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Regulating Hydrogenation Chemoselectivity of α,β -Unsaturated Aldehydes by Combination of Transfer and Catalytic Hydrogenation with Ammonia Borane and Pt/MOL

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Dedication ((optional))

Abstract: Herein, we combine two hydrogenation mechanisms, transfer and catalytic hydrogenation, to achieve higher regulation of hydrogenation chemoselectivity of cinnamyl aldehydes, where transfer hydrogenation with ammonia borane exclusively reduces C=O bonds to get cinnamyl alcohol and Pt-loaded metal-organic layer efficiently hydrogenate C=C bonds to synthesize phenyl propanol with almost 100% conversion rate. The hydrogenation can be carried out under mild conditions without external high pressure hydrogen and applicable to various α,β -unsaturated aldehydes.

Shortage of resources has seriously threatened the high-speed development of modern society because of enormous consumption of limited natural source.^[1] Conversion of biomass provides an alternative, effective route for producing value-added chemicals to answer the current resource crisis. For example, hydrogenation of α,β -unsaturated aldehydes, such as cinnamyl aldehyde (CAL) can produce the reductive products cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and phenyl propanol (HCOL), which are important intermediates in area of fine chemical engineering, especially in preparation of perfume, flavoring, medicine and pharmaceuticals.^[2] However, the concurrence of C-C and C-O double bonds poses many difficulties to achieve highly controllable chemoselectivity for hydrogenation of α,β -unsaturated aldehydes.^[3] It is of significant importance to design a catalytic system for regulating the hydrogenation selectivity to obtain products in demand.

Hydrogenation reactions often involve two mechanisms: catalytic hydrogenation and transfer hydrogenation. The catalysts for catalytic hydrogenation of α,β -unsaturated aldehydes include Pt, Pd, Ru, Ni, Co metal nanoparticles or their alloys, which often showed high activity towards C=C bonds but low selectivity because of thermodynamically favored carbon-carbon group. Various strategies have been developed to design

catalysts for increasing the chemoselectivity of hydrogenation reaction. Steric effect is a straightforward way to increase the selectivity, by considering the different collision probability of C-C and C-O double bonds.^[4] For instance, it has been demonstrated that the selectivity of CAL into COL could be significantly increased through functionalization of the surface of catalyst with long-chain amines or incorporation of metal nanoparticles within metal organic frameworks. Synergistic electronic effect, such as hybridization of metal catalysts with co-catalysts has shown the obviously improved chemoselectivity towards unsaturated alcohols by the interfacial electron-transfer interaction.^[2a, 5] Although the high chemoselectivity can be achieved through catalytic hydrogenation, elaborate design of catalysts and external hydrogen atmosphere are necessities, and the selectivity and activity could be affected by many reaction parameters (temperature, pressure, composition and morphology of catalysts, etc.).

Compared with catalytic hydrogenation, the transfer hydrogenation represents a green strategy for hydrogenation of α,β -unsaturated aldehydes, which utilizes hydrogen donors through self-reducing or catalytic dehydrogenation without requiring high pressure H₂.^[6] Hydrogen donors, such as 2-propanol and formic acid often requires the usage of catalysts at high temperature to initiate the hydrogenation reaction, and metal amidoborane can reduce selectively the C=O but under inert atmosphere. Therefore, it remains a big challenge to regulate the chemoselectivity for hydrogenation of α,β -unsaturated aldehydes at target positions under mild conditions.

Herein, we for the first time developed a mild and green strategy to combine two hydrogenation mechanisms to achieve highly controllable selectivity for hydrogenation of α,β -unsaturated aldehydes. Ammonia borane (AB in short) not only is highly stable to be transported, but also possesses the characteristics of water-solubility, nontoxicity, and high hydrogen content of ca. 19.6 wt%, which have shown the exclusive hydrogenation of C=O to prepare unsaturated alcohols under mild conditions.^[7] Consequently, AB was selected as the hydrogen donor for transfer hydrogenation of α,β -unsaturated aldehydes.

Metal-organic frameworks (MOFs) possessed large surface area, ordered and tunable pores, adjustable structure and exposed active sites, which provided a versatile material platform for catalytic applications,^[8] especially catalytic hydrogenation.^[2a, 3b, 5d, 9] Metal-organic layer (MOL), a kind of two-dimensional MOFs, has attracted increasing research interest due to their thin thickness and exposed active sites reminiscent of typical 2D graphene,^[10] which serve as ideal support for immobilization of metal nanoparticles. Therefore, Pt supported on MOL (Pt/MOL) was used for catalytic

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hydrogenation of α,β -unsaturated aldehydes. By employing AB and Pt/MOL, no external hydrogen atmosphere is required for catalytic hydrogenation, which can be in-situ generated through dehydrogenation of AB by Pt/MOL. The high activity of Pt nanoparticles towards hydrogenation of C=C bonds can produce saturated alcohols thereafter. By combination of these two mechanisms, extremely high activity and selectivity (both conversion rate and selectivity approach 100%) can be achieved to produce unsaturated and saturated alcohols.

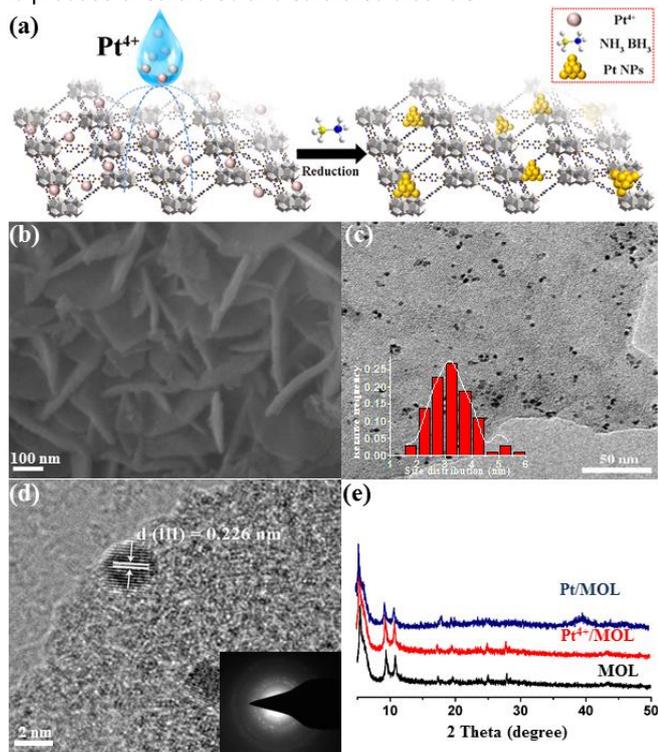


Figure 1 (a) Schematic illustration exhibits the immobilization of Pt NPs on the MOL using AB reduction followed by catalytic hydrogenation of α,β -unsaturated aldehydes with Pt/MOL and AB; (b) SEM image of the Pt/MOL; (c) TEM image of the Pt/MOL (Inset: size distribution of Pt NPs in Pt/MOL); (d) High resolution TEM image of the Pt/MOL (Inset: selected area electron diffraction); and (e) Powder XRD patterns of Pt/MOL, Pt⁺/MOL, and pure MOL.

A microporous zirconium-based MOL with the molecular formula $Zr_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu_2-OH)_6(BPYDC)_9$, ($H_2BPYDC = 2,2'$ -bipyridine-5,5'-dicarboxylic acid),^[89] is used to immobilize active sites homogeneously on the support due to its high stability in water and ethanol and the strong coordination interaction between metal ions and nitrogen atom in bipyridine. As shown in Figure 1a, firstly, a precursor, $H_2PtCl_6 \cdot 2H_2O$, was introduced into the pores of MOL *via* absorption to form Pt⁴⁺/MOL. And then Pt/MOL was prepared through *in situ* reduction of AB during the catalytic hydrogenation. The morphology of the composites was characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as shown in Figure 1b, 1c and 1d. SEM and TEM images confirm the as-prepared composite is thin layered material with a lateral thickness of ca 25 nm and high resolution TEM shows that the average length of Pt nanoparticles with Pt(111) plane (ca 0.226 nm) is ca 3.4 nm,^[89] which are evenly distributed within MOL.^[11] PXRD patterns show that the MOL maintains the same crystal structure after adsorption of Pt⁴⁺ and loading with Pt nanoparticles (Figure 1e).^[89] A broad peak at 39.4 degree is ascribed to Pt NPs, indicating that the tiny Pt NPs were formed, consistent with the TEM image.

The loading of Pt within composites is 10.46 wt%, calculated from the result of inductively coupled plasma-mass spectrometry (ICP-MS). X-ray photoelectron spectroscopy (XPS) spectra of Pt/MOL and Pt²⁺/MOL are shown in Figure S2a and S2b, which show Pt/MOL exhibits 4f_{5/2} and 4f_{7/2} peaks of Pt⁰, Pt²⁺, and Pt⁴⁺ at 70.6 eV and 73.5 eV, 72.6 eV and 75.8 eV, 76.8 eV, respectively.^[12] Moreover, ca. 70% of the Pt are in the reduced state. Nitrogen adsorption analysis (Figure S2c) demonstrates that the BET surface area of Pt/MOL decreases obviously to 244 m² g⁻¹, compared with that of the pure MOL (467 m² g⁻¹), which may result from occupation of parts of pores in MOL with dispersed Pt NPs. Thermogravimetric analysis of MOL and Pt/MOL is well identical with that in published literature (Figure S1).^[89, 13]

Table 1 Hydrogenation of cinnamaldehyde over catalysts.

Entry	Catalyst	Conversion(%)	Selectivity(%)		TON	TOF/h ⁻¹
			B	C		
1 ^a	-	100	100	0	-	-
2 ^b	Pt/MOL	100	0	100	124.3	41.4
3 ^c	Pt NPs	100	40	60	74.6	24.8
4 ^b	MOL	100	100	0	-	-
5 ^d	Pt/MOL + H ₂	59	35	6	73.3 ^e	24.4 ^e
6 ^b	Pt/Uio-66-bpy	100	61	39	48.5	16.2

Reaction conditions: ^a 8 mg NH₃BH₃, 25 °C, 15 min. ^b 6 mg catalyst, 25 mg NH₃BH₃, 70 °C, 3 h. ^c 2 mg H₂PtCl₆·2H₂O, 25 mg NH₃BH₃, 70 °C, 3 h. ^d 6 mg catalyst, 0.4 MPa H₂, 70 °C, 3 h. Same reaction conditions: 0.4 mmol substrates, 5 mL ethanol, 800 rpm. TOF was calculated as quantity of COL converted per mole of total Pt per hour, and TON was calculated as quantity of COL converted per mole of total Pt after 3 h. ^e TOF was calculated as the quantity of CAL converted per mole of total Pt per hour, TON was calculated as the quantity of CAL converted per mole of total Pt after 3 h, and the resource of hydrogen was changed to 0.4 MPa H₂. Catalytic reaction products were analyzed and identified using ¹H NMR.

To access the hydrogenation performance towards α,β -unsaturated aldehydes, CAL was selected as an initial substrate as listed in Table 1. All the reactions were performed in a 25 mL schlenk pressure tube, except that control experiment of H₂ + Pt/MOL was performed in high pressure autoclave to detect the pressure (Entry 5, Table 1). Firstly, the transfer hydrogenation of CAL with AB separately was carried out at various reaction temperature and time (from 25 to 100 °C, from 15 min to 3 h). It is found that CAL could be completely converted at room temperature for 15 min and only COL was obtained exclusively, both conversion rate and selectivity toward hydrogenation of C=O are 100% (Entry 1, Table 1). No dehydrogenation of AB was observed at the tested conditions without any catalyst, demonstrating the conversion of C=O results from the transfer hydrogenation mechanism (Figure S3c and 3d). Subsequently, combination of transfer and catalytic hydrogenation was performed for completely hydrogenate CAL to obtain HCOL. Pt/MOL was used as the catalyst and AB served as hydrogen donor and hydrogen source for catalytic hydrogenation. Interestingly, complete conversion of CAL was observed and only HCOL was found without any byproduct (both conversion rate and selectivity toward full hydrogenation are 100%) (Entry 2, Table 1), values of TON and TOF were 124.3 and 41.4 h⁻¹

respectively. To identify the catalytically active sites, control experiment was also carried out with pure MOL and in-situ formed Pt nanoparticles as catalysts (Entry 3 and 4, Table 1). In the case of pure MOL, although CAL was completely converted, only COL was produced which is the same as that with AB separately, indicating MOL is inactive for hydrogenation. With in-situ formed Pt nanoparticles as the catalyst, both COL and HCOL were found and TOF and TON are only 2/3 times of those of AB/Pt/MOL system, reflecting the high activity of Pt nanoparticles after homogeneously immobilized on MOL. The catalytic hydrogenation mechanism of Pt/MOL is confirmed by the fact that no saturated alcohol was found with pure AB and 0.4 MPa pressure was generated through mixing AB and Pt/MOL at the same temperature and time (Figure S3a and S3b). The catalytic hydrogenation mechanism for C=C can be further confirmed by a control experiment: hydrogenation of COL with AB in the presence of Pt/MOL in an open flask to avoid H₂ dehydrogenated from AB from contacting the COL. It is found that the conversion of COL is extremely low, especially at larger open flask (17% and 1% conversion of COL at 25 and 250 ml flasks, respectively) (Figure S12-S13).

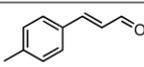
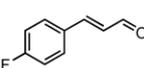
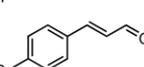
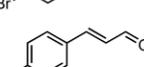
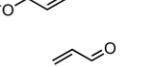
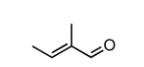
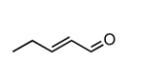
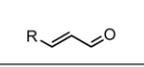
Control experiment of catalytic hydrogenation with pure H₂ was carried out instead of AB through pumping 0.4 MPa H₂ into high pressure autoclave at 70 °C (Entry 5, Table 1), the same pressure as that of in-situ generated H₂ by dehydrogenation of AB (Figure S3a). The conversion of CAL is only 59%, far less than that with AB as hydrogen source, and three hydrogenated products were detected under the same condition, which implies the hydrogenation selectivity can be efficiently regulated through combination of both transfer and catalytic hydrogenation mechanism. The high activity of Pt/MOL for catalytic hydrogenation of α,β -unsaturated aldehydes is further confirmed by comparison with in-situ reduced Pt nanoparticles within UiO-66-bpy, a 3D MOF with the same metal precursor and ligand. As shown in Figure S4b and S4c, 3D UiO-66-bpy were synthesized successfully according to the reported procedure^[14] and characterized by PXRD and SEM (Figure S4a). As-synthesized Pt/UiO-66-bpy combined with AB was applied for the hydrogenation of α,β -unsaturated aldehydes under same conditions. Although conversion of CAL was complete, the mixture products (61% COL and 39% HCOL) were obtained (Entry 6, Table 1). The disparity of catalytic performance between Pt/MOL and Pt/UiO-66-bpy may be ascribed to the unique layers structure of MOL, leading to sufficient contact of active Pt NPs with substrates.

The above-mentioned hydrogenation results show that the hydrogenation chemoselectivity of CAL can be easily regulated through different combinations of two hydrogenation mechanism based on AB and Pt/MOL. Through transfer hydrogenation with AB, exclusive hydrogenation of C=O can be achieved to prepare unsaturated alcohols, and saturated alcohols can be prepared with complete hydrogenation of C=O and C=C through combination of transfer and catalytic hydrogenation. In this hydrogenation process, AB is crucial to accomplish controllable chemoselectivity, which plays three important roles: i) hydrogen donor for selective reduction of C=O; ii) reductant for in-situ formation of Pt nanoparticles on MOL; and iii) hydrogen source for dehydrogenation with Pt/MOL for further catalytic hydrogenation of C=C.

To verify the generality of our combination strategy for hydrogenation, in Entry 8 Table 2 and Entry 4 Table S1, R represented a series of substitute groups of α,β -unsaturated

aldehydes, which were catalyzed under the optimized conditions and the results are tabulated in Table 2. Various α,β -unsaturated aldehydes with aromatic and alkyl groups can be reduced to the related unsaturated alcohols and saturated alcohols in high yields, such as α,β -unsaturated aldehydes containing 4-methylphenyl, 4-fluorophenyl, 4-bromophenyl, 4-methoxyphenyl, dimethyl, ethyl (Entries 1-7, Table 2). In all cases, substrates can be selectively converted into corresponding unsaturated alcohols (B) hydrogenated merely by AB within 15 min at room temperature, proving that the transfer hydrogenation with AB can selectively hydrogenate C=O without breaking C=C.

Table 2 Hydrogenation of other substrates over Pt/MOL.

Entry	Substrate	Conversion(%)	Selectivity(%)		TON	TOF/h ⁻¹
			B	C		
1 ^a		100	0	100	124.3	41.4
2 ^a		100	0	100	124.3	41.4
3 ^b		100	1	99	123.1	30.8
4 ^a		100	1	99	123.1	41.0
5 ^c		100	0	100	124.3	31.1
6 ^d		100	4	96	119.3	29.8
7 ^a		100	4	96	119.3	39.8
8 ^e		100	100	0	-	-

Reaction conditions: ^a 6 mg catalyst, 25 mg NH₃-BH₃, 70 °C, 3 h. ^b 6 mg catalyst, 46 mg NH₃-BH₃, 70 °C, 4 h. ^c 6 mg catalyst, 31 mg NH₃-BH₃, 70 °C, 4 h. ^d 6 mg catalyst, 36 mg NH₃-BH₃, 70 °C, 4 h. ^e 8 mg NH₃-BH₃, 25 °C, 15 min; R represents a series of substitute groups of α,β -unsaturated aldehydes. Same reaction conditions: 0.4 mmol substrates, 5 mL ethanol, 800 rpm. TOF was calculated as quantity of COL converted per mole of total Pt per hour, and TON was calculated as quantity of COL converted per mole of total Pt after 3 or 4 h. Catalytic reaction products were analyzed and identified using ¹H NMR.

Saturated alcohols can be prepared through the combination of transfer hydrogenation and catalytic hydrogenation by adding Pt/MOL. However, the hydrogenation activity of Pt/MOL varies from the substrates, possibly because of the steric and/or electronic effect. Various substituents on the benzene ring have basically no influence on the yield of (C) product, (Entry 1, 2 and 4 in Table 2) the selectivity values of completing reduced product are ~99%. When the substituents are 4-bromophenyl, methyl, or ethyl, the selectivity of corresponding completely reduced products would decrease using the similar conditions (Entry 1, 2 and 3 in Table S1), which may be caused by electron and steric effect, but the selectivity can approach 100% through increasing the reaction time and/or the amount of AB again (Entry 3, 5, and 6 in Table 2). These catalytic results

indicate that combination of Pt/MOL and AB are highly efficient and universal toward the hydrogenation of α,β -unsaturated aldehydes to corresponding two significant products.

The instability of heterogeneous catalysts would restrict their catalytic applications; therefore, the stability and recyclability of as-prepared catalysts were examined by consecutive runs reactions, SEM, TEM, and PXRD (Figure S2a, S2b S5a and S5b).^[8g] Firstly, the recyclability experiment was performed under the same conditions by recycling catalyst after separated by centrifugation and washed with ethanol. Figure S2a exhibits that the selectivity and conversion of Pt/MOL are maintained after five consecutive runs without any activity loss. In addition, the Pt NPs loaded in the MOL were not obviously aggregated after at least five runs reactions as demonstrated by SEM and TEM (Figure S5a and 2b). The PXRD patterns proved the structures are retained after reactions and the Pt NPs are well dispersed as evidenced by the short and broad peak at 39.4 degree (Figure S5b).^[9c] ICP result was also indicative of no detectable leaching of Pt during the reaction. The excellent recyclability may result from that MOL has the ordered pores and strong interaction originated from the BPYDC ligand, which can confine and well disperse the Pt NPs.

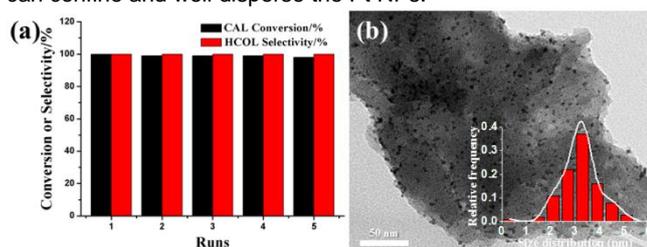


Figure 2. (a) Catalytic recyclability of Pt@MOL for hydrogenation of α,β -unsaturated aldehydes; and (b) TEM image of the Pt@MOL after catalytic reaction. (Inset: size distribution of Pt NPs after reaction).

In summary, we for the first time combine the two hydrogenation mechanism: transfer and catalytic hydrogenation to achieve high regulation of the hydrogenation selectivity of α,β -unsaturated aldehydes. Through transfer hydrogenation with ammonia borane, unsaturated alcohols can be exclusively produced and the saturated alcohols can be selectively synthesized by synergistic action of ammonia borane and Pt-loaded metal-organic layer, the latter of which simultaneously dehydrogenate ammonia borane and hydrogenate the C=C bonds. The combination of two hydrogenation mechanism not only can highly regulate the chemoselectivity of hydrogenation reactions but also avoid the usage of external hydrogen atmosphere. The strategy can be extended to various α,β -unsaturated aldehydes and the catalysts can be recycled for several times without any loss of activity. Unfortunately, only two hydrogenation products could be synthesized in this work. Controllable regulation of three hydrogenation products of α,β -unsaturated aldehydes would be a big challenge and more important, which might be achievable by elaborate design of MOF-based catalysts. We envision that this mild approach would open an avenue for hydrogenation of α,β -unsaturated aldehydes to replace the traditional rigorous methods and the combined strategy would be extendable to other systems, where high regulation of selectivity is required.

Acknowledgements

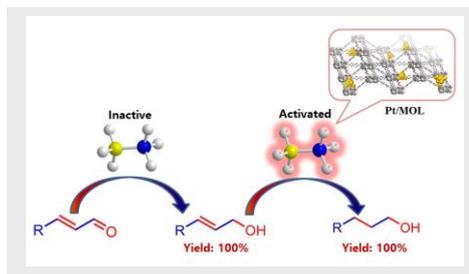
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Keywords: metal-organic layers • α,β -unsaturated aldehydes • ammonia borane • transfer hydrogenation • catalytic hydrogenation

- [1] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044-4098.
- [2] a) M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, L. Gu, W. Hu, H. Zhao, Z. Tang, *Nature* **2016**, *539*, 76-80; b) M. Boudart, *Nature* **1994**, *372*, 320-320.
- [3] a) L. E. Murillo, A. M. Goda, J. G. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 7101-7105; b) S. Bai, L. Bu, Q. Shao, X. Zhu, X. Huang, *J. Am. Chem. Soc.* **2018**, *140*, 8384-8387; c) J. W. Yang, M. T. Hechavarría Fonseca, N. Vignola, B. List, *Angew. Chem. Int. Ed.* **2005**, *44*, 108-110; d) L. Loffreda, F. Delbecq, F. Vigné, P. Sautet, *Angew. Chem. Int. Ed.* **2005**, *44*, 5279-5282; e) S. Zhou, S. Fleischer, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2011**, *50*, 5120-5124.
- [4] H. Liu, Q. Mei, S. Li, Y. Yang, Y. Wang, H. Liu, L. Zheng, P. An, J. Zhang, B. Han, *Chem. Commun.* **2018**, *54*, 908-911.
- [5] a) K. R. Kahsar, D. K. Schwartz, J. W. Medlin, *J. Am. Chem. Soc.* **2014**, *136*, 520-526; b) S. Cao, F. Tao, Y. Tang, Y. Li, J. Yu, *Chem. Soc. Rev.* **2016**, *45*, 4747-4765; c) Y. J. Wang, N. Zhao, B. Fang, H. Li, X. T. Bi, H. Wang, *Chem. Rev.* **2015**, *115*, 3433-3467; d) K. Yuan, T. Song, D. Wang, X. Zhang, X. Gao, Y. Zou, H. Dong, Z. Tang, W. Hu, *Angew. Chem. Int. Ed.* **2018**, *57*, 5708-5713; e) B. Wu, H. Huang, J. Yang, N. Zheng, G. Fu, *Angew. Chem. Int. Ed.* **2012**, *51*, 3440-3443; f) S. Chen, H. Su, Y. Wang, W. Wu, J. Zeng, *Angew. Chem. Int. Ed.* **2015**, *54*, 108-113; g) S. Song, X. Liu, J. Li, J. Pan, F. Wang, Y. Xing, X. Wang, X. Liu, H. Zhang, *Adv. Mater.* **2017**, *29*, 1700495.
- [6] G. Brieger, T. J. Nestruck, *Chem. Rev.* **1974**, *74*, 567-580.
- [7] Y. H. Zhou, Q. Yang, Y. Z. Chen, H. L. Jiang, *Chem. Commun.* **2017**, *53*, 12361-12364.
- [8] a) Q. Yang, Q. Xu, H. L. Jiang, *Chem. Soc. Rev.* **2017**, *46*, 4774-4808; b) L. Chen, R. Luque, Y. Li, *Chem. Soc. Rev.* **2017**, *46*, 4614-4630; c) L. Ma, Y. Liu, Y. Liu, S. Jiang, P. Li, Y. Hao, P. Shao, A. Yin, X. Feng, B. Wang, *Angew. Chem. Int. Ed.* **2019**, *58*, 4221-4226; d) Y. Chen, S. Li, X. Pei, J. Zhou, X. Feng, S. Zhang, Y. Cheng, H. Li, R. Han, B. Wang, *Angew. Chem. Int. Ed.* **2016**, *55*, 3419-3423; e) P. Jin, W. Tan, J. Huo, T. Liu, Y. Liang, S. Wang, D. Bradshaw, *J. Mater. Chem. A* **2018**, *6*, 20473-20479; f) D. Bradshaw, A. Garai, J. Huo, *Chem. Soc. Rev.* **2012**, *41*, 2344-2381; g) R. Dai, F. Peng, P. Ji, K. Lu, C. Wang, J. Sun, W. Lin, *Inorg. Chem.* **2017**, *56*, 8128-8134.
- [9] a) N. Zhang, Q. Shao, P. Wang, X. Zhu, X. Huang, *Small* **2018**, *14*, 1704318; b) Z. Guo, C. Xiao, R. V. Maligal-Ganesh, L. Zhou, T. W. Goh, X. Li, D. Tesfagaber, A. Thiel, W. Huang, *ACS Catal.* **2014**, *4*, 1340-1348.
- [10] a) M. Zhao, Q. Lu, Q. Ma, H. Zhang, *Small Methods* **2017**, *1*, 1600030; b) L. Cao, Z. Lin, W. Shi, Z. Wang, C. Zhang, X. Hu, C. Wang, W. Lin, *J. Am. Chem. Soc.* **2017**, *139*, 7020-7029.
- [11] H. Zhang, Y. Liu, H. Wu, W. Zhou, Z. Kou, S. J. Pennycook, J. Xie, C. Guan, J. Wang, *J. Mater. Chem. A* **2018**, *6*, 20214-20223.
- [12] a) C. Feng, G. Xu, H. Liu, J. Lv, Z. Zheng, Y. Wu, *J. Electrochem. Soc.* **2013**, *161*, B1-B8; b) J. Fang, D. Li, Y. Shao, J. Hu, *J. Mater. Chem. A* **2016**, *4*, 14213-14221.
- [13] M. Mihet, G. Blanita, M. Dan, L. Barbu-Tudoran, M. D. Lazar, *J. Nanosci. Nanotechnol.* **2019**, *19*, 3187-3196.
- [14] a) H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim, W. Zhou, *J. Am. Chem. Soc.* **2013**, *135*, 10525-10532; b) L. Chen, X. Chen, H. Liu, Y. Li, *Small* **2015**, *11*, 2642-2648.

COMMUNICATION

Two hydrogenation mechanism, transfer and catalytic hydrogenation are combined to achieve higher regulation of hydrogenation chemoselectivity of cinnamyl aldehydes, where transfer hydrogenation with ammonia borane exclusively reduces C=O bonds to get cinnamyl alcohol and Pt-loaded metal-organic layers efficiently hydrogenate C=C bonds to synthesize phenyl propanol with almost 100% conversion rate without external H₂.



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Regulating Hydrogenation Chemoselectivity of α,β -Unsaturated Aldehydes by Combination of Transfer and Catalytic Hydrogenation with Ammonia Borane and Pt/MOL

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