Synthesis of atomic platinum with high loading on metal-organic sulfide

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ABSTRACT Synthesis of ultrafine noble metal with sizes down to nanoscale and even atomic scale is of great significance for heterogeneous catalysis. However, the metal loading is usually kept below 2 wt% due to the aggregation tendency at higher metal contents. Herein, by mimicking the multicentered metal sulfur cluster of metalloenzyme, a bioinspired synthesis of isolated noble metal atoms on the metal-organic sulfide (MOS) framework was reported. The sulfur-rich framework featuring $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ cluster as the building block and dithiol as the linking node was constructed *via* chemical bonding and employed to support atomic metal species. Remarkably, highly dispersed platinum atoms with a loading amount as high as 18.5 wt% on the underlying sulfur-rich framework could be obtained after reduction. By increasing the number of benzene rings in the dithiol, the pore size and even the wettability of the MOS frameworks could be modulated. The general applicability of the synthesis could also be extended to the synthesis of atomic Pd. Furthermore, the Pt-loaded MOS could serve as the catalyst for selective hydrogenation of phenylacetylene to styrene in both organic solvent and pure water. Density function theory calculation demonstrated that the atomic Pt sites in the sulfur-rich coordination environment could activate H_2 molecules and chemoselectively catalyze the semi-hydrogenation of phenylacetylene to styrene through moderately low energy barriers. The metalation of such a versatile MOS framework will shed light on the synthesis of bioinspired catalytic materials with well-defined structures for more diverse applications.

Keywords: bioinspired, metal-organic sulfide, multicentered catalyst, single atoms

INTRODUCTION

Atomically dispersed metals on substrates with well-defined structure and high atom utilization efficiency have received enormous scientific interest, especially in heterogeneous catalysis [1–7]. Because the atomically dispersed metal sites with high surface energy highly tend to agglomerate, the loading of the transition metal-based single-atom catalysts is usually constrained to 2 wt%. Reducing the metal content and applying structural defects or voids are the two most common strategies

to stabilize metal atoms on the support. Although the resulting atomically dispersed catalysts exhibit remarkable activity per metal atom, the overall catalytic performance is limited on a gram basis of catalysts. In the natural prototype of such an atomic metal site, the metalloenzyme features the well-defined metal site in the secondary coordination environment [8,9]. For example, the common nitrogenase features active-site iron-molybdenum cofactor (FeMo-co) containing well-defined Fe and Mo sites in the sulfur-rich environment and the active sites of the widely distributed hydrogenase are comprised of sulfur-bridged bimetallic centers [10,11]. Sulfur compounds poison most industrial catalysts, but nature relies heavily on sulfur-rich environments for catalytic transformations [12]. Inspired by such delicate design and versatile metal-sulfur chemistry, the iron, molybdenum, or nickel complexes in homogeneous catalysis have been widely studied [13–19].

Exploring the interaction between the noble metal and sulfur for metal atom or nanoparticles formation as heterogeneous catalysts has also been well proceeded in the catalysis community. For example, Zheng *et al.* [20] reported a novel deposition method using thiourea-coordinated metal complex to load noble metal atoms onto two-dimensional chalcogenides. By introducing sulfur into carbon materials, the strong interaction between the noble metal and sulfur could serve the purpose of anchoring and stabilizing the noble metal atom. The porous sulfur-containing carbon materials were widely used for atomically dispersing platinum (Pt) or other noble metals based on the sulfur-tethering strategy [21–24]. Due to the complexity and inhomogeneous nature of doping S into carbon materials, such a strategy could involve tedious steps, and further increasing the Pt loading will eventually lead to the aggregation of the metal atoms. Further exploring the sulfur-containing framework materials should be appealing due to the homogeneous and abundant distribution of sulfur in such easy-to-prepare porous materials [25–29]. Kanatzidis and co-workers [30,31] demonstrated that by breaking the Pt–S bond in the chalcogel through reduction, the well-dispersed supported Pt nanoparticles in the underlying framework could be obtained. Lu *et al.* [32] utilized the thioether-containing covalent organic framework for the confined growth of ultrafine Pt nanoparticles. Recently, the metal-organic sulfide (MOS) was proposed by replacing the regular hard acid and base coordination bonds of the metal-

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organic framework materials with the soft-base linkage based on sulfido and thiolate for connecting $[\text{Mo}_3\text{S}_{13}]^{2-}$ clusters [33]. Previous studies demonstrated the potential of the sulfur-rich framework for the homogeneous dispersing of noble metal nanoparticles; however, confining noble metal atoms with high loading capacity on such materials has rarely been reported. Due to the rich chemistry of the MOS framework and the large affinity between noble metals and sulfur, the exploration of MOS for supporting metals to construct confined catalytic centers is desired.

In this work, by mimicking the metal-sulfur interaction in metalloenzyme, the investigation of bioinspired MOS for supporting atomic Pt as catalyst was reported. The substituted trinuclear $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ clusters act as building blocks with dithiol as linking nodes, and 1,4-benzenedithiol (*p*-BDT)-linked MOS (*uni*-MOS) [34], biphenyl-4,4'-dithiol-linked MOS (*bi*-MOS), and *p*-terphenyl-4,4''-dithiol-linked MOS (*ter*-MOS) could be obtained. Through a facile *in-situ* synthetic strategy, the obtained MOS was demonstrated to be capable of loading atomically dispersed Pt species (abbreviated as Pt-*uni*-MOS, Pt-*bi*-MOS, or Pt-*ter*-MOS). Remarkably, the Pt loading amount on *uni*-MOS as high as 18.5 wt% could be obtained without aggregation. By adopting the Pd precursor, the atomic Pd could be also obtained, confirming the general applicability of the current synthesis strategy. Further evaluation in the selective hydrogenation of phenylacetylene (PA) confirmed the intriguing catalytic performance of the highly loaded Pt atoms on *uni*-MOS (91% conversion in 2 h, and selectivity toward styrene up to 90%). Furthermore, the resulting Pt-*uni*-MOS maintained its catalytic activity in three cycles without aggregation, suggesting the stability of the current catalytic system. The density function theory (DFT) calculation was conducted, demonstrating that the H_2 -activation and subsequent PA semi-hydrogenation are thermodynamically feasible over Pt-*uni*-MOS.

RESULTS AND DISCUSSION

Preparation and structural characterization of *uni*-, *bi*-, *ter*-MOS, and Pt loaded counterparts

As schematically shown in Fig. 1 (Fig. S1 in Supplementary information, SI), the anchoring of metal onto MOS was

accomplished by adding metal salt (such as PtCl_2) during MOS synthesis, which involved coordination assembly of molybdenum-sulfur clusters and thiolate. Specifically, the $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ cluster formed by replacing terminal S_2^{2-} on $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster by bromide anions (Fig. S2), which further reacted with dithiols (Figs S3–S7) to form MOS (Fig. S8) [35–37]. The abundant and well-dispersed sulfur element in the framework of MOS materials could be regarded as the ideal anchoring sites for stabilizing noble metal atoms (Fig. S9a). The valence state in Pt-4S might be balanced by Br^- , whose presence was confirmed by Br 3d X-ray photoelectron spectroscopy (XPS) spectrum in Fig. S9b. By chemical reduction of PtCl_2 -MOS with NaBH_4 (Fig. S10a), the metalated MOS could be obtained (Pt-*uni*-MOS, Pt-*bi*-MOS, or Pt-*ter*-MOS). The Cl residue was detected by XPS. No Cl 2p signal could be observed after reduction (Fig. S10b–d), suggesting the complete removal of the Cl ligand [23]. The inductively coupled plasma (ICP) analysis indicated that the weight ratio of Pt species in Pt-*uni*-MOS was as high as 18.5 wt%.

Further characterizations were performed to validate the proposed compositions of *uni*-MOS (Fig. S11a). The Fourier transform infrared (FTIR) spectra of *uni*-MOS, metal-containing PtCl_2 -*uni*-MOS and Pt-*uni*-MOS, did not show the typical signal near 2500 cm^{-1} that was attributable to S–H stretching modes of *p*-BDT (Fig. S11b). The absence of dangling S–H demonstrated that *p*-BDT was fully deprotonated and coordinated to the clusters in *uni*-MOS support [38]. It was worth mentioning that the oxidation of sulfhydryl groups could not be excluded. Raman spectroscopy was further employed to investigate the chemical environment. As shown in Fig. S11c, the S–H vibration at 2564 cm^{-1} in *p*-BDT vanished in the spectra of *uni*-MOS, PtCl_2 -*uni*-MOS, and Pt-*uni*-MOS, agreeing well with the FTIR results. The combination of the phenyl ring breathing mode [39,40], C–H in-plane bending, C–S stretching (1066 cm^{-1}), and phenyl ring stretching (1562 cm^{-1}), demonstrated that the benzene rings were the connection linkers in *uni*-MOS. The absence of the 520 cm^{-1} band that was assigned to the S–S stretching suggested that there was no apparent oxidation of S-groups during the syntheses (Fig. S11d) [41,42]. The solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy was further performed to confirm the presence of thiophenyl. By referring to the peak of

Figure 1 Schematic illustration for synthesizing Pt-loaded MOS. Color code in models: Mo, light blue; S, yellow; Br, orange; Pt, brown; Cl, green; wiggly lines, connecting to the repeated structure.

carbons in *p*-BDT (129.44 ppm) (Fig. S12a), the chemical shift of carbons on *uni*-MOS showed slight shifts to 126.59 and 135.22 ppm, which were assigned to α and β carbons on the benzene, respectively (Fig. S12b). The changes of chemical shift suggested the occurrence of deprotonating and coordination in the synthesis of *uni*-MOS, which was in agreement with the conclusion of FTIR. The ^{13}C CP-MAS NMR spectra of PtCl_2 -*uni*-MOS and Pt-*uni*-MOS also showed two peaks (Fig. S12c, d). These results indicated that *p*-BDT units served the role of connecting in *uni*-MOS materials. The digestion experiment was performed by digesting the *uni*-MOS in D_2SO_4 , which was followed by diluting with DMSO-d_6 for ^1H NMR analysis [43]. As shown in Fig. S13, the ^1H NMR spectrum of the digestion product clearly showed the hydrogens on the α and β carbons of $[\text{NEt}_4]^+$. The negative charge of the MOS framework could be balanced by the $[\text{NEt}_4]^+$. The above results confirm that the synthesized MOS materials are comprised of molybdenum sulfur clusters and *p*-BDT.

By increasing the benzene length in the linking dithiols, the obtained *bi*-MOS or *ter*-MOS demonstrated interesting properties (Fig. 2a) [44]. The successful synthesis of *bi*-MOS or *ter*-MOS was confirmed by FTIR, Raman, and NMR characterizations (Figs S14–S17). The porosity and wettability are regarded as two important parameters to improve the mass transfer process in heterogeneous catalysis [45–47]. The specific surface areas of Pt-*bi*-MOS ($37\text{ m}^2\text{ g}^{-1}$) and Pt-*ter*-MOS ($73\text{ m}^2\text{ g}^{-1}$) were measured to be higher than that of Pt-*uni*-MOS ($17\text{ m}^2\text{ g}^{-1}$), which agreed well with the longer linking dithiols in the former two counterparts (Fig. 2b). Interestingly, the pore volume was also observed to increase in the trend of Pt-*uni*-MOS, Pt-*bi*-MOS, and Pt-*ter*-MOS, which also correlated well with the linker lengths (Fig. 2c). Owing to the presence of longer organic linkers in the material, *bi*-MOS and *ter*-MOS are more hydrophobic than *uni*-MOS (Fig. 2d and Fig. S18). However, by

loading PtCl_2 followed by NaBH_4 reduction, the resultant Pt-*ter*-MOS still maintained hydrophobicity while the other two counterparts were superhydrophilic (Fig. 2e and Fig. S19).

From the powder X-ray diffraction (XRD) spectra in Fig. S20, no characteristic diffraction peaks of Pt nanoparticles could be observed by comparing with the standard spectrum of Pt nanocrystal (JPCDS 04-0802). Both transmission electron microscopy (TEM) images (Fig. 3a and Fig. S21a, b) and high-resolution TEM (HRTEM) image (Fig. 3b) showed that Pt nanoparticles were indiscernible on the underlying materials. High-angle annular dark-field scanning TEM (HAADF-STEM) images (Fig. S21c) provided the direct evidence for the absence of Pt nanoparticles. Energy-dispersive X-ray spectroscopy (EDS) mapping images (Fig. 3c) suggested the homogeneous distribution of the elements. The above results implied that Pt species were present in the supporting material but indiscernible in conventional TEM.

To gain direct atomic-level insight into the dispersion of Pt species, the spherical aberration-corrected HAADF-STEM analysis was performed. As shown in Fig. 3d, e and Fig. S22, numerous isolated Pt atoms were strikingly observed as brighter spots on *uni*-MOS. Interestingly, Pt species maintained atomic dispersion on *bi*-MOS and *ter*-MOS with increased numbers of benzene rings in the dithiol, indicating the universality of MOS supports for loading single atoms (Fig. 3f, g). More characterization results in Figs S23–S30 further supported such a conclusion. PtCl_2 -*uni*-MOS XPS was employed to investigate the oxidation states of Pt species (Fig. S31). The fitting analysis of Pt $4f_{7/2}$ XPS spectrum for Pt-*uni*-MOS showed two peaks. The peak at 72.48 eV matches the Pt oxidation state in PtCl_2 -*uni*-MOS, while the other one at 71.53 eV is between the binding energies of metallic Pt and Pt^{2+} , indicating the existence of $\text{Pt}^{\delta+}$ in the material [48].

The successful synthesis of Pt-*uni*-MOS prompted us to use

Figure 2 (a) Schematic illustration of the connection between Mo cluster and dithiols in *uni*-MOS, *bi*-MOS, and *ter*-MOS. N₂ adsorption and desorption isotherms (b) and (c) pore size distributions of Pt-*uni*-MOS, Pt-*bi*-MOS, and Pt-*ter*-MOS. Water contact angle characterizations on (d) *uni*-MOS, *bi*-MOS, and *ter*-MOS, (e) Pt-*uni*-MOS, Pt-*bi*-MOS, and Pt-*ter*-MOS, respectively.

Figure 3 Characterization of Pt-uni-MOS, Pt-bi-MOS, and Pt-ter-MOS. (a) TEM image of Pt-uni-MOS. (b) HRTEM image of Pt-uni-MOS. (c) EDS mapping of the composition elements (Pt, S, and Mo) in Pt-uni-MOS, respectively. The spherical aberration-corrected HAADF-STEM images of (d, e) Pt-uni-MOS, (f) Pt-bi-MOS, and (g) Pt-ter-MOS, respectively.

uni-MOS as the supporting material for dispersing Pd species, which could further verify the general applicability of the MOS synthesis strategy reported herein. 20%-Pd-uni-MOS was obtained by using NaBH_4 to reduce 20%-Pd(OAc) $_2$ -uni-MOS which was prepared through the similar synthesis procedure of 20%-PtCl $_2$ -uni-MOS. As expected, the TEM images (Fig. S32), TEM EDS mapping images (Fig. S33), and the powder XRD spectra (Fig. S34a) showed convincing evidence that no Pd nanoparticles existed in the material. The XPS of Pd 3d (Fig. S34b) confirmed the existence of Pd $^{\delta+}$, which was keeping a positive valence state between Pd 0 (Pd 0 3d $_{5/2}$, ~335.10 eV) and Pd $^{2+}$. These findings suggested that uni-MOS was an excellent supporting material for high loading isolated metal atoms.

X-ray absorption analysis of Pt-uni-MOS

For further understanding of the electronic and coordination structures of Pt atoms, X-ray absorption fine structure spectroscopy was adopted. Fig. 4a shows the normalized X-ray absorption near-edge structure (XANES) spectra of Pt-uni-MOS, the Pt foil, and PtO $_2$. The near-edge feature of Pt-uni-MOS shifted into higher energy compared with that of Pt foil. The absorption edge of Pt-uni-MOS was located between that of Pt foil and PtO $_2$ reference, identifying the unoccupied density of d state of Pt and also indicating Pt atoms in Pt-uni-MOS with positive charges. As shown in Fig. 4b, the Fourier transform k^3 -weighted of extended X-ray absorption fine structure (EXAFS) provided the direct coordination environment of atomic Pt sites in Pt-uni-MOS. EXAFS spectra of Pt-uni-MOS presented a strong single peak at 1.9 Å attributed to the coordination between Pt and S, and no metal Pt-Pt contribution can be observed. As a comparison, the Pt-Pt contribution was located

at 2.6 Å in standard Pt foil reference. The EXAFS spectra in R space further ruled out the presence of metallic Pt or PtO $_x$ nanoparticles in Pt-uni-MOS. To reveal quantitative structural parameters of Pt centers in Pt-uni-MOS, a least-squares EXAFS curve fit was carried out. The best-fitting results of Pt-uni-MOS, Pt foil, and PtO $_2$ were shown in Fig. S35, where the fitting curves could best match with the experimental data (see Table S1). Based on these fitting results, the calculated coordination number of Pt atoms in Pt-uni-MOS was 4 with an average Pt-S bond length of 2.32 Å. EXAFS spectroscopy thus revealed that each atomic Pt site was coordinated with four sulfur atoms to form a Pt-S $_4$ configuration. Such a tetracoordinate macrocyclic M-X $_4$ model is thermodynamically stable in the field of metalloproteins or organometallics [49,50]. From the Wavelet transform (WT) spectrum (Fig. 4c), the intensity maxima at ~10 Å $^{-1}$ was assigned to Pt-Pt contribution in Pt foil. For Pt-uni-MOS (Fig. 4d), the contour plots displayed only one intensity maximum at ~7.8 Å $^{-1}$, which further suggested the atomic dispersion of Pt in Pt-uni-MOS. The above data further confirm that the Pt atoms indeed exist as single atoms in the underlying MOS.

Selective PA hydrogenation of Pt-uni(bi, ter)-MOS

The catalytic behavior of Pt-uni-MOS was evaluated in selective hydrogenation of PA to styrene as a model reaction [51–53]. First, the reaction was performed in different reaction conditions to get the optimum reaction conditions (Tables S2, S3). Then, uni-MOS with different Pt loadings (0–20 wt%) were prepared to evaluate the impact of metal contents on the catalytic performance (Table 1, Entries 1–4 and 8). In a typical run, the 20%-Pt-uni-MOS showed an optimized efficiency in terms of conversion (91%) and selectivity toward styrene (90%). Although

Figure 4 X-ray absorption studies. (a) Pt L₃-edge XANES profiles of Pt-uni-MOS, PtO₂, and Pt foil. (b) Pt L₃-edge EXAFS profiles of Pt-uni-MOS, Pt foil, and PtO₂. The contour plots of WT for (c) Pt foil and (d) Pt-uni-MOS.

Table 1 Catalytic performances of MOS-supported atomic Pt catalysts in hydrogenation of PA

Entry ^a	Catalyst ^b	Conversion ^c (%)	Yield ^c (%)		Selectivity ^c (%)
			2a	2b	
1	20%-Pt-uni-MOS	91	82	9	90
2	15%-Pt-uni-MOS	97	83	14	86
3	10%-Pt-uni-MOS	86	77	9	90
4	5%-Pt-uni-MOS	74	68	6	92
5	20%-PtCl ₂ -uni-MOS	38	35	3	93
6	20%-Pt-bi-MOS	95	80	15	84
7	20%-Pt-ter-MOS	93	82	11	88
8	uni-MOS	0	–	–	–
9	bi-MOS	0	–	–	–
10	ter-MOS	0	–	–	–

a) Reaction conditions: PA (0.75 mmol), catalyst (5 mg), H₂ (1 MPa), reaction time (2 h), stirring rate (600 r min⁻¹), temperature (110°C), solvent (*N,N*-dimethylformamide, 3 mL). b) See text for a definition of terms. c) Determined by gas chromatography-mass spectrometry.

the 15%-Pt-uni-MOS demonstrated the highest conversion (97%), the selectivity dropped to 86%. Further reducing the Pt loading to 10% and 5%, the conversions decreased to 86% and 74%, while the selectivities were at a similar level (90% and 92%, respectively). However, 20%-PtCl₂-uni-MOS gave only 38% conversion (Table 1, Entry 5), indicating the detrimental role of Cl in hydrogenation. These results suggest that Pt^{δ+} could be the critical catalytic active site for the selective hydrogenation of PA. The catalysts showed slightly lower selectivity toward styrene when the conversion approaching 100% (Table S4). The increased porosity and hydrophobicity could be beneficial to enhancing catalytic ability. Therefore, bi-MOS and ter-MOS supported Pt were also employed in PA semi-hydrogenation. As expected with higher Brunauer-Emmett-Teller (BET) surface

area and more pores, 20%-Pt-bi-MOS and 20%-Pt-ter-MOS showed slightly better performance in terms of conversion, but the selectivities toward styrene were inferior to that of 20%-Pt-uni-MOS (Table 1, Entries 6, 7). Furthermore, the pure uni(bi, ter)-MOS did not show any catalytic performance in hydrogenation (Table 1, Entries 8–10). In addition, the hydrogenation of PA was also performed in pure water. As shown in Table S5, the most hydrophobic 20%-Pt-ter-MOS gave 69% conversion while the hydrophilic uni- or bi-MOS counterparts gave the inferior performances. The difference in conversion was partly ascribed to the limited mass transfer of PA due to its poor solubility in water. The chemical microenvironment especially the hydrophobic 20%-Pt-ter-MOS could effectively trap PA in water, which was thought to contribute to the enhanced catalytic

activity. Importantly, 20%-Pt-*uni*-MOS showed constant conversion and selectivity toward styrene in consecutive three cycles of PA semi-hydrogenation (Fig. 5a). The post-analysis of the recycled sample confirmed the remaining atomic dispersion of Pt (Fig. 5b and Fig. S36). The nearly identical chemical states of Pt and S in the XPS (Fig. 5c, d) also indicated the high stability of the system.

Compared with other reported catalysts in the literature (Table S6), the catalytic ability of these MOS-based atomic Pt catalysts is indeed moderate. First, the unsatisfactory catalytic performance might be due to the unmatching pore size of the catalysts with the molecular size of PA. Second, the NEt^+ cations balancing the negative charges carried by the clusters could block the pores, which are therefore not accessible for the substrate molecules. Last but not least, the abundant S content in the supporting material (Figs S37–S39), a typical poison to the catalytic sites, could harm the performance. The versatile MOS chemistry and the enormous progress in the metal-organic framework field will bring more possibilities for modulating the catalytic performance of MOS-supported metal catalysts [33]. The availability of ditopic, tritopic, and even hexatopic linker offers more opportunities for the development of new MOS as supporting materials to host metal sites [54,55].

DFT calculations of PA chemoselective hydrogenation on Pt-*uni*-MOS

DFT calculations were conducted to investigate the reaction mechanism of PA semi-hydrogenation, using a simplified model of $\text{Pt}(\text{SH})_4$ (Fig. S40). The equilibrium geometries of $\text{Pt}(\text{SH})_4$ with different spin multiplicities were optimized at B3LYP (D3BJ)/def2-SVP level. Among all possible multiplicities, the energy configuration of the triplet ground state of $\text{Pt}(\text{SH})_4$ with a typical planar equilibrium geometry was revealed to be the lowest and thus was employed in the following calculations

(Table S7). As shown in Fig. 6a, the semi-hydrogenation of PA could be divided into two steps, and the possible transition state (TS) in the first step may be intermediate with one H atom, adding to the terminal of alkynyl. We then searched the possible configurations of TS and successfully identified the structure. Monitoring variation of electronic structures along intrinsic reaction coordinate (IRC) path can provide further insight into the semi-hydrogenation reaction (Fig. 6b). To better visualize the evolution of the electronic structure in the course of the reaction, we further analyzed the wave functional information using the same level of theory and method as indicated above. Isosurface maps of spin density (the difference between α and β density) [56,57] were shown in Fig. 6c. The unpaired electrons were not shown in the reactants at the initial state of the reaction. As the reaction progresses, single electrons are mainly distributed between H^*H^* at the TS, which is then transferred to the carbon atom attached to the benzene ring. Similar information can also be obtained from visual inspection of the orbital distribution (Fig. 6c). The electron from H^* gradually enters π^* lowest unoccupied molecular orbital (LUMO) of a terminal carbon atom from PA, demonstrating the change of carbon hybrid orbitals from sp to sp^2 [58,59].

Furthermore, the second step of styrene hydrogenation was also investigated and the corresponding IRC path was presented in Fig. S41. Different from the semi-hydrogenation process of PA, one H^* is added to the terminal carbon atom of ethenyl, which is followed by the reaching of TS and termination of IRC. Matching of H^* with π^* LUMO of a terminal carbon atom from ethenyl can be seen both from the isosurface map of spin density distribution (Fig. S42). Thus, the styrene first reacts with one H atom at the terminal site, forming an intermediate product. Then, the final ethylbenzene product will be obtained following an exothermic process.

In addition, to reveal the occurrence of PA hydrogenation

Figure 5 (a) Reusability test of Pt-*uni*-MOS. (b) Spherical aberration-corrected HAADF-STEM image of the recycled catalyst. (c) Pt 4f and (d) S 2p XPS spectra comparison between the recycled sample and pristine sample.

Figure 6 (a) Proposed pathway of semi-hydrogenation of PA. (b) Total Gibbs free energy *versus* IRC along the reaction pathway with the derived energy barrier indicated. (c) Isosurface maps of spin density corresponding to points I–V. Pt, brown; S, yellow; H, white; C, light blue. HOMO: highest occupied molecular orbital.

under the experimental condition (temperature 383.15 K, pressure 1 MPa), the energy barrier $\Delta G^\ddagger$ of the reaction describes the Gibbs free energy (G) of TS abstracted by that of the starting species was calculated. For the semi-hydrogenation of PA, $\Delta G^\ddagger$ is 33.8 kcal mol⁻¹ under the experimental condition (Fig. 6b) [60]. With the reaction proceeding over TS, the rest of the whole reaction path is downhill in energy which ends up with a product characteristic of equilibrium geometry V and much lower energy compared with the starting reactant. Therefore, the simulated energy barrier and the obtained reaction rate constant (Section 5.3 in SI) of styrene hydrogenation together corroborate the proposed reaction pathway.

CONCLUSIONS

In summary, we reported a strategy for synthesizing supported atomic metal with high loading based on the interaction between the noble metal and sulfur in the MOS. A Pt loading as high as 18.5 wt% supported on MOS could be obtained, which showed intriguing catalytic activity and selectivity for PA semi-hydrogenation. Such strategy could also be extended to the synthesis of atomic Pd and even 30.9 wt% loading could be obtained. The DFT calculations confirm that the atomic Pt sites in the sulfur-rich coordination environment is thermodynamically capable of activating H₂ and chemoselective hydrogenation of PA. Further

diversifying MOS chemistry and metalation strategy would provide more opportunities to construct biomimetic materials for versatile catalytic applications.

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Author contributions Liu J conceived the idea and designed the experiments. Liu J and Yang L cowrote the paper. Yang L and Bai J synthesized and characterized the samples and further analyzed the results. Yang L and Liu W performed the catalytic tests. Kan X performed the DFT calculations. All authors discussed and commented on the manuscript.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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金属有机硫化物框架用于制备高载量单原子Pt

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摘要 原子级分散的贵金属位点在多相催化中具有广阔的应用前景。然而当金属含量较高时极易引起团聚, 因此其负载量通常限制在2 wt%以下。本研究中, 通过模拟金属酶的多中心金属硫簇, 基于金属有机硫化物(MOS)框架仿生合成了高载量贵金属单原子催化剂。以[Mo₃S₇Br₆]²⁻团簇和二硫醇分别为组装单元和连接结构, 通过化学键合构筑MOS框架材料, 并在上述合成过程中原位负载贵金属盐。进一步通过NaBH₄还原, 制备出负载型的Pt单原子催化剂, 且负载量高达18.5 wt%。通过改变二硫醇中苯环的数量, 可以调节MOS框架的孔径及浸润性。此外, 制备得到的Pt-MOS单原子催化剂, 可以在有机溶剂或纯水中选择性将苯乙炔加氢生成苯乙烯。密度泛函理论计算表明, 富硫配位环境中的原子Pt位点可以有效活化H₂分子, 并通过较低的反应能垒高选择性地催化苯乙炔半氢化为苯乙烯。这种基于金属有机硫化物的金属化策略将启发人们合成结构明确的仿生催化材料, 在未来有望实现更多样化的应用。