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Highly Networked Platinum-Tin Nanowires as Highly Active and Selective Catalysts towards Unsaturated Aldehyde Semihydrogenations

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Abstract: The selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols is an important process for many industrial applications, while the realization of excellent conversion efficiency and selectivity remains significant challenge. Herein, we reported the preparation of a class of networked Pt-tin nanowires (Pt-Sn NWs) for selectively hydrogenating unsaturated aldehydes to the desired unsaturated alcohols. The optimized Pt_{1.5}Sn NWs deliver high conversion efficiency for cinnamaldehyde (CAL) hydrogenation (98.1 %) and excellent selectivity to cinnamyl alcohol (COL) (90.6 %), which outperform the Pt_{1.5}Sn nanoparticles (NPs) as well as the Pt NPs. The high performance of Pt_{1.5}Sn NWs can also be expanded to other α,β -unsaturated aldehydes hydrogenation. X-ray photoelectron spectroscopy reveals that the high ratio of metallic Pt in the Pt_{1.5}Sn NWs boosts the CAL conversion and high content of Sn favors the C=O hydrogenation, respectively, which leads to the excellent activity and selectivity.

Keyword: Platinum, Tin, Networked Nanowires, Selective Hydrogenation, Unsaturated Aldehyde

The selective hydrogenation of α,β -unsaturated aldehydes has aroused great attention because it involves significant steps to yield the widely-used unsaturatured alcohols for the synthesis of various fine chemicals, particularly in the field of pharmaceuticals, flavourings and perfumes.^[1-4] A typical example is the selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL), which is the critical process for desired industrial products. However, CAL hydrogenation involves in multiple products owing to the competitive hydrogenation between C=C double bond and C=O double bond, making it difficult to achieve high selectivity to the targeted products, particularly in the heterogeneous catalysis.^[1, 5, 6] In addition, the hydrogenation of C=O is more unfavorable than that of C=C mainly because of the thermodynamics favor of C=C hydrogenation over C=O hydrogenation, which easily lead to the selective formation of hydrocinnamaldehyde (HCAL) rather than the desired COL.^[2, 7, 8] Therefore, improving the efficiency and selectivity of the CAL hydrogenation to the desirable COL is challenging and significant.

Platinum (Pt)-based nanomaterials were widely studied and demonstrated as the effective catalysts for hydrogenation.^[8-15] However, monometallic Pt is difficult to selectively hydrogenate C=O when served as the main sites, mainly because the thermodynamic favor of C=C hydrogenation over C=O hydrogenation.^[16-18] To promote the catalytic efficiency and selectivity as well as minimize the usage of Pt, the classical strategy is to fabricate bimetallic Pt-based nanostructures for enhancing the selectivity because of the modulated electronic structure and surface atom arrangement.^[19-21] Therefore, the introduction of second non-noble metals into Pt for the enhanced hydrogenation has attracted tremendous attention.^[21-30] Despite the intense achievements, the development of unique nanostructures with excellent efficiency and selectivity towards the hydrogenation of α,β -unsaturated aldehydes is still far from desirable.

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Herein, we reported the preparation of a new class of networked bimetallic Pt-tin nanowires (Pt-Sn NWs) with controlled compositions for the enhanced selective CAL hydrogenation.^[31] The abundant oxidized Sn presented on the surface of Pt-Sn NW promotes the activation of C=O while decreases the activation of C=C. It turned out that the networked Pt-Sn NWs showed the excellent activity for the CAL hydrogenation, and exhibited the increased selectivity to the desired COL and decreased selectivity to hydrocinnamyl alcohol (HCOL) with the Sn content of Pt-Sn NWs increased. Particularly, the optimized Pt_{1.5}Sn NWs delivered an outstanding activity of nearly 100% conversion and excellent selectivity to COL (90.6%), which is superior to those of Pt_{1.5}Sn nanoparticles (NPs) and Pt NPs, showing a new class of Pt-based catalysts for α,β -unsaturated aldehydes hydrogenation with excellent efficiency and selectivity.

We prepared the networked Pt-Sn NWs through a simple wet-chemical approach, in which potassium tetrachloroplatinate (II) (K₂PtCl₄) and tin (II) chloride (SnCl₂) were used as the metal precursors, benzoin was chosen as shape-controlled agent, polyvinylpyrrolidone (PVP) was applied as capping agent, and ethylene glycol (EG) was selected as solvent. The homogeneous mixture was heated at 200 °C for 5 h in a Teflon-lined stainless-steel autoclave (see the Experimental Section for details). Through the optimization of synthetic conditions, the benzoin was considered as an essential shape-controlled agent for the preparation of well-defined PtSn NWs (**Figure S1**). The product was first characterized by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) (**Figure 1a**) and transmission electron microscopy (TEM) (**Figure 1b**), which clearly revealed that the ultrathin networked nanostructures consisted of the interlaced NWs with an average diameter of 2.7 ± 0.8 nm (**Figure 1b** inset). The atomic ratio of Pt to Sn for the NWs was calculated to be around 1.5 : 1, by scanning electron microscopy energy-dispersive spectrometer (SEM-EDS) (**Figure 1c**), which fit well with their feeding ratio and thus termed as Pt_{1.5}Sn NWs. The

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crystalline nature of the networked $Pt_{1.5}Sn$ NWs was characterized by X-ray diffraction (XRD) (**Figure 1d**). The representative diffraction peaks at 38.9°, 45.2°, 65.9°, and 79.3° are close to the (111), (200), (220) and (311) planes of Pt_3Sn (JCPDS No. 35-1360), in consistent with the selected area electron diffraction (SAED) (**Figure 1a**, inset), confirming the formation of the alloyed $Pt_{1.5}Sn$ NWs. We further characterized the NWs by high resolution TEM (HRTEM) and STEM. As shown in **Figure 1e**, the HRTEM image of the NWs displays the interplanar spacing of 0.230 nm, corresponding to the (111) plane of Pt_3Sn (JCPDS No. 35-1360), in agreement with the XRD result. Moreover, a number of kinks with defects and atoms steps were observed in the inset of **Figure 1e**, which can offer vital chances for the enhanced catalytic system.^[32, 33] The alloyed structure of $Pt_{1.5}Sn$ NWs was also confirmed by the HAADF-STEM elemental mapping (**Figure 1f**), where the homogeneous distributions of Pt and Sn in the whole NW were observed.

Interestingly, the presented wet-chemical synthetic method for networked NWs is facile and robust, which can be extended to the synthesis of other noble metal alloy NWs, including networked Ru_{1.5}Sn NWs, Rh_{1.5}Sn NWs, and Ir_{1.5}Sn NWs (**Figure S2**). Although networked Pt-Sn NWs with different compositions were obtained by varying the content of Sn precursor supplied (**Figure S3**), only the pure Pt nanoparticle can be obtained in the absence of Sn precursor (**Figure S4**), indicating that the introduction of Sn precursor is critical for the formation of NWs. To comprehend the composition and structure features of these different Pt-Sn NWs, we further characterized SEM-EDS and XRD characterizations. The SEM-EDS spectra show that the atomic ratios of the Pt-Sn NWs were all coherent with the their own feeding ratios and the composition of spherical Pt_{1.5}Sn NPs was close to that of Pt_{1.5}Sn NWs and Pt₄Sn NWs are analogous to that of Pt_{1.5}Sn NWs, all which show obvious peak shift

benchmark with those of the Pt NPs and the standard Pt₃Sn XRD card (JCPDS No. 35-1360), revealing the alloyed properties of the these Pt-Sn NWs.

The as-prepared Pt NPs, $Pt_{1.5}Sn$ NPs and $Pt_{1.5}Sn$ NWs were then evaluated as catalysts for the selective hydrogenation of CAL. **Figure 2a** shows the possible reaction pathways of CAL hydrogenation, where the hydrogenation of C=O double bonds yields the targeted COL, that of C=C double bonds produces HCAL, and the consecutive hydrogenation of either COL or HCAL produces HCOL.^[15, 34] Although COL is industrially desired product, the hydrogenation of C=O double bonds is more unfavorable than that of C=C double bonds according to the thermodynamics and kinetics.^[8, 22, 34] To this end, the kinetic mechanisms of Pt NPs, $Pt_{1.5}Sn$ NPs and $Pt_{1.5}Sn$ NWs for the hydrogenation of CAL were carefully investigated by the comparison of the time-tracing reactions. Before the catalytic tests, the catalysts were dispersed in a mixed solution of CAL and ethanol. The reactions were performed in the stainless-steel autoclave with fixed stirring speed at near room temperature and definite hydrogen pressure. The loading amounts of Pt were fixed at 2 mg for all the Ptbased catalysts, which were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The specific catalytic conversion efficiency and selectivity were presented in **Figure 2b-2d**. As shown in **Figure 2b**, the Pt NPs shows a low selectivity to the desired COL. With the reaction time changes from 15 min to 60 min, the conversion efficiency of the whole product increases gradually with no obvious selectivity to COL, HCAL or HCOL. With the similar spherical shape as Pt NPs, the Pt_{1.5}Sn NPs exhibited a stable selectivity of roughly 83 % to COL and the conversion efficiency strengthened from 27.2 % to 87.3 % for the duration of 60 min reaction (**Figure 2c**), revealing the enhanced conversion efficiency and selectivity achieved by the introduction of Sn. The networked Pt_{1.5}Sn NWs with similar composition but different shape compared with Pt_{1.5}Sn NPs were further explored for the hydrogenation of

CAL in details. As shown in Figure 2d, the product after 15 min reaction shows 55.3 % conversion efficiency and high selectivity of 87.2 % to the targeted COL, and negligible selectivity to HCAL and HCOL. As reaction time is extended to 30 min, the conversion efficiency of product increases to 94.3 % and the selectivity to COL is up to 88.9 %, whereas the selectivity to HCAL or HCOL is still extremely low. With the reaction going to 45 min, the content of COL product slowly increases to 89.6 % while the conversion efficiency maintains above 90 %, indicating the excellent catalytic efficiency and the COL selectivity. When reaction time is 60 min, the selectivity to COL and the conversion of product have slight improvements with limited selectivity to HCOL. These time-tracing conversion efficiency and intermediates changes for the hydrogenation of CAL revealed several attractive features as follows: (1) Pure Pt NPs is unfavorable for selectively hydrogenating CAL to COL but can promote the conversion efficiency due to the high active sites from ultrasmall nanostructure,^[16] (2) Pt-Sn alloy can favor the adsorption of C=O double bonds to the desirable COL, and (3) the networked NWs structure is of more active sites and higher utilization efficiency to hydrogenate CAL than spherical NPs likely due to the unique nanostructure and alloy effect.^[35, 36] Furthermore, we also studied the stability of Pt_{1.5}Sn NWs for CAL hydrogenation by five recycle tests, where the selectivity to COL keeps high, while the conversion efficiency drops from 99.4% to 34.0%, which may be attributed to the heavy aggregation of the catalysts (Figure S8).

To deeply understand the role of Pt-Sn NWs in the selective CAL hydrogenation, a series of composition-controlled networked Pt-Sn NWs and spherical Pt-based NPs were further investigated. For a comprehensive evaluation of the catalytic properties of CAL hydrogenation, these Pt-based catalysts with the same Pt loadings were carried out under the same experimental conditions. As shown in **Table 1** and **Figure S9a**, the Pt_{1.5}Sn NWs exhibit the best selectivity (90.6 %) to COL and excellent conversion (98.1 %) among all the Pt-Sn

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NWs within 1 h. Particularly, the hydrogenation products of C=C are negligible (the selectivities of both HCAL and HCOL are less than 10 %), which displays the optimal composition of Pt-Sn NWs for the adsorption of C=O double bonds to the desirable COL. In the case of the networked Pt₂Sn NWs, almost 100 % conversion of the product and 87.6 % selectivity to COL and 12.2 % selectivity to HCOL are observed, indicating that distinct selective hydrogenation of C=O. With decreasing the Sn content, the networked Pt₃Sn NWs is of same high CAL conversion (99.7 %), in which negligible catalytic performance for selective activation of C=C (3.3 %) while the selectivity toward COL decreases to 69.1 % with that of HCOL increases to 27.6 %, suggesting the interaction with the C=O and further hydrogenation of COL to HCOL. Remarkably, the lowest Sn content of networked Pt₄Sn NWs shows roughly 100 % CAL conversion within 1 h, with a relatively high selectivity of 84.7 % to HCOL and limited selectivity to COL or HCAL. The preferential absorption of C=O diminishes distinctly, attributing to the consecutive hydrogenation of COL. Moreover, the spherical Pt_{1.5}Sn NPs with the same composition as the optimal Pt_{1.5}Sn NWs was also compared (Table 1 and Figure S9b), which exhibited relatively high conversion (87.3 %) and high selectivity toward COL (86.3 %) despite inferior to that of Pt_{1.5}Sn NWs, indicating the favorable hydrogenation of the C=O rather than that of the C=C for the compositioncontrolled Pt_{1.5}Sn nanomaterials. On the other hand, to gain better understanding of the role of Sn on the reaction, the activity of pure Pt NPs was further explored for comparison. Although no noticeable selectivity to the desired COL, HCAL or HCOL was found, Pt NPs benefitted the hydrogenation of CAL due to the appearance of good conversion efficiency (76.3 %).^[10] This result confirms that pure Pt NPs interact with both C=O and C=C without performing the specific selective CAL hydrogenation to the definite products.^[5] With the introduction of Sn in Pt NPs, the Pt_{1.5}Sn NPs exhibited superior performance to activate C=O to the desired COL. Furthermore, the increased selectivity to the targeted COL (from 14.5 % to 90.6 %) and decreased selectivity to HCOL (from 84.7 % to 8.2 %) with the Sn content increased in

various Pt-Sn NWs, in which $Pt_{1.5}Sn$ NWs presented the excellent conversion and enhanced selectivity to the targeted COL, indicating the well-tunable adsorption of C=O bonds to the desired COL in the $Pt_{1.5}Sn$ NWs.

Significantly, the high activity and selectivity of $Pt_{1.5}Sn$ NWs can be expanded to other *a*, β -unsaturated aldehydes hydrogenation, where the desirable other industrially unsaturated alcohol can be readily realized by hydrogenating corresponding *a*, β -unsaturated aldehydes (**Table 2** and **Figure S10**). For example, as a typical unsaturated aldehyde, furfural (FAL) hydrogenation can be happened under mild reaction by adding the $Pt_{1.5}Sn$ NWs, in which the FAL hydrogenation was of 100 % conversion efficiency and the C=O was readily hydrogenated to furfuryl alcohol with especial high selectivity (99.2 %). Similar phenomenon also appeared in the 3-methyl-2-butenal (MBL) hydrogenation, which exhibited 100 % conversion with pretty high selectivity to 3-methyl-2-butenol (91.0 %) and low selectivities to 3-methyl butyraldehyde as well as the over-hydrogenation product. For the hydrogenation of crotonaldehyde (CTL), high conversion efficiency (88.8 %) and selectivity of C=O to crotyl alcohol (71.3 %) were also achieved under mild condition by using $Pt_{1.5}Sn$ NWs as the catalysts.

The enhanced activity and selectivity for the CAL hydrogenation on the compositioncontrolled Pt-Sn NWs can be related to the chemical states of Pt and Sn. We thus investigated the surface states of these Pt-based nanomaterials by X-ray photoelectron spectroscopy (XPS). As shown in **Figure 3a**, the Pt in these Pt-based nanomaterials are all composed of the metallic state Pt (Pt⁰) and oxidized state Pt (Pt²⁺). The binding energy of Pt⁰ shifts slightly to higher position with the content of Sn increased in the Pt-Sn NWs, which is higher than that of Pt NPs, revealing the electron-transferred effect from electropositive Sn to electronegative Pt. The Sn 3d XPS spectra of these Pt-Sn nanomaterials are also analyzed in **Figure 3b**, which can be split into two doublets peaks of Sn²⁺ and Sn⁴⁺ with no distinct metallic Sn is

observed, revealing the presence of abundant oxidized Sn on the surface of these Pt-Sn NWs and the Pt₁₅Sn NPs. Furthermore, the atomic ratios of Pt^{0}/Pt^{2+} and the corresponding conversion efficiency are plotted in Figure 3c, in which the composition-controlled Pt-Sn NWs shows higher Pt^{0}/Pt^{2+} ratio than the Pt NPs while the Pt^{0}/Pt^{2+} ratio of the Pt-Sn NWs is higher than that of Pt_{1.5}Sn NPs, indicating the addition of Sn leads to the improved atomic ratio of Pt⁰/Pt²⁺. In addition, all these Pt-Sn NWs showed almost 100 % conversion for the CAL hydrogenation, where the conversion efficiency is higher than that of the Pt_{1.5}Sn NPs and Pt NPs with the Pt₁₅Sn NPs excelled the Pt NPs. The change in the Pt^{0}/Pt^{2+} atomic ratio is in consistent with the activity trends of CAL hydrogenation, where the increased the Pt^{0}/Pt^{2+} atomic ratio results in the improved hydrogenation activity, indicating that the metallic Pt is the main active sites for the hydrogenation.^[37] Moreover, the atomic ratios of Sn/Pt were further calculated and the selectivity for hydrogenating CAL to COL of various catalysts are shown in Figure 3d. The Sn/Pt ratio of the various Pt-Sn NWs increased with Sn content increased, indicating the successful introduction of Sn into Pt-Sn NWs. The high Sn/Pt ratio in Pt1.5Sn NPs further demonstrated the existence of high content Sn. Especially, the volcanotype plot of Sn/Pt ratios matched well with the corresponding selectivity plot for the CAL hydrogenation to COL. Lowering the Sn/Pt ratio in the various Pt-Sn NWs associated with the decrease of the COL selectivity, indicating that abundant oxidized Sn boosts the COL selectivity and can turn the selectivity to desired COL. The addition of oxidized Sn in Pt favored the hydrogenation of C=O double bonds to COL, which was also confirmed by comparing the Sn/Pt ratio plot and selectivity plot of the Pt_{1.5}Sn NPs and pure Pt NPs (Figure **3d**).

In summary, we have demonstrated a facile method for the preparation of a class of Pt-Sn NWs with networked structure and controlled composition. Benefitting from the unique structure and alloy effect, the networked $Pt_{1.5}Sn$ NWs exhibit promising performance for

selective hydrogenation of CAL to the industrially required COL, outperforming both the spherical $Pt_{1.5}Sn$ NPs and the spherical Pt NPs. The Pt-Sn NWs show the increased selectivity (from 14.5 % to 90.6 %) to the targeted COL and decreased selectivity (from 84.7 % to 8.2 %) to over-hydrogenation HCOL with the content of Sn increased. XPS studies demonstrated that the enhanced activity arises from the high ratio of metallic Pt and the high COL selectivity attributes to high content of Sn. The present work provides a promising strategy to enhance the hydrogenation reaction through precise structure and composition tuning of the alloyed catalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] C. H. Hao, X. N. Guo, Y. T. Pan, S. Chen, Z. F. Jiao, H. Yang, X. Y. Guo, J. Am.

Chem. Soc. 2016, 138, 9361.

- [2] F. Zaera, ACS Catal. 2017, 7, 4947.
- [3] K.-H. Dostert, C. P. O'Brien, F. Ivars-Barceló, S. Schauermann, H.-J. Freund, J. Am.

Chem. Soc. 2015, 137, 13496.

[4] A. Karakulina, A. Gopakumar, İ. Akçok, B. L. Roulier, T. LaGrange, S. A. Katsyuba,

S. Das, P. J. Dyson, Angew. Chem. Int. Ed. 2016, 55, 292.

- [5] K. R. Kahsar, D. K. Schwartz, J. W. Medlin, J. Am. Chem. Soc. 2014, 136, 520.
- [6] S. Rana, S. B. Jonnalagadda, *RSC Adv.* **2017**, *7*, 2869.

10.1002/cctc.201800238

- [7] J. R. McManus, E. Martono, J. M. Vohs, ACS Catal. 2013, 3, 1739.
- [8] G. Kennedy, L. R. Baker, G. A. Somorjai, Angew. Chem. Int. Ed. 2014, 126, 3473.
- [9] F. Kallmeier, T. Irrgang, T. Dietel, R. Kempe, Angew. Chem. Int. Ed. 2016, 55, 11806.
- [10] S. Rösler, J. Obenauf, R. Kempe, J. Am. Chem. Soc. 2015, 137, 7998.
- [11] M. Tamura, D. Yonezawa, T. Oshino, Y. Nakagawa, K. Tomishige, *ACS Catal.* 2017, 7, 5103.
- [12] X. Wang, D. Liu, S. Song, H. Zhang, J. Am. Chem. Soc. 2013, 135, 15864.
- [13] M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, L. Gu, W. Hu, H. Zhao, Z. Tang, *Nature* 2016, *539*, 76.
- [14] L. Bai, X. Wang, Q. Chen, Y. Ye, H. Zheng, J. Guo, Y. Yin, C. Gao, *Angew. Chem.Int. Ed.* 2016, 55, 15656.
- [15] E. Castillejos, P.-J. Debouttière, L. Roiban, A. Solhy, V. Martinez, Y. Kihn, O. Ersen,K. Philippot, B. Chaudret, P. Serp, *Angew. Chem. Int. Ed.* 2009, *48*, 2529.
- [16] 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.
- [17] D. S. He, D. He, J. Wang, Y. Lin, P. Yin, X. Hong, Y. Wu, Y. Li, *J. Am. Chem. Soc.***2016**, *138*, 1494.
- [18] D. Y. Chung, S. W. Jun, G. Yoon, S. G. Kwon, D. Y. Shin, P. Seo, J. M. Yoo, H. Shin,
 Y. H. Chung, H. Kim, B. S. Mun, K. S. Lee, N. S. Lee, S. J. Yoo, D. H. Lim, K. Kang, Y. E.
 Sung, T. Hyeon, *J. Am. Chem. Soc.* 2015, *137*, 15478.
- [19] S. Guo, D. Li, H. Zhu, S. Zhang, N. M. Markovic, V. R. Stamenkovic, S. Sun, *Angew. Chem. Int. Ed.* 2013, *52*, 3465.
- [20] L. Dai, S. Mo, Q. Qin, X. Zhao, N. Zheng, *Small* **2016**, *12*, 1572.
- [21] S. Chen, H. Su, Y. Wang, W. Wu, J. Zeng, Angew. Chem. Int. Ed. 2015, 54, 108.
- [22] B. Wu, H. Huang, J. Yang, N. Zheng, G. Fu, Angew. Chem. Int. Ed. 2012, 51, 3440.

- [23] V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. Mayrhofer, C. A. Lucas, G. Wang, P. N. Ross, N. M. Markovic, *Nat. Mater.* 2007, *6*, 241.
- [24] W. Du, G. Yang, E. Wong, N. A. Deskins, A. I. Frenkel, D. Su, X. Teng, J. Am. Chem.Soc. 2014, 136, 10862.
- [25] P. Wang, K. Jiang, G. Wang, J. Yao, X. Huang, *Angew. Chem. Int. Ed.* 2016, 55, 12859.
- [26] Q. Chen, Y. Yang, Z. Cao, Q. Kuang, G. Du, Y. Jiang, Z. Xie, L. Zheng, *Angew*.*Chem. Int. Ed.* 2016, 55, 9021.
- [27] Y. Wu, S. Cai, D. Wang, W. He, Y. Li, J. Am. Chem. Soc. 2012, 134, 8975.
- [28] K. D. Gilroy, A. Ruditskiy, H.-C. Peng, D. Qin, Y. Xia, Chem. Rev. 2016, 116, 10414.
- [29] B. Y. Xia, H. B. Wu, X. Wang, X. W. Lou, J. Am. Chem. Soc. 2012, 134, 13934.
- [30] J. Fennell, D. He, A. M. Tanyi, A. J. Logsdail, R. L. Johnston, Z. Y. Li, S. L. Horswell, J. Am. Chem. Soc. 2013, 135, 6554.
- [31] W. Wang, F. Lv, B. Lei, S. Wan, M. Luo, S. Guo, Adv. Mater. 2016, 28, 10117.
- [32] M. Zhu, Q. Shao, Y. Pi, J. Guo, B. Huang, Y. Qian, X. Huang, *Small*, 2017, 13, 1701295.
- [33] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, Z. L. Wang, *Science* 2007, *316*, 732.
- [34] S. Song, X. Liu, J. Li, J. Pan, F. Wang, Y. Xing, X. Wang, X. Liu, H. Zhang, *Adv. Mater.* 2017, 1700495.
- [35] L. Bu, J. Ding, S. Guo, X. Zhang, D. Su, X. Zhu, J. Yao, J. Guo, G. Lu, X. Huang, *Adv. Mater.* 2015, 27, 7204.
- [36] L. Cademartiri, G. A. Ozin, Adv. Mater. 2009, 21, 1013.
- [37] C. J. Kliewer, M. Bieri, G. A. Somorjai, J. Am. Chem. Soc. 2009, 131, 9958.



Figures



Figure 1. (a) HAADF-STEM image and SAED pattern in the inset, (b) TEM image and size distribution pattern of the product in the inset, (c) SEM-EDS, (d) XRD pattern, (e) HRTEM image, and (f) HAADF-

STEM image and elemental mappings of the networked $Pt_{1.5}Sn$ NWs. Dashed lines and red dots in (e) indicate the defects and atom steps, respectively.



Figure 2. (a) Scheme of hydrogenation pathway of CAL. Time-tracing reactions of (b) Pt NPs, (c) $Pt_{1.5}Sn$ NPs and (d) $Pt_{1.5}Sn$ NWs for selective hydrogenation of CAL to COL, HCAL and HCOL. Reaction conditions: catalyst (contains 2 mg Pt), CAL (0.8 mmol), ethanol (5 mL), stirred speed (500 rpm), 30 °C, and H₂ (3 MPa).



Catalysts	T (°C)	Time (h)	Conv. (%)	Select. (%)		
				COL	HACL	HCOL
Pt _{1.5} Sn NWs	30	1	98.1	90.6	1.2	8.2
Pt ₂ Sn NWs	30	1	99.3	87.6	0.2	12.2
Pt ₃ Sn NWs	30	1	99.7	69.1	3.3	27.6
Pt ₄ Sn NWs	30	1	99.9	14.5	0.8	84.7
Pt _{1.5} Sn NPs	30	1	87.3	86.3	6.7	7.0
Pt NPs	30	1	76.3	39.4	33.2	27.4

Table 1. Selective hydrogenation of CAL by different catalysts.

Table 2. Selective hydrogenation of different α,β -unsaturated aldehydes with Pt_{1.5}Sn NWs.

FAL		MBL		CTL		
	S.		and a second	3	and a star	
Substrat	Т	Time	Conv.	Select. (%)		
es	(°C)	(h)	(%)	C=O	C=C	C=C
						С=О
FAL	40	2	100	99.2	0.8	0
MBL	40	2	100	91.0	9.0	0
CTL	40	1	88.8	71.3	4.0	24.7



Figure 3. (a) Pt 4f XPS spectra. (b) Sn 3d XPS spectra of various catalysts. (c) Plots of atomic ratios of Pt^{0}/Pt^{2+} and conversion of CAL toward different Pt-based catalysts and the corresponding conversion efficiencies for CAL hydrogenation. (d) Plots of atomic ratios of Sn/Pt and selectivity to COL toward different Pt-based catalysts.



The table of contents entry

Composition-controlled networked Pt-Sn nanowires (NWs) were successfully prepared through a facile wet-chemical approach. The Pt-Sn NWs show a volcano-type activity and selectivity of cinnamaldehyde hydrogenation to cinnamyl alcohol (COL) as a function of Sn content. The optimized Pt_{1.5}Sn NWs is highly active and selective towards cinnamaldehyde hydrogenation with the conversion of 98.13 % and the COL selectivity of 90.62 %, as well as towards the other α,β -unsaturated aldehydes hydrogenation.

Keyword: Platinum, Tin, Networked Nanowires, Selective Hydrogenation, Unsaturated Aldehyde

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Highly Networked Platinum-Tin Nanowires as Highly Active and Selective Catalysts towards Unsaturated Aldehyde Semihydrogenations

TOC figure

