Article

Chemoselective transfer hydrogenation to nitroarenes mediated by oxygen-implanted MoS₂

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ABSTRACT

We present an efficient approach for the chemoselective synthesis of arylamines from nitroarenes and formate over an oxygen-implanted MoS₂ catalyst (O-MoS₂). O-MoS₂ was prepared by incomplete sulfidation and reduction of an ammonium molybdate precursor. A number of Mo−O bonds were implanted in the as-synthesized ultrathin O-MoS₂ nanosheets. As a consequence of the different coordination geometries of O (MoO₂) and S (MoS₂), and lengths of the Mo−O and Mo−S bonds, the implanted Mo−O bonds induced obvious defects and more coordinatively unsaturated (CUS) Mo sites in O-MoS₂, as confirmed by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, high resolution transmission electron microscopy, and extended X-ray absorption fine structure characterization of various MoS₂-based materials. O-MoS₂ with abundant CUS Mo sites was found to efficiently catalyze the chemoselective reduction of nitroarenes to arylamines.

1. Introduction

Functionalized arylamines [1–3] and their derivatives, such as imines and aromatic azo compounds [4,5], are widely used for the synthesis of dyes, pigments, agrochemicals, pharmaceuticals pesticides, herbicides, and other fine chemicals [6]. Previous studies on the reduction of nitroarenes to anilines have been mainly focused on supported catalysts containing d_6–d_{10} noble metals and active Ni-based catalysts [7–13]. A crucial issue for the general application of these heterogeneous catalysts for nitro reduction is their selectivity. Different methods, including metal particle size tailoring [14–16], use of alloy nanoparticles [17–19], metal-support cooperative effect regulation [20–22], and solvent and additive screening, have been employed to promote catalyst selectivity. Taking into account the complex synthesis and oxidizable nature of these noble metal catalysts, there is a strong incentive to develop nitroarene reduction processes with efficient and robust catalysts based on non-precious metals [23–30], which can catalyze the reaction in less harmful solvents and do not require many additives.

Compared with catalytic hydrogenation using H₂ as the hydrogen source, the convenient and selective transfer hydrogenation process has drawn much attention. As an important hydrogen storage process [31,32], transfer hydrogenation using formic acid provides an attractive alternative to the catalytic hydrogenation of nitroarenes; however, few active heterogeneous catalysts based on non-precious metals have been

reported [33–35].

For the reduction of nitroarenes with formate, Llusar and co-workers [36] confirmed that coordinative unsaturated (CUS) Mo sites in cubane-type $[Mo_3S_4X_3(dmpe)_3]^+$ clusters played a crucial role in the transformation of formate to the active hydrogen species for nitroarene reduction. Taking into account the similar structural skeleton of $[Mo_3S_4X_3(dmpe)_3]^+$ clusters and MoS_2, we postulate that MoS_2 could be a robust and easily prepared catalyst for reduction reactions. However, it has been both theoretically and experimentally proved that while the edge sites of MoS_2 that have CUS Mo sites are catalytically active, the mostly exposed basal planes are inactive [37–39]. Chemical and mechanical exfoliation methods can increase the number of active sites [40–42]. Therefore, in light of the high-aspect-ratio architecture of MoS_2 nanosheets, a novel strategy should be developed to change the mostly exposed MoS_2 basal planes to be catalytically active.

It is anticipated that the fractional replacement of S with O in the MoS_2 crystalline lattice may create extra CUS Mo sites because the ligand geometries of O (MoO_2) and S (MoS_2), and the lengths of the Mo−O and Mo−S bonds are remarkably different [43,44], which could induce lattice distortion and defects. However, it is rather challenging to obtain such a structure via post-modification, because perfect MoS_2 basal planes consisting of closed shell Mo centers and strong Mo−S bonds can either endure post-modification or will be completely changed. Therefore, one possible way to implant O into the MoS_2 lattice should be via bulk synthesis.

Encouraged by previous studies of MoS_2 in photonic and electrocatalytic applications [45–48], we successfully synthesized oxygen-implanted MoS_2 (designated as O-MoS_2) via incomplete sulfidation and reduction of a molybdate precursor ($[Mo_7O_{24}]^{6-}$). The presence of deliberately left Mo−O or Mo=O bonds in the O-MoS_2 lattice was confirmed by XPS and Raman spectroscopy characterization. HRTEM observations revealed that the as-synthesized O-MoS_2 had a coiled nanosheet morphology with highly distorted crystal lattice and defect-rich zones on its basal planes. EXAFS indicated the existence of four-fold and five-fold CUS Mo sites. As a result of the lattice defects, abundant active CUS Mo sites existed in the O-MoS_2, which functioned as active sites in the hydrogen transfer reduction of nitroarenes with formate in water.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used as obtained without further purification.

2.2. Catalyst preparation

The preparation of the O-MoS_2 was adapted from Xie et al [46]. Typically, 3.70 g $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (3 mmol, AHM) and 6.85 g thiourea (90 mmol) were dissolved in 105 mL distilled water and placed in an autoclave. The autoclave was tightly sealed in air and then placed in an oven thermally stabilized at 180 °C for 24 h, after which the autoclave was removed from the oven and allowed to naturally cool to room temperature. The solid product was centrifuged, washed with distilled water and ethanol, and then dried at 60 °C under vacuum. The final dry solid was O-MoS_2. O-MoS_2-Ar was also prepared by treating O-MoS_2 in an Ar flow at 250 °C for 3 h.

The chemical exfoliation of commercial 2H-MoS_2 (designated as ceMoS_2) was adapted from Chou et al [49]. 700 mg of 2H-MoS_2 powder was immersed in 10 mL of n-butyllithium (1.6 mol/L in hexane) and stirred for 48 h under Ar protection. After the stirring, 20 mL hexane was added to the mixture, and 0.36 mL H_2O was then added dropwise over 10 min under Ar flow. After 0.5 h, a further 200 mL of H_2O was added to the mixture. The mixture was then sonicated for 2 h to achieve exfoliation. The ceMoS_2 nanosheets were then centrifuged and washed with water and ethanol five times, and the final products were obtained after vacuum drying at room temperature.

MoO_3/2H-MoS_2 (MoO_3, 5 wt%) was prepared by impregnating 2H-MoS_2 (1.0 g) in 8 mL of AHM solution (61 mg). The extra solvent was evaporated on a metal heating plate at 120 °C. The obtained dry solid was then annealed at 500 °C for 2 h in Ar flow (30 mL/min). MoO_2/2H-MoS_2 (MoO_2, 5 wt%) was obtained by adding 2H-MoS_2 (1.0 g) to 8 mL of phosphomolybdic acid solution (7.5 g/L). The extra solvent was evaporated on a metal heating plate at 120 °C. The obtained dry solid was then reduced at 500 °C for 2 h in a H_2/N_2 (1/9) flow (30 mL/min) [28]. Partially oxidized 2H-MoS_2 (2H-MoS_2-O_2) was prepared by treating 2H-MoS_2 in an air flow (30 mL/min) at 400 °C for 0.5 h.

2.3. Characterization

X-ray diffraction (XRD) analyses were conducted on a Rigaku D/Max 3400 powder diffraction system with Cu K_α radiation (λ = 1.542 Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VGESCALAB MK2 spectrometer equipped with an Al K_α X-ray source ($h\nu$ = 1486.6 eV) operated at a voltage of 12.5 kV. The binding energy (BE) was calibrated with the C 1s signal (284.6 eV) as a reference. Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) equipped with a CCD detector using a He/Ne laser with a wavelength of 532 nm. High-resolution transmission electron microscopy (HRTEM) was carried out on an FEI Tecnai F30 electron microscope at an accelerating voltage of 300 kV.

X-ray absorption fine structure (XAFS) spectral measurements at the Mo K-edge (E_0 = 20000 eV) were performed at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under "top-up" mode with a constant current of 240 mA. The XAFS data were recorded under transmission mode with ion chambers. The energy was calibrated according to the absorption edge of pure Mo foil. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energy $\mu(E)$ were processed using background subtraction and normalization procedures, and are reported as "normalized absorptions". For the extended X-ray absorption fine