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Article

A MoS₂ nanocatalyst with surface-enriched active sites for the heterogeneous transfer hydrogenation of nitroarenes

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ABSTRACT

A highly efficient and reusable plane-curved and interlayer-expanded MoS₂ nanocatalyst with increased exposure of active sites was prepared. The catalyst was used for the heterogeneous hydrogen transfer reaction of nitroarenes with hydrazine monohydrate as a reductant under mild reaction conditions without pressure and base, which was different from other hydrogen transfer systems that require the presence of a base (e.g., propan-2-ol/KOH). The sandwiching of carbon between the MoS₂ nanosheets increased the distance between the layers of MoS₂ and exposed more Mo sites, resulting in superior catalytic performance compared with that of bulk MoS₂ catalyst. The active hydrogen (H*) generated from N₂H₄ could directly transfer to the –NO₂ groups of nitrobenzene to form aniline followed by N₂ emission, which was confirmed by detecting the gas emission with mass spectrometry during the decomposition of hydrazine or the co-existence of nitrobenzene and hydrazine.

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1. Introduction

Aromatic amines are widely used as important intermediates for the industrial production of agrochemicals, pharmaceuticals, antioxidants, dyes, and polymers. The transformation of nitro compounds into anilines represents an important reaction in organic synthesis in the laboratory and industry [1,2]. The use of heterogeneous catalysts demonstrates several advantages over homogeneous systems, such as easy recovery and recycling of the catalysts. One of the most widespread cat-

alytic processes is the catalytic hydrogenation using transition metal (Pt, Pd, Ru, Au, and Ni) catalysts with H₂ for the hydrogenation of nitroarenes [3–7]. Another route for the hydrogenation of nitroarenes is hydrogen transfer reduction, which is safer and more ecofriendly compared with the hydrogenation reduction process with hazardous molecular hydrogen as a reductant. Different kinds of hydrogen sources (such as HCOOH, HCOONH₄, PhSiH₃, propan-2-ol/KOH, H₂NNH₂) have been applied for the catalytic transfer hydrogenation of nitro compounds [8–11]. Among them, hydrazine has many ad-

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vantages such as avoiding the use of a flammable gas, autoclaves, and bases, producing harmless by-products (N_2 and H_2O) [12], and simplifying the reactor; therefore, the use of hydrazine for the reduction of $-\text{NO}_2$ has attracted extensive attention [13–17].

Molybdenum disulfide (MoS_2) is a kind of layered inorganic compound consisting of S-Mo-S layers coupled through weak van der Waals interactions, which has been widely used for the hydrodesulphurization process [18,19] and HER [20,21]. It has been shown that the catalytic activity could be improved by reducing the size of the MoS_2 particles [22,23] and the layers of MoS_2 [24,25] because the activity is normally ascribed to the edge sites and the vacancies on the plane (such as S vacancy, unsaturated Mo sites) of the MoS_2 nanoclusters [26–29]. Therefore, exfoliated MoS_2 nanosheets exhibit enhanced catalytic performance for the hydrodesulphurization of dibenzothiophene [24], but they easily aggregate, resulting in low activity or the loss of catalytic performance. If the single-layer MoS_2 nanosheets are uniformly partitioned by the insertion of carbon or other materials, their aggregation is effectively inhibited, which improves their catalytic performance and stability [19].

Beller et al. [30] proposed that molybdenum(IV) complexes bridged by several sulfide ligands could be used as homogeneous catalysts for the transfer hydrogenation in the co-presence of HCOOH and NEt_3 , whereas limited activity was observed for lower nuclearity MoS_2 . Bulk MoS_2 and an oxygen-implanted MoS_2 catalyst have been used to catalyze the transfer hydrogenation of nitroarenes to the corresponding anilines with hydrazine as the hydrogen source in a closed tube or pressure bottle with or without Ar protection [31,32]; however, these processes are unsafe because of the increased pressure owing to the formation of nitrogen. The catalytic behavior of few-layer MoS_2 catalyst has not been reported for the reduction of nitroarenes under the presence of hydrazine.

Herein, our objective was to develop an inexpensive, easily prepared, and recyclable nonprecious metal catalyst that enables the reduction of nitroarenes under safe and mild conditions (e.g., under low temperature, normal pressure, and without base). Interlayer-expanded MoS_2 obtained by inserting carbon was synthesized by using a hydrothermal method followed by calcination under a hydrogen atmosphere. The material exhibited a high abundance of Mo sites and curved interlayers. In the transfer hydrogenation of nitroarenes with hydrazine, the few-layer and plane-curved MoS_2 with more Mo sites showed higher activity than that of bulk MoS_2 . The catalyst also exhibited high stability and could be reused at least 7 times, and displayed excellent chemoselectivity for the reduction of the nitro group in the presence of other functional groups such as halogens, ethers, and CN groups.

2. Experimental

2.1. Materials

Nitroarenes (99%) were purchased from Aladdin Reagent Co. Ltd., Shanghai, China. Glucose, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, anisole, hy-

drazine monohydrate (85%), and ethanol (AR) were supplied by China Medicine Group Shanghai Chemical Reagent Company. Thiourea and sulfur powder (99%) were obtained from Aladdin Co.

2.2. Preparation of catalysts

The interlayer-expanded MoS_2 catalyst ($\text{MoS}_2@\text{C}$) was prepared by a one-pot hydrothermal synthesis by inserting amorphous carbon in MoS_2 according to a literature procedure [33]. In a typical synthesis process, 0.30 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (molybdenum source) and 0.40 g thiourea (sulphur source) were dissolved in 60 mL deionized water, and then 1.00 g of glucose was added into the solution as a carbon source. The obtained clear solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 240 °C for 24 h. After cooling naturally, the black precipitate was collected by filtration, washed with deionized water, and dried at 80 °C for 12 h. The dried black powder was annealed at 800 °C for 2 h in a stream of 10% H_2/Ar (200 mL min^{-1}) and the product was denoted as $\text{MoS}_2@\text{C}$. The bulk MoS_2 was synthesized by a similar process as for the synthesis of $\text{MoS}_2@\text{C}$ but without adding glucose. Carbon powder (denoted as C) was also synthesized by a similar hydrothermal process by only adding glucose as a carbon source, and the S, N co-doped carbon powder (S,N-doped C) was also synthesized by a similar process by only adding glucose and thiourea as a carbon source and sulphur/nitrogen source, respectively.

2.3. Catalytic reaction

The nitroarene reduction reactions were carried out in a 25 mL round-bottom flask containing a certain amount of catalyst, 1.23 g of nitrobenzene (10 mmol), 1.5–4.0 equivalents (equiv.) of hydrazine monohydrate, 0.57 g of anisole as an internal standard, and 2 mL ethanol as solvent. The flask was connected to a water-cooled condenser and the mixture was heated in an oil bath for a set period of time. When the reaction was completed, ethanol was added and the mixture was accurately diluted to 25 mL in a volumetric flask. The products were analyzed with a gas chromatogram (Agilent 7890A) equipped with a FID detector.

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2500PC diffractometer with a $\text{Cu } K_\alpha$ radiation source operating at 50 kV, 300 mA. The mesostructure and morphology of the samples were characterized by transmission electron microscopy (TEM) on a FEI T12 with an accelerating voltage of 120 kV. Scanning electron microscopy (SEM) images were taken using an FEI Nano450 scanning electron microscope operated at 10–15 kV. An energy dispersive spectroscopy (EDS) spectrometer was attached to an FEI Nano450 SEM to analyze the element composition of the samples. Nitrogen adsorption-desorption data were measured with a Micromeritics ASAP 2020 analyzer at 77 K. Prior to the measurements, the

samples were degassed at 120 °C for 12 h. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.02 to 0.20. The pore size distribution (PSD) was calculated from adsorption data of isotherms using the Barrett-Joyner-Halenda (BJH) model. The surface chemistry of the samples was investigated using an ESCALAB 250 instrument with Al $K\alpha$ X-rays (1486.6 eV).

3. Results and discussion

Fig. 1 shows the XRD patterns of bulk MoS₂ and MoS₂@C synthesized by the hydrothermal method [33]. It indicated that both samples were 2H phase, which was consistent with a hexagonal structure (JCPDS 87-2416). The (002) plane ($2\theta = 14.4^\circ$, d -spacing = 0.614 nm) of MoS₂ was not observed in MoS₂@C, whereas the diffraction peak observed at $2\theta = 8.3^\circ$ for MoS₂@C indicated an increased interlayer distance from 0.614 ($d(002)$ of MoS₂) to 1.061 nm. It has been reported that the structure of MoS₂ with a few layers cannot exhibit the (002) reflection [34,35]; therefore, the absence of the (002) diffraction peak indicated that MoS₂@C had a single layer or few layers structure. Moreover, a new peak at $2\theta = 17.7^\circ$ with d -spacing of ~ 0.500 nm for the MoS₂@C sample suggested the formation of a new lamellar structure with carbon sandwiched between the MoS₂ nanosheets [33,36]. In fact, it is well known that the $d(002)$ -spacing of bulk MoS₂ and graphite are 0.62 and 0.34 nm, respectively. Therefore, the 0.500 nm $d(002)$ -spacing of the peak at $2\theta = 17.7^\circ$ was between the $d(002)$ of bulk MoS₂ (0.62 nm) and carbon (0.34 nm). Furthermore, the d -spacing of the peak at $2\theta = 8.3^\circ$ for MoS₂@C was ~ 1.061 nm, which was only twice that of the peak at $2\theta = 17.7^\circ$, suggesting that the d -spacing of the peak at $2\theta = 8.3^\circ$ may be the distance between the adjacent MoS₂ nanosheets after the insertion of a carbon layer between them. Therefore, it is possible that the peak at $2\theta = 17.7^\circ$ represents the spacing between the MoS₂ layer and the carbon layer. The obvious broadening of the (100) and (110) diffraction peaks for MoS₂@C indicated the formation of nanosized domains with a defect-rich structure along the basal

[37,38]. A weak diffraction peak at $2\theta = 25.8^\circ$ was observed, which was attributed to the (002) plane of carbon. Furthermore, no molybdenum oxides (MoO₂ or MoO₃) and molybdenum carbides were observed in MoS₂ or MoS₂@C, as revealed by XRD.

The morphologies of the samples characterized by SEM are shown in Fig. 2. As shown in Fig. 2(A) and (B), bulk MoS₂ consisted of stacked sheets with a micrometer-sized scale. The morphology of MoS₂@C shown in Fig. 2(C) and (D) was a flower-like spherical architecture with a size of hundreds of nanometers (~ 200 nm).

The microstructure of the samples was further clarified by HRTEM (Fig. 3). The bulk MoS₂ sample showed a perfect layered sheet with an interlayer distance of ~ 0.622 nm in the (002) plane (Fig. 3(A) and (B)), which was similar with the hexagonal lattice of the MoS₂ phase. The HRTEM images of MoS₂@C (Fig. 3(C) and (D)) show that MoS₂@C comprises few-layered nanosheets with an enlarged layer distance, ~ 1.09 or 1.43 nm, which was larger than that of bulk MoS₂. One- or two-layers of amorphous carbon inserted into the MoS₂ layers can be observed, which enlarged the distance between the two (002) planes of MoS₂ (Fig. 3(D)). The distance between two adjacent MoS₂ (002) planes and the carbon layer was ~ 0.510 nm, which may contribute to the diffraction peak at $2\theta = 17.7^\circ$ (Fig. 1). A curved (002) plane in MoS₂@C can also be observed (Fig. 3(D)) owing to the dispersion of MoS₂ in amorphous carbon during the hydrothermal process [33]. Such an expanded interlayer distance could improve the structural stability and expose more active edges. In fact, curved and distorted basal planes have also been shown to contribute to catalytic activity [37] except for the edges. Therefore, MoS₂@C could exhibit better activity than bulk MoS₂. N₂ adsorption-desorption data (Fig. 3(E)) indicated that interlayer-expanded MoS₂@C shows higher specific surface areas ($89 \text{ m}^2 \text{ g}^{-1}$) than that of bulk MoS₂ ($17 \text{ m}^2 \text{ g}^{-1}$). Moreover, the BJH pore size distribution (Fig. 3(F)) showed that MoS₂@C exhibited a pore size of ~ 20 nm.

Fig. 1. The XRD patterns of the MoS₂ materials.

Fig. 2. SEM images of MoS₂ (A, B) and MoS₂@C (C, D).

Fig. 3. TEM images of MoS₂ (A, B) and MoS₂@C (C, D); N₂ adsorption-desorption curves (E) and pore size distributions (F) of MoS₂ and MoS₂@C; The deconvolution of high-resolution Mo 3d spectra (G) and S 2p spectra (H) of the catalysts.

The elemental compositions characterized by EDS (Table 1) show that the atomic ratio of Mo and S for MoS₂@C was ~ 0.67 , which was larger than that in MoS₂ (~ 0.53). The weight content of MoS₂ in MoS₂@C calculated according to the content of Mo was approximately 48.3 wt% (Table 1). The compositional analysis by XPS revealed that the atomic ratio of Mo and S was ~ 0.63 (MoS₂) and ~ 0.71 (MoS₂@C) (Table 1), which was slightly higher than the results obtained by EDS. The high-resolution Mo 3d XPS spectra (Fig. 3(G)) of the samples showed two peaks with binding energies of 229.5 ± 0.1 eV and 232.6 ± 0.1 eV, corresponding to the Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, which are characteristic of dominant Mo (IV) in the products. The high-resolution S 2p XPS spectra (Fig. 3(H)) exhibited two binding energies of 162.3 ± 0.1 eV and 163.5 ± 0.1 eV, corresponding to S 2p_{3/2} and S 2p_{1/2}, respectively, which was consistent with the S (–2) valence state. Furthermore, the peak at 235.6 ± 0.1 eV (Fig. 3(G)) corresponded to the oxygen bonding with Mo, confirming the existence of S–Mo (VI)–O bonds [39]. These unique Mo sites with O- and S-bonding provide more active defect sites and unusual electronic properties [40,41]. Consequently, such an interlayer-expanded MoS₂@C with high specific surface areas and a mesoporous structure exposes more edges and active sites on a curved (002) basal plane, which may display excellent catalytic activity.

Table 2 displays the catalytic behavior of various materials for nitrobenzene reduction to aniline under different condi-

tions. In the absence of any catalyst, only 4.7% of nitrobenzene conversion was observed after 5 h at 80 °C (Table 2, entry 1). The complete conversion of nitrobenzene was obtained after the addition of bulk MoS₂ catalyst, but a low selectivity to aniline was obtained (70.1%; Table 2, entry 2). Nitrobenzene was fully converted to aniline with a selectivity of >99% (Table 2, entry 4) when MoS₂@C was used as a catalyst. Moreover, the selectivity to aniline over MoS₂@C catalyst was still higher than 95% with 1.5 equiv. of hydrazine hydrate (Table 2, entry 5 and 6), whereas an inferior aniline selectivity of 55.4% was obtained under the same conditions over MoS₂ (Table 2, entry 3), suggesting superior catalytic performance of the MoS₂@C catalyst containing an interlayer-expanded and curved (002) plane. No reaction occurred without N₂H₄ (Table 2, entry 7), which suggested that MoS₂ itself could not reduce nitrobenzene to aniline. In previous studies, the carbonyl group (C=O) on the surface of oxidized carbon materials was considered to contribute to the conversion of nitrobenzene, with hydrazine hydrate as the reductant [42]. Although C–O groups existed (Fig. 4(A)) in the sample of C (synthesized by a similar process as that for MoS₂@C, without adding Mo and S precursors), as shown in Table 2, entry 13, weak activity of C was obtained. Furthermore, the C 1s XPS spectra for C and MoS₂@C had a similar shape (Fig. 4(A)). Therefore, the existing C–O groups in the MoS₂@C also did not contribute the catalytic performance. Both sulfur powder and S,N-C (synthesized by a similar process

Table 1

The element analysis of the catalysts according to EDS and XPS.

Catalyst	EDS/XPS (at%)				Mo/S (EDS/XPS)	MoS ₂ content (wt%)
	Mo	S	C	O		
MoS ₂	34.6/23.6	65.3/37.4	—/29.3	—/9.7	0.53/0.63	—
MoS ₂ @C	5.8/11.2	8.6/15.8	71.9/63.7	13.7/9.3	0.67/0.71	48.3

Table 2Catalytic activity of different catalysts for the reduction of nitrobenzene ^a.

Entry	Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	N_2H_4 (equiv.)	Con. (%)	Sele. (%)	Yield (%)	TOF ^h (s^{-1})
1	Blank	—	4	4.7	97.6	4.6	—
2	MoS_2	17	4	99.5	70.1	69.7	1.24
3	MoS_2	17	1.5	55.1	55.4	30.5	0.54
4	$\text{MoS}_2@\text{C}$ ⁱ	89	4	99.6	99.8	99.4	3.66
5	$\text{MoS}_2@\text{C}$	89	3	99.5	99.5	99.0	3.65
6	$\text{MoS}_2@\text{C}$	89	1.5	72.1	97.7	70.4	2.59
7	$\text{MoS}_2@\text{C}$	89	0	—	—	—	—
8 ^b	$\text{MoS}_2@\text{C}$	89	4	99.4	93.9	93.3	8.59
9 ^c	$\text{MoS}_2@\text{C}$	89	4	99.8	99.8	99.6	6.11
10 ^d	$\text{MoS}_2@\text{C}$	89	4	99.6	98.2	97.9	3.60
11 ^e	$\text{MoS}_2@\text{C}$	89	4	99.7	82.5	82.3	6.05
12 ^f	$\text{MoS}_2@\text{C}$	89	4	99.7	97.9	97.6	0.15
13	C	419	4	3.9	98.2	3.8	—
14	S,N-doped C	339	4	3.4	97.2	3.3	—
15	Sulphur	—	4	3.7	97.0	3.6	—
16 ^g	$\text{MoS}_2@\text{C}$	89	4	99.6	98.6	98.2	3.62

^a Reaction conditions: 5 mg catalyst, 10 mmol (1.23 g) substrate, 2 mL ethanol, 80 °C for 5 h. ^b 10 mg catalyst at 80 °C for 1 h. ^c 15 mg catalyst at 80 °C for 1 h. ^d Without solvent. ^e The amount of substrate was increased to 20 mmol (2.46 g) with 5 mg catalyst, at 80 °C for 5 h. ^f Reaction temperature: at 30 °C for 120 h. ^g The $\text{MoS}_2@\text{C}$ reused for the seventh time.

^h TOF: turnover frequencies calculated based on the total amount of MoS_2 (mmol) and the production of aniline (mmol) in the reaction system at the corresponding reaction time (h).

ⁱ The weight fraction of MoS_2 in $\text{MoS}_2@\text{C}$ is 48.3% (Table 1) and the amount of MoS_2 in 5 mg $\text{MoS}_2@\text{C}$ is 2.415 mg (~0.0151 mmol).

Fig. 4. (A) C 1s spectra of $\text{MoS}_2@\text{C}$ and C; (B) Hot filtration experiment. Reaction conditions: 10 mmol nitrobenzene, 4 equiv. of hydrazine hydrate, ethanol 2 mL, 5 mg $\text{MoS}_2@\text{C}$, 80 °C.

as that for $\text{MoS}_2@\text{C}$, without adding Mo precursor) could not convert nitrobenzene to aniline (Table 2, entry 14 and 15). Under the same reaction conditions (reaction temperature, reaction time, the amount of catalyst, and reductant), the $\text{MoS}_2@\text{C}$ gives an aniline yield at 99.4% with a TOF of 3.66 s^{-1} (Table 2, entry 4), which was higher than that of bulk MoS_2 with a TOF of 1.24 s^{-1} and an aniline yield of 69.7% (Table 2, entry 2). A hot filtration experiment (Fig. 4(B)) indicated that the transfer hydrogenation using hydrazine as a reducing agent over $\text{MoS}_2@\text{C}$ was a heterogeneous reaction. These results demonstrated that MoS_2 was responsible for the transfer hydrogenation of nitrobenzene, and MoS_2 with a few curved layers exhibited high activity.

The conversion of nitrobenzene over $\text{MoS}_2@\text{C}$ still reached 99% with aniline selectivity of 98.2% under solvent-free condi-

tions (Table 2, entry 10). Even if the amount of nitrobenzene was increased to 20 mmol without increasing the amount of $\text{MoS}_2@\text{C}$, the complete conversion of the substrate was achieved with 82% aniline selectivity (Table 2, entry 11). Furthermore, in contrast to conventional catalytic systems using other hydrogen sources [8,9,14,31,32], our reaction was conducted under milder alkali-free conditions (80 °C without pressure) and without using noble metal catalyst [10]. In a further study, we conducted the reaction at a lower temperature (30 °C). Complete conversion of nitrobenzene to aniline was obtained with 97.8% selectivity (Table 2, entry 12). Increasing the amount of $\text{MoS}_2@\text{C}$ reduced the time for the conversion of nitrobenzene to 1 h (Table 2, entry 8 and 9). Significantly, the $\text{MoS}_2@\text{C}$ catalyst could be easily recovered by filtration at least seven times with little reduction in its activity (Table 2, entry

Fig. 5. TEM images of MoS₂@C after reaction for the first run (A, B, C) and the seventh run (D, E, F). (G) ATR IR spectra of several catalyst.

16). The TEM images (Fig. 5(A–F)) and ATR IR spectra (Fig. 5(G)) results indicated that there was no obvious difference between the fresh and used MoS₂@C catalyst, conforming the structural stability of the catalyst.

The diimide (HN=NH) is considered to be the active intermediate formed in mixtures of hydrazine and oxidizing agents such as oxygen-copper ion or H₂O₂-copper ion in the presence of a weak proton source and could transfer hydrogen resulting in the formation of aniline or a –C–C– bond [43–45]. A control experiment under a nitrogen atmosphere showed similar activity to that under an air atmosphere (Table 3, entry 1), which indirectly indicated that the diimide was not acting as a reagent in the present catalytic system. However, we cannot exclude the formation of diimide in our open catalytic system because the reaction was not protected from the atmosphere. Furthermore, no conversion of nitrobenzene was observed when hy-

drazine was replaced by ammonia (Table 3, entry 2), suggesting that it was impossible to transfer hydrogen from ammonia to nitrobenzene. Similar activity was obtained if the catalyst was mixed with hydrazine or nitrobenzene at 80 °C for 0.5 h before the addition of another reactant (nitrobenzene or hydrazine) (Table 3, entry 3 and 4). Therefore, the sequence of the addition of the reactants was not essential to obtain an active system. Generally, the hydrogenation process of nitroarenes can occur through two routes: direct reduction and an indirect condensation pathway [7]. The feasibility of this second route was investigated by using azoxybenzene (-AZO) or azobenzene (-AZ) as reactants. When -AZO was used as a reactant, the selectivity for aniline was 52.3% (Table 3, entry 5) and another side-product (AZ) was obtained in 47.7% yield. The reduction of -AZ reached a conversion of 79.9%, whereas only 40.7% selectivity of aniline was obtained (Table 3, entry 6). When nitrosobenzene (PhNO) was used as a substrate, its conversion was 99.7% in 1 h under the same conditions (Table 3, entry 7) and the selectivity to aniline was 90.1%, indicating that the reduction of PhNO to PhNH₂ occurred faster than that of PhNO₂ to PhNO (Table 3, entry 8). Moreover, the complete conversion of nitrobenzene to aniline occurred after 1 h when the amount of MoS₂@C was increased (Table 2, entry 9). Therefore, the formation of aniline in the presence of the MoS₂@C preferentially takes place through the direct reduction route.

The gas product was analyzed by mass spectrometry to further study the reaction mechanism. As shown in Fig. 6, no H₂ ($m/z = 2$) was detected in the gas phase with or without nitrobenzene, suggesting that the reduction of nitrobenzene occurred through a transfer hydrogenation route and the formation of an active H⁺ could be stabilized on the surface of MoS₂. When only hydrazine was mixed with MoS₂@C at 80 °C, NH₃ ($m/z = 17$) was the main gas product owing to the decomposition of hydrazine [46]. The main gas product changed to N₂ ($m/z = 28$) when nitrobenzene and hydrazine co-existed (Fig. 6(B)), which indicated that the addition of nitrobenzene

Table 3

Catalytic activity of MoS₂@C under different conditions ^a.

Entry	Substrate	Con. (%)	Sele. (%)
1 ^b	Nitrobenzene	99.7	99.7
2 ^c	Nitrobenzene	<0.1	—
3 ^d	Nitrobenzene	99.9	99.6
4 ^e	Nitrobenzene	99.9	98.6
5 ^f	Azoxybenzene	65.3	52.3
6 ^g	Azobenzene	79.9	40.7
7 ^h	Nitrosobenzene	99.7	90.1
8 ⁱ	Nitrobenzene	85.1	60.1

^a Reaction conditions: 5 mg MoS₂@C catalyst, 10 mmol (1.23 g) nitrobenzene, 4 equiv. of hydrazine, 2 mL ethanol, 80 °C for 5 h.

^b N₂ protection.

^c 4 equiv. of 28 wt% of ammonia water as reductant to replace hydrazine.

^d After stirring nitrobenzene at 80 °C for 0.5 h, adding 4 equiv. of hydrazine.

^e After stirring hydrazine at 80 °C for 0.5 h, adding nitrobenzene.

^f 1 mmol azoxybenzene (-AZO) as a substrate.

^g 1 mmol azobenzene (-AZ) as a substrate.

^h 1 mmol nitrosobenzene (-NO) as a substrate at 80 °C for 1 h.

ⁱ 1 h.

Fig. 6. The mass spectrometry (MS) analysis of the hydrazine decomposition (A) and nitrobenzene reduction with hydrazine (B) using MoS₂@C catalyst. Conditions: 5 mg MoS₂@C, 80 °C, no solvent, He as the carrier gas. (A) 40 mmol N₂H₄; (B) 10 mmol nitrobenzene with 40 mmol N₂H₄.

changed the decomposition route of N₂H₄ and triggered the N₂ emission ($2\text{PhNO}_2 + 3\text{N}_2\text{H}_4 \rightarrow 2\text{PhNH}_2 + 3\text{N}_2 + 4\text{H}_2\text{O}$) [46]. Therefore, hydrazine decomposition over MoS₂@C without nitrobenzene may preferentially occur through breakage of the N–N triple bond, resulting in the formation of large quantities of ammonia, which is unable to transfer hydrogen to –NO₂ (Table 3, entry 2). These results indicated that the formation of

aniline was through direct hydrogen transfer from hydrazine to –NO₂ groups followed by N₂ emission.

To study the general applicability of MoS₂@C catalyst for the transfer hydrogenation of nitroarenes, several kinds of nitroarenes were tested. The results in Table 4 indicate that good conversion (>90%) for all the substrates and selectivity (>95%) for the corresponding anilines could be obtained, which demonstrated excellent chemoselectivity for the reduction of the nitro group in the presence of functional groups such as halogen, ether, and CN groups. However, the procedure was not good for the selective reduction of the nitro group in the presence of C=C groups (Table 4, entry 13); this could be attributed to the formation of diimide (HN=NH), which could transfer the hydrogen to the –C=C– bond, resulting in the formation of a –C–C– bond [45].

Bulk MoS₂ with a perfect layered structure exposes a few active edges, which results in inferior activity. In contrast, the interlayer-expanded MoS₂ prepared by inserting carbon between the MoS₂ layers exhibited more Mo sites at the edges and on the surface of a curved (002) plane, which leads to a highly efficient performance. Because the reaction goes through a direct transfer hydrogenation process from N₂H₄ to –NO₂, the MoS₂@C could abstract and stabilize hydrogen from N₂H₄ forming active H* on its surface, which further transfers to the –NO₂ groups to obtain aniline. Therefore, the reduction of nitrobenzene occurs in step-by-step N–H bond dissociation to form active H*, which is stabilized by an active Mo site on the surface of MoS₂, and then the –NO₂ group is reduced by active H* followed by emission of N₂.

4. Conclusions

The interlayer-expanded MoS₂ with a high abundance of Mo sites on the surface of a curved (002) plane could convert nitrobenzene to aniline much more efficiently than bulk MoS₂ using hydrazine as a reductant via a hydrogen transfer process under mild reaction conditions without pressure and base. The active hydrogen (H*) generated from N₂H₄ could directly transfer to –NO₂ to form aniline followed by N₂ emission. The cata-

Table 4

The substrate scope of the MoS₂@C catalyst ^a.

Entry	Substrate	Product	Con. (%)	Sele. (%)
1			99.8	98.2
2			99.8	98.8
3			99.7	96.6
4			99.8	97.6
5			99.8	99.2
6			99.6	99.1
7			99.7	97.6
8 ^b			99.8	99.8
9 ^b			92.7	99.8
10			96.9	96.1
11			96.9	99.6
12			98.9	97.3
13 ^c			98.1	30.1

^a 5 mg MoS₂@C catalyst, 1 mmol substrate, 4 equiv. of hydrazine, 2 mL ethanol, 80 °C for 5 h.

^b 5 mmol substrate.

^c 0.5 mmol, 4 equiv. of hydrazine, 4 mL ethanol, 100 μL *m*-xylene as an internal standard.

lyst exhibited excellent chemoselectivity for the reduction of the nitro group in the presence of halogen, ether, and CN groups. However, it was not good for the selective reduction of the nitro group in the presence of C=C bonds. It is necessary to further investigate the corresponding protocols to improve the chemoselectivity of the catalyst.

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Graphical Abstract

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A MoS₂ nanocatalyst with surface-enriched active sites for the heterogeneous transfer hydrogenation of nitroarenes

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Interlayer-expanded and plane-curved MoS₂ obtained by carbon insertion exhibits highly catalytic performance for the transformation of nitrobenzene to aniline under mild conditions without base and pressure.

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表面暴露活性位点的MoS₂纳米催化剂催化硝基化合物的非均相氢转移反应

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摘要: MoS₂具有独特的二维层状结构, 被广泛用于加氢脱硫过程以及HER反应, 而且可以通过减少MoS₂的颗粒尺寸以及层数来进一步改善其催化活性. 通过剥离方法得到的MoS₂纳米片虽然表现出优良的加氢脱硫活性, 但容易团聚使其循环使用性能很差. 如果通过引入纳米碳将单层的MoS₂纳米片进行有效“隔离”, 则可明显降低团聚的可能性, 从而改善其催化性能和稳定性. 本文通过一步水热法制备出了碳嵌入的MoS₂纳米颗粒(MoS₂@C), 将其应用于硝基苯类化合物的氢转移反应中表现出了非常好的催化性能. 进一步通过粉末X射线衍射(XRD)、X射线光电子能谱(XPS)、透射电子显微镜(TEM)和在线质谱检测等手段研究了层间距增加的MoS₂催化剂在硝基苯类化合物的氢转移反应中催化性能提升的原因.

XRD, SEM和TEM结果表明, 通过引入碳材料可以明显增加MoS₂的层间距, 同时减小其颗粒尺寸, 而且使MoS₂表现出弯曲的(002)晶面. 由于存在一定的曲率, 这种(002)晶面也会表现出一定的催化能力. 氮气物理吸附结果表明, 这种MoS₂@C复合物具有较高的比表面积(89 m² g⁻¹)和明显的介孔结构(~20 nm), 在催化反应中有利于底物扩散, 进而改善催化性能. XPS结果显示, 与体相的MoS₂相比, MoS₂@C表面暴露出更多的不饱和Mo原子(Mo/S = 0.71 (MoS₂@C) vs Mo/S = 0.63 (MoS₂)), 形成了独特的S-Mo-O结构以及缺陷结构. 在硝基苯类化合物的氢转移反应中, 层间距增加的MoS₂@C由于暴露出更多的活性位和具有弯曲的(002)晶面, 表现出了更高的催化活性(TOF = 3.66 s⁻¹ vs 1.24 s⁻¹ (MoS₂)).

通过质谱对反应过程的追踪发现, 在只有肼存在的条件下, MoS₂@C催化肼分解的主要气相产物是氮气. 这说明MoS₂@C能够使肼发生N–N键的断裂. 而当肼和硝基苯同时存在的条件下, 质谱检测的气相产物主要是氮气, 表明硝基苯的存在可以诱导肼逐步发生N–H键断裂, 在催化剂表面形成活性的H物种, 进而转移到硝基苯上使其还原得到苯胺. 使用偶氮苯和氧化偶氮苯作为反应底物, 发现MoS₂@C很难使其还原为苯胺, 这说明在该催化体系中, 硝基苯的还原过程主要是沿着直接路径(硝基苯-亚硝基苯-苯胺)进行的.

关键词: 二硫化钼; 增加的层间距; 氢转移反应; 硝基苯还原; 无碱体系

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