

Bimetallic Pt-Sn nanoparticles on hydrogenated MoO_x for the selective hydrogenation of functionalized nitroarenes

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Abstract: Hydrogenating functionalized nitroarenes to the corresponding anilines is of great importance in fine chemical industry, which requires high-performance catalysts with good activity and selectivity. Herein, hydrogenated MoO_x (H-MoO_x) supported bimetallic Pt-Sn (Pt-Sn/H-MoOx) was developed to accomplish selective and efficient hydrogenation. In the case of 4nitrostyrene, the outstanding selectivity of 4-vinylaniline (~ 93%) with a high turnover frequency (0.094 s⁻¹) was achieved at a mild condition (T = 30 °C, P_{H2} = 1 atm.). The evidenced metal-support interactions contributed to the efficient turnover on ultrafine nanoparticles, and the atom-rearranged bimetallic Pt-Sn surface promoted the selectivity owing to the preferred adsorption of nitro group. The good efficiency for various functionalized nitroarenes further verified the promise of $Pt-Sn/H-MoO_x$ in chemoselective hydrogenation.

Introduction

Functionalized anilines, the valuable intermediates for manufacturing dyes, pigments, pharmaceuticals and agrochemicals, are usually produced via nitroarenes reduction.¹¹⁻ ^{2]} Non-catalytic processes, including either Béchamp (with Fe/HCl as reducing system) or sulfide reduction (with H₂S or NaSH as reducing agent), are employed for the reduction, which however produce a large amount of waste and cause serious environmental problems.^[3] Catalytic systems using renewable and green reagents, e.g., H₂, provide feasible alternatives.^[4-5] When other reducible groups, such as C=C, C=C, C-X (X: CI, Br and I), C=N and C=N, are present in the same molecule, the catalytic reduction of nitro group in a selective manner remains the great challenge.^[6] Particularly, the C=C bond is more reactive than the nitro group, resulting in difficulty to selectively reduce nitro in its presence.^[3] Meanwhile, the activity is another important criterion, which is however sacrificed to ensure the selectivity. It is challenging to explore efficient catalysts with both good selectivity and high activity. The Pt-group catalysts (e.g.,

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Pt, Pd and Rh) with satisfied activity suffer seriously low selectivity, because the undesired C=C hydrogenation is kinetically and thermodynamically more favored than $-NO_2$.^[7] And, Au and Ag showing chemoselectivity for nitro group are unfortunately prohibited by the poor activity, requiring high temperature or extreme H₂ pressure.^[8-9] A feasible engineering is desired to improve the both of activity and selectivity.

Introducing other metal elements to construct bimetallic catalysts is feasible to rearrange metal surface.[10-11] Because the isolation of active metal atoms will afford geometric and electronic variation, bimetallic catalysts show the noticeable enhancement in activity, selectivity and stability in comparison with their monometallic counterparts.^[10-11] As one of the promising bimetallic catalysts, Pt-Sn delivers the selectivity of functionalized aniline in nitroarenes reduction, but the poor activity, which might be associated with its inert supports (e.g., SiO₂ and carbon) without effective metal-support interactions (MSI).^[12] Noticeably, MSI arising from reducible oxides usually leads to the varied catalytic turnover.^[13] Very recently, hydrogenated molybdenum oxides (H-MoOx) with controlled H doping and partial reduction emerge as promising supports or additives, because the metallic band states can enhance the electronic interactions with loading metals.^[14-15] The rich valence states of Mo (+6, +5, +4, +3, and +2) further ensure the manipulated electronic MSI toward efficient catalytic hydrogenation.[16]

Herein, a rational combination of bimetallic nanocatalysts with interactive metal-oxide supports is introduced to promote the both of activity and selectivity for nitroarenes hydrogenation. As shown in Scheme 1, H-MoO_x nanorods (NRs) supported Pt (Pt/H-MoO_x) and Pt-Sn (Pt_mSn_{100-m}/H-MoO_x) are one-step fabricated, in which the H₂ spillover from as-formed Pt or Pt-Sn nanoparticles (NPs) enables the controlled H-doping into parent MoO₃. The MSI on H-MoO_x supports results in the decreasing size of Pt NPs with increasing temperature during reduction, and the controlled introduction of Sn gradually rearrange Pt atoms on their bimetallic surface. The hydrogenation of 4-nitrostyrene (4-NS) to 4-vinylaniline (4-VA), holding the great challenge in chemoselective nitroarenes hydrogenation, is studied as the probe reaction. Combining the MSI associated with H-MoO_x and the atom-rearranged bimetallic surface, the optimal Pt₄₀Sn₆₀/H-MoO_x delivers an efficient and selective hydrogenation of 4-NS to 4-VA, performing among the best of current metal-based catalysts.

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Scheme 1. Schematic illustration for the fabrication of Pt/H-MoO_x and Pt-Sn/H-MoO_x composites. T denotes for temperature.

Results and Discussion

The MoO_3 NRs, derived from $Mo_3O_{10}(C_6H_8N)_2$ ·2H₂O via calcination under air flow (Figures S1-S3 in Supporting Information), are used as the reducible supports for Pt and Pt-Sn. This results in a series of rod-like catalysts after reduction (Figure S4 and Table S1 in Supporting Information). The H-MoO_x supported Pt and Pt-Sn received at varied temperature (T) are denoted as Pt/H-MoOx-T and PtmSn100-m/H-MoOx-T, respectively. The hydrogen temperature-programmed reduction (H₂-TPR) was conducted to confirm the reduction of Pt and Pt-Sn below 300 $^{\circ}$ C on MoO₃ (Figure 1a). It's obvious that the introduction of Sn increases the temperature for Pt reduction, implying the formation of bimetallic phases. A considerable Hdoping into MoO_3 support is further indicated by the H_2 consumption around 300 °C, which is obviously lower than that of bare MoO_3 (> 480 °C). The easier H-doping is associated with the H₂ spillover from as-form Pt or Pt-Sn NPs to MoO₃ surface. The chemisorbed hydrogen molecules can dissociate at Pt or Pt-Sn sites to highly active hydrogen atoms, which migrate to the surface of MoO_3 , and further diffuse into the bulk.^[17] The Hdoping into MoO₃ can be confirmed by UV-vis diffuse reflection spectra (UV-vis DRS), which show the new adsorption at 400 ~ 600 nm after reduction (Figure S5 in Supporting Information). Furthermore, the acidity of the above samples was analyzed by NH₃ temperature-programmed desorption (NH₃-TPD). As shown in Figure 1b, the amount of NH₃ desorbed from the parent MoO₃ nanorods is negligible, indicating the low density of acidic sites. After the reduction at higher temperature, the signal for NH₃ desorption on Pt/H-MoO_x obviously increases (e.g., Pt/H-MoO_x-400, -500, and 600), consistent with the acidic sites arising from the enhanced H-doping in H-MoOx.^[15] Particularly, the emerging NH₃ desoprtion at high temperature should be ascribed to the Lewis acidic sites. By contrast, introducing Sn to construct bimetallic Pt-Sn only generates a slight enhancement in surface acidity (Figure 1c).

Accordingly, the structural variation relying on reduction temperature is investigated by X-ray diffraction (XRD). As



Figure 1. (a) H_2 -TPR profiles of MoO₃, Pt/MoO₃ and Pt-Sn/MoO₃. NH₃-TPD profiles of (b) Pt/H-MoO_x obtained via reduction at varied temperature, and (c) $Pt_mSn_{100-m}/H-MoO_x$ -400 with different Sn content.

displayed in Figure 2a, all the as-obtained Pt/H-MoO_x show the characteristic diffraction peaks of Pt(111) and Pt(200) at 39.8° and 46.2°, respectively. Beside the peaks of H-MoO_x at 2θ = 38.0° and 42.7° [18] Pt/H-MoOx-300 also presents others associated with residual MoO₃, which disappear after further reduction at 400 ~ 600 °C. Obviously, the H-doping into MoO₃ is enhanced by heating. As the Pt loading is cut down to the onetenth (i.e. 0.15 wt% Pt), a deep reduction of MoO₃ to MoO₂ at only 400 °C is observed (Figure S6 in Supporting Information), implying the promoted H2-spillover on smaller Pt NPs. Interestingly, the peaks of Pt(111) and Pt(200) becoming broad and weak with increasing temperature, suggest the decreasing Pt size. This is further evidenced by TEM observation (Figure S7 in Supporting Information). Such unexpected decrease of Pt size should be ascribed to the strong interactions with H-MoOx supports,^[19-20] which are gradually doped by hydrogen upon heating. The further interpretation will be included in the following discussion of X-ray photoelectron spectroscopy (XPS).

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Figure 2. XRD patterns of (a) Pt/H-MoO_x obtained at varied temperature for reduction and (b) Pt_mSn_{100-m}/H -MoO_x reduced at 400 °C.



Figure 3. TEM and HR-TEM images, and the corresponding particle-size distribution of (a) 1.4% Pt/H-MoO_x-400 and (b) 2.7% Pt_{40}Sn_{60}/H-MoO_x-400 (Pt loading: 1.4 wt%). (c) EDS pattern and (d) HAADF-STEM images of Pt_{40}Sn_{60}/H-MoO_x-400, as well as the corresponding elemental mapping.

Furthermore, the introduction of Sn also leads to structural variation (Figure 2b). In comparison with Pt/H-MoOx, only the peaks for H-MoO_x are detected by XRD in a series of Pt_mSn₁₀₀₋ m/H-MoOx, and those for Pt-Sn alloys are absent, suggesting the ultra-small NPs. This can be further verified by TEM investigation, taking Pt/H-MoOx and Pt40Sn60/H-MoOx for comparison (Figures 3a and 3b). The average size of Pt in 1.4%Pt/H-MoOx is about 6.0 ± 0.5 nm, while that in 2.7%Pt₄₀Sn₆₀/H-MoO_x (Pt: 1.4 wt%) is obviously reduced to $3.5 \pm$ 0.5 nm. In their HRTEM images, the characteristic lattices of Pt and Pt-Sn alloy are well observed on 1.4%Pt/H-MoOx and 2.7%Pt₄₀Sn₆₀/H-MoO_x (insets of Figures 3a and 3b), respectively. The attached energy dispersive spectra (EDS) also identify the loading of the corresponding metals on H-MoO_x supports (Figure 3c and Figure S8 in Supporting Information). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Figure 3d) displays the uniform distribution of Mo, O, Pt and Sn in Pt₄₀Sn₆₀/H-MoO_x-400, identifying the welldispersed Pt-Sn NPs on H-MoO_x supports. To further ensure the presence of both Pt and Sn on metal NPs, the linear scanning EDS analysis was conducted on a slightly larger Pt-Sn NPs (Figure S9 in Supporting Information). The correlative distribution of Pt and Sn along Pt-Sn particles indicates the formation of bimetallic Pt-Sn NPs.

XPS was carried out to study the chemical state of elements in Pt/H-MoO_x and Pt_mSn_{100-m}/H-MoO_x. Figures 4a and 4b display the profiles of Mo 3d and Pt 4f on 1.4%Pt/H-MoO_x, respectively.



Figure 4. XPS spectra of (a) Mo 3d and (b) Pt 4f in Pt/H-MoO_x received after reduction at different temperature. XPS profiles of (c) Mo 3d, (d) Pt 4f and (e) Sn 3d for Pt₄₀Sn₆₀/H-MoO_x-400 and Pt/H-MoO_x-400.

After a reduction at 300 °C, the Mo 3d profiles can be deconvoluted into four peaks, ascribed to the Mo 3d_{5/2} and 3d_{3/2} of Mo⁶⁺ and Mo⁵⁺ species.^[21] With further reduction at higher temperature (400 ~ 600 °C), the species of Mo4+ emerges, consistent with the enhanced reduction of MoO₃ upon heating. The corresponding evolution was observed in Pt 4f (Figure 4b). The Pt/H-MoOx-300 shows a doublet at 71.3 and 74.7 eV, associated with the 4f7/2 and 4f5/2 of metallic Pt.[22] With the increasing reduction temperature, such peaks are obviously shifted to higher binding energy, indicating the positively charged Pt (Pt^{δ^+}) due to their interactions with H-MoO_x. According to the previous experimental discovery and theoretical calculation,^[16] the effective H-doping and reduction of MoO₃ can lead to the metallic band configuration, which promotes the MSI with loading metals. It's remarkable that such interactions can be varied by controlling the reduction degree in H-MoO_x supports. Owing to such electronic interactions gradually enhanced by Hdoping,^[19-20] the size of Pt will decrease as the temperature increases during reduction (c.f. Figure 2a).

When Sn is introduced, negligible variation is observed in the binding energy of Pt and Mo (Figure 4c and 4d). Both of 1.4%Pt/H-MoO_x-400 and 2.7%Pt₄₀Sn₆₀/H-MoO_x-400 present the positive Pt^{δ+} species. In addition, the Sn in 2.7%Pt₄₀Sn₆₀/H-MoO_x-400 is mainly represented by Sn⁰, as well as some oxidized species (Figure 4e). Meanwhile, the strong electronic interactions associated with H-MoO_x are still obvious in bimetallic Pt-Sn/H-MoO_x, as indicated by the blue-shift owing to H-doping in their Pt 4f XPS profiles (Figure S10 in Supporting Information). As a result, the size of Pt-Sn NPs decreases with the increasing temperature in reduction (Figure S11 in Supporting Information), consistent with the situation of Pt/H-MoO_x. These well confirm the strong MSI for both Pt and Pt-Sn on the interactive H-MoO_x supports.



Figure 5. (a) Schematic illustration for the hydrogenation of 4-NS, and the performance over (b) 1.4%Pt/H-MoO_x received at different reduction temperature and (c) Pt_mSn_{100-m}/H-MoO_x-400 (fixed Pt loading of 1.4 wt%) with varied Sn/Pt ratio. Reaction condition: 1 mmol of 4-NS, catalyst (Pt : 4-NS = 0.002), P_{H2} = 1 atm, 30 mL of EtOH, 30 °C, 1 hour.

The hydrogenation of 4-nitrostyrolene (4-NS) to 4vinylaniline (4-VA) was employed as the probing reaction for the above catalysts. The typical hydrogenation routes are shown in Figure 5a. The desired 4-VA is obtained via the direct hydrogenation of nitro group, while the C=C hydrogenation results in the undesired 4-ethylnitrobenzene (4-ENB).^[23] The partially-hydrogenated products of 4-VA and 4-ENB can be further hydrogenated to 4-ethylaniline (4-EA). Figure 5b presents the activity of Pt/H-MoOx relying on the temperature adopted for catalyst reduction. With the temperature increasing from 300 to 600 °C, the Pt/H-MoO_x shows an obvious improvement in 4-NS conversion. Unfortunately, the poor selectivity of 4-VA is delivered by the above Pt/H-MoOx, as low as ~ 40% on Pt/H-MoOx-300, -400, and -500. And no 4-VA is detected on Pt/H-MoO_x-600. Thus, an enhancement on selectivity is essentially demanded.

Bimetallic Pt-Sn NPs were constructed to improve the selectivity of 4-VA, in which a moderated reduction at 400 °C was adopted. The introduction of Sn visibly increases the 4-VA selectivity from 44% to a maximum of 93%, with the Sn/Pt molar ratio from 0 to 1.5 (Figure 5c). And, no obvious variation in 4-NS conversion is observed on these $Pt_mSn_{100-m}/H-MoO_x$. The promoted selectivity by bimetallic Pt-Sn is further confirmed on $Pt_mSn_{100-m}/H-MoO_x$ that is reduced at varied temperature, i.e.,



Figure 6. (a) Product distribution over 2.7%Pt₄₀Sn₆₀/H-MoO_x-400 (Pt: 1.4 wt%). (b) Cycling catalytic test of 4-NS hydrogenation over 2.7%Pt₄₀Sn₆₀/H-MoO_x-400, Reaction condition: 1 mmol of 4-NS, catalyst (Pt : 4-NS = 0.002), *P*_{H2} = 1 atm, 30 mL of EtOH, 30 °C, 1 hour.

300 ~ 600 °C (Figure S12 in Supporting Information). Among them, the 2.7%Pt₄₀Sn₆₀/H-MoO_x-400 remarkably fulfils the high selectivity as well as the good activity. And the relatively low selectivity on Pt-Sn/H-MoO_x-600 should be ascribed to easy hydrogenation of 4-NS on ultrafine and positively-charged Pt-Sn NPs, in which function groups show negligible difference in their adsorption or activation on highly active metals. By contrast, although Pt/SiO₂ and Pt/C show high activity, they suffer the obvious decrement as Sn is introduced (Table S2 in Supporting Information), suggesting that the MSI associated with H-MoO_x also contributes to the high activity on Pt-Sn.

Figure 6a gives the details of product distribution on $Pt_{40}Sn_{60}/H-MoO_x-400$. With a mild condition (30 °C, 1 bar H₂), the main product is the desired 4-VA, and by-products of 4-ENB and 4-EA are kept at a low level. Almost complete conversion of 4-NS is observed after 120 minutes, reaching the maximum yield of desired 4-VA. At this point, the 4-VA selectivity is as high as 90%. Remarkably, such selective performance is superior to that of previously reported metal and bimetal catalysts, e.g., Pt/Ti-WOx^[22] (sel.: 66%), Pt@MFI zeolite^[24] (sel.: 80%) and RhIn/SiO₂^[23] (sel.: 84%). Noticeably, higher temperature (e.g., 80 °C) or H₂ pressure (10 ~20 bar) is usually required to reach the good activity,^[22,24] which can be easily accomplished by a mild reaction (30 °C, 1 bar H₂) on Pt₄₀Sn₆₀/H-MoO_x. In addition, the Pt₄₀Sn₆₀/H-MoO_x-400 exhibits good stability. In the consecutive 6 cycle operation, negligible decrease in activity and selectivity is observed (Figure 6b)).

The promotion of 4-NS hydrogenation is obviously associated with H-MoO_x support. According to the previous experimental discovery and theoretical calculation,^[16] the effective H-doping into MoO₃ can lead to the large density states within band gap, showing the strong MSI with loading metals.

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Figure 7. Schematic illustration for the hydrogenation of 4-NS over (a) Pt/H- MoO_x and (c) Pt-Sn/H- MoO_x , and (b) CO-PTD profiles of MoO_3 , Pt/H- MoO_x and Pt-Sn/H- MoO_x .

Such interactions in Pt/H-MoO_x are enhanced by improving Hdoping and partial reduction in H-MoO_x, as a result of increasing temperature in reduction. Thus, the Pt NPs on H-MoO_x surface diminish in size (Figure 2a and S7 in Supporting Information), and more importantly they are positively-charged due to the charge redistribution on interfaces (Figure 4b). These variations should be responsible for the superior activity on Pt/H-MoO_x, as shown in Figure 7a. In addition, the surface acidity of H-MoO_x supports should be noticed. The enhanced acidity due to Hdoping, espeically the emerging Lewis acidic sites confirmed by NH₃-TPD (Figure 2b), will promote the adsorption of substract with large π electrons. However, it doese not favor the selective conversion to 4-VA.

Introducing Sn leads to the obvious improvement in selectivity, probably due to the atom-rearranged bimetallic surface. We conducted CO temperature-programmed desorption (CO-TPD) to investigate the surface evolution after Sn introduction (Figure 7b). Regarding the negligible CO desorption on bare MoO_3 , the visible CO adsorption on Pt/H-MoO_x and

Pt_mSn_{100-m}/H-MoO_x is rationally contributed by Pt and Pt-Sn, respectively. On Pt/H-MoOx-400, two broad peaks located at 150 ~ 250 °C and 300 ~ 400 °C are clearly observed, which can be ascribed to the linear (α) and bridge (β) modes of CO chemisorption,^[25] respectively. After the introduction of Sn, the β peak obviously decreases, indicating the diminishing bridge adsorption of CO on bimetallic NPs.[26-27] This variation indicates the formation of bimetallic surface, in which Pt sites isolated by Sn atoms don't prefer the bridge CO adsorption. In this way, the different configuration of 4-NS on Pt and Pt-Sn surface should be taken into account for the varied hydrogenation selectivity. In general, π adsorption mode is energetically favoured for an alkenyl moiety on Pt and Rh.[23,28] As for 4-NS, it's further demonstrated that both of vinyl moiety and aromatic ring were bound to Pt-group metals,^[23,29] requiring the 4-NS activation on neighbor metal atoms in the view of Balandin multiplet theory. By contrast, only nitro group was adsorbed on metal towards nitro hydrogenation,^[23] i.e., the activation on single metal-site. Due to the isolated Pt atoms on bimetallic Pt-Sn surface, the adsorption of vinvl mojety on multiple Pt atoms will be resitrictied while, the activation of nitro group on single Pt site is insusceptible (Figure 7c). Meanwhile, the oxytropic Sn atoms possessing strong interactions with nitro group also facilitate the preferential adsorption and activation.^[30] Therefore, the selective hydrogenation is promoted on bimetallic Pt-Sn surface.

Furthermore, our Pt₄₀Sn₆₀/H-MoO_x-400 can be considered in a sense as a universal catalyst for nitroarenes hydrogenation (Table 1). The results clearly confirm that the chemoselective hydrogenation of nitro group can be performed in the presence of various groups like olefins, halogens and carboxylic acid. For nitrobenzene, a selectivity of desired aniline as high as 91% is observed (entry 1, Table 1), in which the by-products of phenylhydroxylamine and azobenzene are negligible. Similar with the reduction of 4-NS, the selective hydrogenation of 3-NS to 3-VA (sel.: 80%) is also achieved at a mild condition (entry 2, Table 1). In the case of halogenated nitrobenzenes (entries 3 ~ 6, Table 1), the selectivity of the corresponding halogenated anilines can be maintained at a high level (94 ~ 98%), with an almost complete conversion of subtracts. No dehalogenation products are detected after reaction, which are usually the byproducts on Pt mono-metal catalysts.^[12] As the good examples for carboxyl functionalized nitroarenes, 3-nitrobenzoic and 4nitrobenzoic can be efficiently hydrogenated to the corresponding animobenzoic acid (entries 7 and 8, Table 1), showing the high selectivity >99%. These results well verify $Pt_mSn_{100\text{-}m}/\text{H-MoO}_x \quad \text{as} \quad a \quad p \text{ romising} \quad \text{catalyst} \quad \text{for}$ the chemoselective hydrogenation of nitroarenes.

Conclusions

In summary, bimetallic Pt-Sn catalyst loading on $H-MoO_x$ was developed for the chemoselective hydrogenation of functionalized nitroarenes. Strong electronic interactions arising from $H-MoO_x$ supports were evidenced, which led to the efficient hydrogenation on diminishing metal NPs with positive charge. Via introducing Pt-Sn bimetallic catalysts, the highly selective



Table 1. Hydrogenation of various functionalized nitroarenes over $Pt_{40}Sn_{60}/H\text{-}MoO_x\text{-}400.^{[a]}$

^[a] Reaction conditions: 1 mmol of substrate, 2.7%Pt₄₀Sn₆₀/H-MoO_x-400 (Pt : substrate = 0.002), 30 mL of EtOH, P_{H2} = 1 bar. Reaction time: ^[b] 6 hours, ^[c] 4 hours, ^[d] 2 hours.

hydrogenation with superior activity was accomplished. As a result, the Pt-Sn/H-MoO_x presents the selective hydrogenation of 4-NS to 4-VA (TOF: 0.094 s⁻¹, VA sel.: ~93%) at a mild condition (T = 30 °C, P_{H2} = 1 atm.), performing among the best of ever reported metal-based catalysts. Showing the efficiency for various functionalized nitroarenes, our Pt-Sn/H-MoO_x is promising in chemoselective hydrogenation. It is envisioned that the precise control over the interfaces between bimetallic catalysts and oxide supports would further boost the catalytic applications.^[31]

Experimental Section

Materials

All reagents were purchased from commercial sources and in analytical or reagent grade when possible. Ammonium heptamolybdate tetrahydrate (AHM), ethanol and aniline were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Hydrochloric acid was purchased from Guangzhou Chemical Reagent Factory. H₂PtCl₆, SnCl₂, SiO₂, and CNT were purchased from Aladdin. All aqueous solutions were prepared using ultrapure water (> 18 M Ω).

Catalyst preparation

Synthesis of MoO₃ NRs: The synthesis of MoO₃ NRs was conducted according to our previous report^[32]: 2.48 g of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in 40 mL of distilled water, and then 3.34 g of aniline was added in the above solution. Afterwards, 1 M HCl aqueous solution was dropwise added with magnetic stirring at room temperature until white precipitate appeared (pH 4~5). After stirring at 50 °C in oil bath for 4 hours, the Mo₃O₁₀(C₆H₈N)₂·2H₂O was received. Finally, MoO₃ NRs were harvested after calcining Mo₃O₁₀(C₆H₈N)₂·2H₂O at 400 °C for 2 hours under air flow.

Synthesis of Pt/H-MoO_x, Pt-Sn/H-MoO_x, Pt/SiO₂, Pt-Sn/SiO₂ Pt/C and Pt-Sn/C catalysts: An impregnation method was introduced for the synthesis. Typically, supports (MoO₃, SiO₂, or active carbon) were impregnated with H₂PtCl₆ or H₂PtCl₆-SnCl₂ solution, and then were stirred at 80 °C in oil bath until dried. The solids were reduced with a stream of 5 vol% H₂/Ar at target temperature for 2 hours (H-MoO_x supported catalysts: 300 ~ 600 °C; SiO₂ and carbon supported catalysts: 400 °C).

Physical characterization

SEM was taken on a ZEISS ULTRA55. TEM, HRTEM, EDS and elemental mapping investigations were carried out with a JEOL JEM 2100F. XRD analysis was performed on Bruker D8 diffractometer using Cu K α radiation (λ = 1.54056 Å). XPS was processed on a Thermo scientific (Escalab 250Xi), using C 1s (284.6 eV) as a reference. The metal loading was determined by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The H₂-TPR, CO-TPD and NH₃-TPD were conducted on a Quantachrome CHEMBET PULSAR TPR/TPD. Catalytic performance measurement

Catalytic performance measurement

The hydrogenation of nitroarenes were performed in 300 mL Parr 5500 series compact reactor which was assembled with Parr 4848 reactor controller. In a typical reaction, catalyst and nitroarenes (n_{Pt} : $n_{nitroarenes} = 0.002$) were dispersed into the 30 mL of ethanol. The reactor was sealed and purged with H_2 to remove the air for 5 times, and then the reactor was heated to the desired temperature. And the products were analyzed by Shimadzu HPLC-20 with a UV-detector. To calculate the turn-over frequency (TOF), it is assumed that all of Pt contributes to catalytic hydrogenation. The TOF value for 4-VA formation was determined by the target product generated on per Pt per second.

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Layout 1:

FULL PAPER

Bimetallic Pt-Sn catalysts supported by hydrogenated MoO_x (Pt-Sn/H-MoO_x) delivered both high selectivity and activity for the selective hydrogenation of functionalized nitroarenes at a mild condition. The atom-rearranged bimetallic Pt-Sn surface and the electronic metalsupport interactions with H-MoO_x contributed to the remarkably improved selectivity and activity, respectively.



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