

Supporting Information

NiWO₄ nanoparticles : a promising catalyst for hydrodesulfurization

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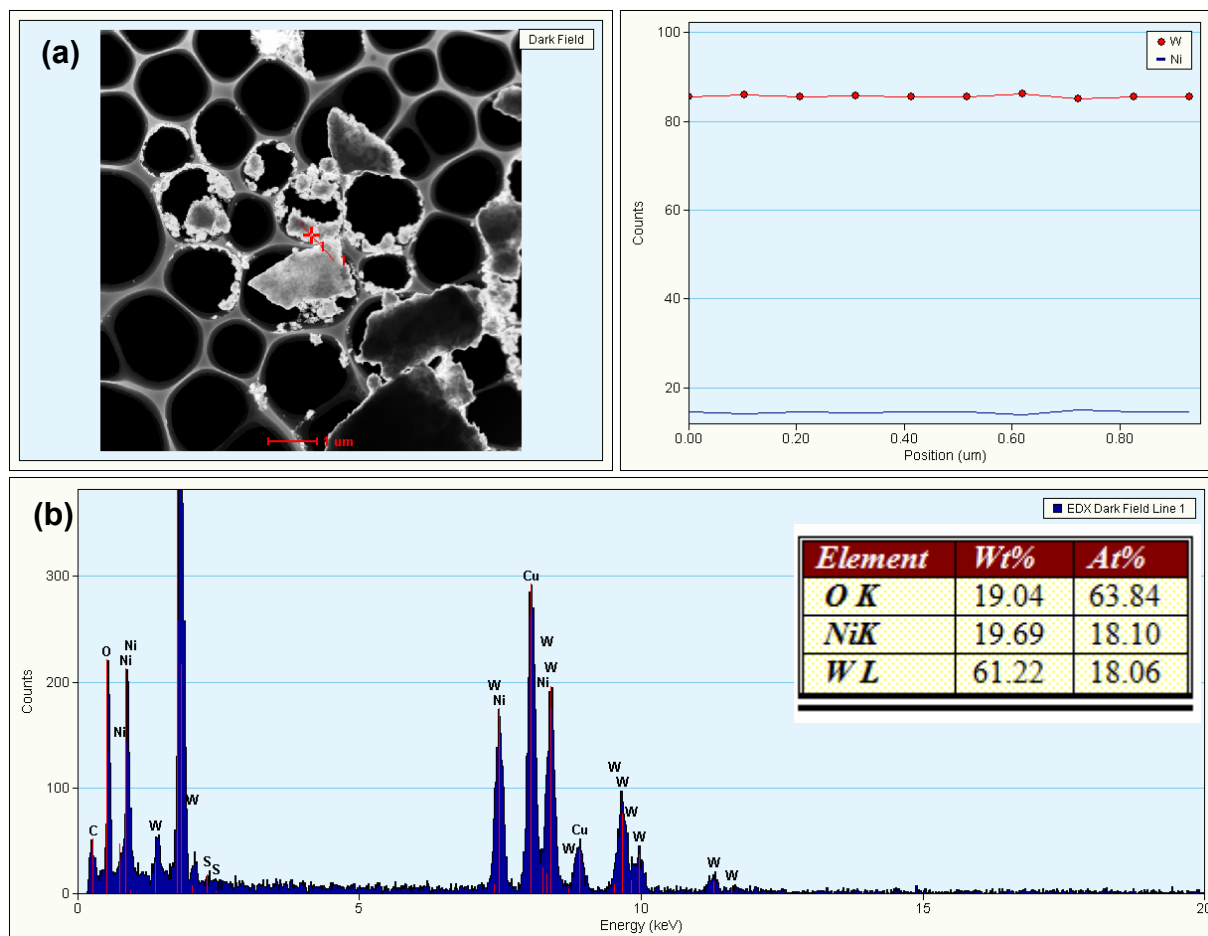
Materials synthesis and characterization

Synthesis of NiWO₄ nanoparticles

NiWO₄ nanoparticles were synthesized like following. Na₂WO₄•2H₂O (3.3 g, 0.01mol) was dissolved in 60 mL deionized water to form a transparent solution. Then, Ni(NO₃)₂•6H₂O (2.9 g, 0.01mol) was added into the solution under magnetic stirring. After half hour, the mixture was transferred into a Teflon-lined stainless steel autoclave, and then hydrothermally treated at 453 K for 4 h. Finally, products were filtered, washed **using deionized water about 5-6 L** and dried at 393 K for 4 h.

Characterization of NiWO₄ nanoparticles

X-ray powder diffraction (XRD) measurements were carried out on a Siemens D500 diffractometer (Cu K α radiation, wavelength = 1.54 Å, graphite monochromator) operating with a **voltage** of 30 kV. Diffractograms were recorded with the range of $2\theta = 5-65^\circ$ with a 0.05° step. The morphology was characterized by a **Jeol** 2010 transmission electron microscopy (TEM) operating at 200 kV. Elemental analysis was carried out with the energy dispersive X-ray spectrometer (EDX) attached to TEM instrument. EDX analysis is shown in SFig.1. Nitrogen adsorption-desorption was obtained using an ASAP model 2010 (Micromeritics) automated analyzer. The samples were outgassed at 423 K overnight under a residual pressure of 1 Pa. The total surface area was determined using the Brunauer–Emmett–Teller (BET) method. Temperature-programmed sulfidation (TPS) were carried out in a flow microreactor equipped with a Varian Cary 50 UV–Vis spectrometer to measure the evolution of H₂S at a fixed wavelength of 200 nm. **The catalyst was 0.15 g and the sulfidation was fulfilled using the gas mixture of H₂S, H₂ and Ar (H₂S:H₂:Ar=1:4:5) with a flow rate of 40 ml min⁻¹.** TPS patterns were registered during the sulfidation of the catalyst by monitoring the H₂S evolution versus temperature with UV – Vis.



SFig. 1 EDX analysis for as-synthesized NiWO₄ nanoparticles (a) EDX line analysis across a range about 1 μm, revealing atomic ratio of Ni/W is almost constant; (b) EDX elemental analysis, revealing the mole ratio of Ni:W:O is close to 1:1:4.

Catalytic experiments

Hydrodesulfurization of thiophene

The catalytic experiment was examined using a single-pass microreactor. The catalysts were crushed and sieved to select particles with the size in the 40–60 mesh range in order to eliminate diffusive effects. 1.5 g of catalyst was loaded in the constant temperature zone.

Prior to the catalytic tests, the catalysts were sulfided in situ using a *n*-hexane solution-containing 5 wt% CS₂ with a flow rate of 0.2 ml min⁻¹ under the hydrogen pressure of 4.0 MPa (180 ml min⁻¹). The sulfiding feed was injected at 423 K and the temperature was subsequently raised to 643 K and maintained 4 h at this value to ensure complete sulfidation. The feed was then switched to the reactant feed (*n*-hexane solution containing 10 wt% thiophene). The flow rate of reaction feed is 0.2 ml min⁻¹.

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The reaction temperatures were 553 K and 573 K, respectively. The whole reaction products were analyzed on-line every 30 min using a gas chromatograph (CE 2000) equipped with a capillary column (OV-17, length 25 m, internal diameter 0.25 mm). The tube between the reactor outlet and chromatograph inlet was heated at 523 K in order to maintain the products in the gas phase. The data reported in this paper were collected when the steady state was reached (*ca.* 24 h).

Hydrodesulfurization of 4,6-dimethyldithiophene (4,6-DMDBT)

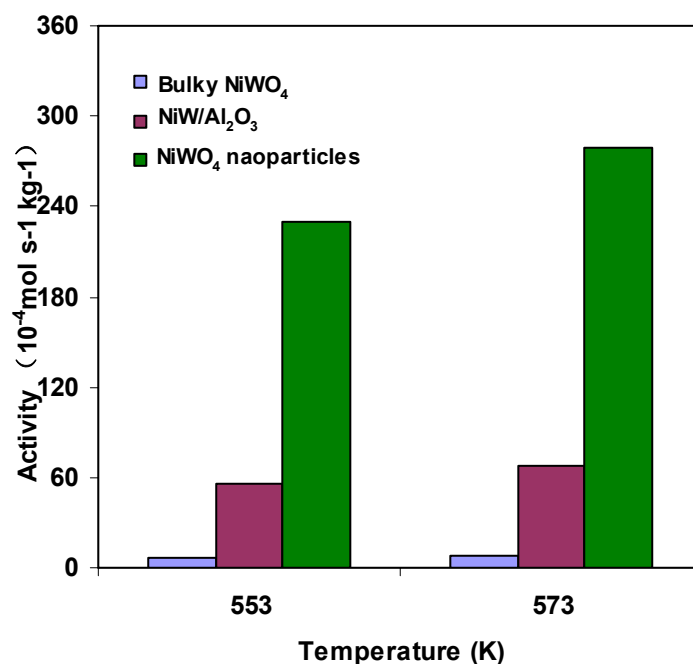
The whole reaction procedures are similar to those of thiophene except the followings:

Firstly, the sulfiding solution was *n*-decane solution containing 5 wt% CS₂.

Secondly, the reactant feed was *n*-decane solution containing 0.45 wt% 4,6-DMDBT and 0.45 wt% *n*-decalin as internal reference for quantitative analysis.

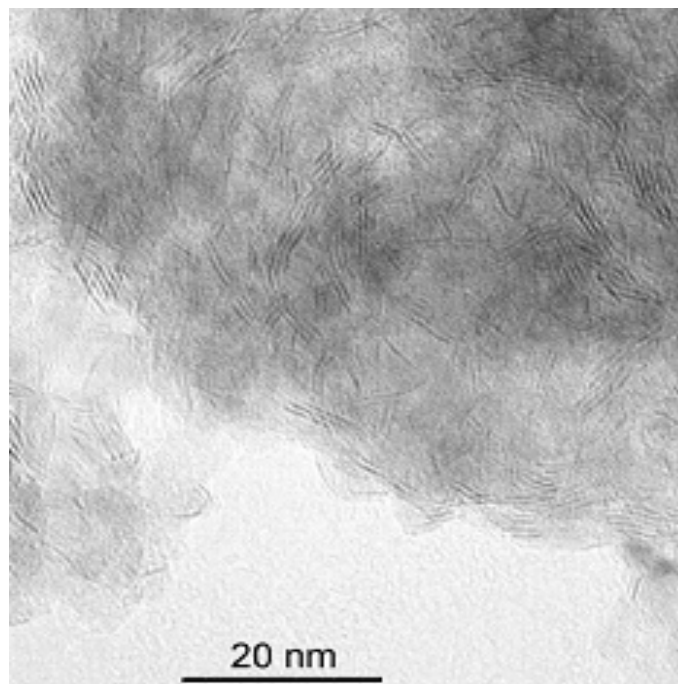
Thirdly, after 24 h reaction the reaction effluents were condensed and analyzed by chromatography.

SFig.2 shows the catalytic activities for 4,6-DMDBT HDS of various catalysts. Through the calculation, it can be seen that the catalytic activity of NiWO₄ nanoparticles is over 1.23 fold than that of NiW/Al₂O₃ on the metal basis.



SFig. 2 Catalytic activities for 4,6-DMDBT HDS of various catalysts.

Characterization for referenced catalysts



SFig. 3 TEM image for the in-situ sulfided NiW/Al₂O₃, revealing the average stacking layers are 3-4.