting selectivity (over 81%) of saturated aldehydes. Corresponding ¹HNMR spectra for the products were supplied in Supporting Information (Figure S18-S27).



[a] Reaction conditions: Catalyst (25 mg), Substrates (1 mmol), ethyl acetate (10 mL), 100 °C and 2 MPa H_2 , 2 h). [b] The reaction time is 4 h.

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Figure 6. (a, c) Kinetic profiles of the CAL conversion by the Pt-Fe(Ni₃)/UiO-66 catalyst (X, CAL conversion) and (b, d) Arrhenius plot of formation of COL from CAL at different temperature. Reaction conditions: Catalyst (25 mg), CAL (0.132 g, 1 mmol), ethyl acetate (10 mL) and 2 MPa H_2 .

The kinetic curves of CAL hydrogenation under different temperature (363, 368, 373, and 378 K) and corresponding Arrhenius plots are displayed in Figure 6.^[21b,22] The -ln(1 - X) is proportional to the reaction time t, where X represents CAL conversion. This plot is in accordance with the definition of a first-order reaction. On the basis of this curve, the rate constants k at different temperatures can be calculated. As we all known, the Arrhenius equation is expressed as $lnk = lnA - E_a/RT$, where E_a and A represent reaction apparent activation energy and pre-exponential factor, respectively. For the Pt-Fe/UiO-66 catalytic system, the value of E_a is 37.6 kJ mol⁻¹, which slightly higher than the findings of Zhao et al., who reported an E_a of 24.7

kJmol⁻¹ over Pt/Fe₃O₄ catalyst.^[21b] For the Pt-Ni₃/UiO-66 catalytic system, the E_a has been calculated to be 19.9 kJ/mol. This value agreed with the findings of Fu et al., who reported an E_a of 18.8 kJmol⁻¹ over 3.5 wt%Pt/G catalyst.^[22] In comparison to Pt- and Pd-based catalysts, the lower E_a values suggest Pt-Fe(Ni₃)/UiO-66 catalysts are quite suitable for selective hydrogenation of CAL.

The possible reaction routes of CAL adsorption and activation with the Pt-Fe(Ni₃)/UiO-66 catalyst, according to the aforementioned discussion, were also proposed in Figure 7. Pt species have partially occupied d-orbitals, which can donate delectrons to the σ^* antibonding orbital of H₂, resulting in weakening and cleaving H-H bonds, forming hydrides.[4a,7a] Adsorption and activation of CAL on the catalyst surface was based on the types of the active metals related to different adsorbed patterns (Figure S13 and Figure 7a-d).^[5a,23] Among these adsorption patterns, the C=C π -complex and di- σ mode can facilitate the preferential activation of C=C bonds. However, the di- σ_{co} and end-on mode enhanced the reactivity for C=O group and generated the desired alcohols. For the Pt-Fe(Ni₃)/UiO-66 catalytic system, C=O group was activated and weakened via end-on bonding interaction ($\Delta E_{ads} = -0.45 \text{ eV}$) on the electron-deficient Fe surface, which attributed to the lone pair of oxygen for carbonyl group can be attracted preferentially because of anticlinal folded Pt-Fe skin (Figure S14).[24] Meanwhile, the dissociated hydrogen molecules are transferred to attack and activate CAL to form COL. For the Pt-Ni₃/UiO-66 catalytic system, the differences in product distribution can be rationalized based on the extended Huckel calculations of Delbecg and Sautet. As shown in Table S6, Ni species showed unstable four-electron interactions due to a narrower d-band width compared to Fe, and the strong interactions between the conjugated C=C bond and the Ni surface form di- σ mode (ΔE_{ads} = -1.18 eV) lead to the favorable adsorption behavior of C=C group, thereby notably enhancing the catalytic selectivity of CAL.[5a,25]



Figure 7. Optimized adsorption patterns of CAL on the surface of Pt-Fe (111) (a-b) and Pt-Ni₃ (111) (c-d); The corresponding adsorption energies are labelled; (e) The possible reaction routes for SH of CAL to COL or HCAL on the surface of Pt-Fe/UiO-66 and Pt-Ni₃/UiO-66, respectively.

Conclusion

In summary, the structurally alloyed Pt-Fe(Ni₃)/UiO-66 catalysts show unique electronic structure and catalytic properties for SH of α,β -unsaturated aldehydes in comparison with singlecomponent Pt catalyst. For the SH of cinnamaldehyde, Fe favors C=O bond hydrogenation (conv. 99.9%, sel. 94.3%), while Ni was more selective for C=C bond hydrogenation (conv. 99.9%, sel. 93.8%) on-demand. Comprehensive characterizations and periodic DFT calculations demonstrate that charge density of Pt species is recombinated after introducing 3d-transition metals (Fe, Ni), which is essential for the high chemoselectivity of cinnamaldehyde to cinnamic alcohol and phenylpropanal, respectively. This study provides an important insight related to rational control of catalytic selectivity via bicomponent nanocatatalysts with precise electron modification, enhanced catalytic properties. Besides, the introducing of secondary component not only directly reduces the expensive Pt usage in the environment-benign catalysts, which emerges satisfactory industrial application potential.

Experimental Section

Catalyst preparation

The UiO-66 was prepared according to the previous report.^[12b] Experimental details and structure information of UiO-66 is provided in supporting information (Figure S15). On the other hand, 10.0 mg (0.02 mmol) of H₂PtCl₆·6H₂O, 5.4 mg (0.02 mmol) of FeCl₃·6H₂O, 2 mL of PVP aqueous solution (0.3 wt %), and 100 mL of deionized water, were added to 250 mL flask. Subsequently, 2.5 mL of NaBH₄ aqueous solution (0.1 mol/L) was added drop by drop after stirring at room temperature for 1 h. After stirring for another 1 h, 0.1 g of UiO-66 powder was added. Stirring was continued at room temperature overnight, and product was collected through filtration (8000 r/min, 5 min), washed by ethanol and distilled water three times, dried in vacuum for 24 h at 80 °C, then pyrolyzed in air for 2 h at 300 °C.

The strategy for the preparation of Pt-Ni₃/UiO-66 was similar to that of Pt-Fe/UiO-66 except that NiCl₂·6H₂O (7.6 mg, 0.06 mmol) was used instead of FeCl₃·6H₂O.

The strategy for the preparation of $Pt-Fe(Ni_3)/ZrO_2$ and $Pt-Fe(Ni_3)/CNT$ were similar to that of Pt-Fe/UiO-66 except that UiO-66 was used instead of ZrO_2 and CNT.

The strategy for the preparation of $Pt-Co(Co_3)/UiO-66$ and $Pt-Sn(Sn_3)/UiO-66$ were similar to that of $Pt-Fe(Ni_3)/UiO-66$.

Meanwhile, single-component Pt/UiO-66, Fe/UiO-66 and Ni/UiO-66 were synthesized by the similar aforesaid protocol without second metal (Fe, Ni) introducing.

For comparison, MOFs-supported bicomponent catalysts with Pt:Fe(Ni) nominal molar ratios of 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4 were synthesized via aforementioned method.

DFT Calculations

The structural models for the Pt-Fe and Pt-Ni₃ nanostructure in the present DFT calculation were constructed according to the previous report.^[5a, 25] All the crystalline phase structure, electronic density of states (DOS), electron localization function (ELF) and Bader charge analysis were calculated by the Vienna Ab-initio Simulation Package (VASP). The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerh (PBE) was used to describe the exchange-correlation effects.^[26] The Pt-

Fe(111) structural model was built using a quadruple-layer p(5x5) slab with 4 metal layers. Furthermore, a vacuum of 15 Å in the z direction was built to separate the neighboring cells. The Pt-Ni₃(111) structural model was built also by p(5x5) supercell with 4 layers. The cutoff energies were set to be 400 eV, which have been tested extensively in supporting information (Figure S16 and S17). The Monkhorst-Pack k-point sampling were set to be 4x4x1 and 6x3x1 for Pt-Fe and Pt-Ni₃ models, respectively. The convergence criteria for the ionic relaxation loop and electronic self-consistent iteration were set to 10^{-4} eV and 10^{-5} eV/Å, respectively. The stability of the adsorbed CAL on the catalyst surface was described via chemisorption energy ΔE_{ads} , which is defined by the following equation:

 $\Delta E_{ads} = E_{slab+cal} - E_{slab} - E_{cal}$

Where $E_{slab+cal}$ is the energy of the catalyst with the adsorbed CAL, E_{slab} is the energy of pure catalyst, and E_{cal} is the energy of the isolated CAL.

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Keywords: Bimetallic catalysts • MOFs • Selectivity hydrogenation • Electronic effects • DFT

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In this work, we report a convenient strategy to fabricate bimetallic nanostructures with 3d-transition non-noble metal (Fe, Ni) modified Pt nanoparticles directly supported on porous metal-organic frameworks, which can function as a switch for selective hydrogenation of α , β -unsaturated aldehydes towards potential products on-demand.