Constrained Growth of MoS_2 Nanosheets within a Mesoporous Silica Shell and Its Effects on Defect Sites and Catalyst Stability for H_2S Decomposition

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Abstract: A synthetic approach has been developed to encapsulate nanosized MoS_2 within a mesoporous silica shell. MoO_2 nanocores were first synthesized and coated with mesoporous silica, then converted to $MoS_2@SiO_2$. The MoS_2 nanosheets in $MoS_2@SiO_2$ are short, few-layered and highly curved, resulting in a high density of active catalytic sites. The $MoS_2@SiO_2$ catalyst was used for the decomposition of hydrogen sulfide (H_2S) to hydrogen gas and sulfur solid, demonstrating high catalytic turn-over frequency and thermal stability. Conversion was stable at 55% for up to 38h at 800°C for $MoS_2@SiO_2$, and short-term conversion was up to 67% with the nickel-doped catalyst.

Keywords: molybdenum disulfide, hydrogen sulfide, core-shell

1. Introduction

Molybdenum disulfide (MoS2) is a 2D transition-metal-dichalcogenide that forms a graphene-like layered structure, with inter-layer bound by weak van-der-Waals forces and a spacing of 0.61 nm.[1] MoS_2 has catalytic applications in hydrodesulfurization, hydrodeoxygenation, hydrodenitrogenation and synthesis gas conversion to alcohols. The active sites of MoS_2 are at edge sites at the end of nanosheets, or defects/sulfur vacancies along the basal plane.[2] Also, the bandgap of the MoS_2 nanosheets change when the number of layers is less than five. Hence, to improve catalytic activity of MoS_2, the nanosheets should ideally be small, thin, with sharp angles. Top-down synthesis methods such as exfoliation produce large crystals, while bottom-up synthesis method like chemical vapor deposition produces uniform large nanosheets with low density of edge sites.[3] Hydrothermal or solvothermal would be most suitable to synthesized nanosized MoS_2 nanoparticles. However, nanosized particles often agglomerate at high temperatures and lose long-term stability. Hence, MoS_2 should be synthesized nano-sized, but also well-supported or encapsulated to prevent sintering.

2. Experimental

MoO_2 nanocores were first synthesized by surfactant-assisted hydrothermal treatment, using ammonium heptamolybdate and polyvinylpyrrolidone (PVP) in water-ethanol co-solvent, treated at 180°C for 16 h. The MoO_2 cores were then coated with mesoporous silica shell using cetyltrimethylammonium chloride (CTAC) as surfactant and tetraethylorthosilicate (TEOS) as silica source, in water-ethanol co-solvent. Finally, $MoO_2@SiO_2$ was converted to $MoS_2@SiO_2$ by hydrothermal treatment with thioacetamide in water at 200°C for 24 h (Figure 1, top right). Co and Ni doping can be achieved by adding nitrate salts during the last step. Decomposition of H_2S was carried out in a quartz tube with 40 ml/min gas flow of 2500 ppm H_2S in N_2 with 50 mg of catalyst from 500-800°C at 1 atm. H_2 product was measured using gas chromatography (GC). Detailed information can be found in our publication.[4]

3. Results and discussion

The synthesized core-shell $MoS_2@SiO_2$ (Figure 1, left) has a 60 nm core comprising many MoS_2 nanosheets with high curvature, few layers and disoriented shape, which provides a high density of defect sites (active sites). The MoS_2 core is surrounded by mesoporous silica, confirmed by N_2 physisorption and

TEM imagery. XRD analysis shows low crystallinity, Raman analysis shows highly-strained nanosheets, and XPS analysis shows high concentration of defect sites.

When tested for H_2S decomposition, $MoS_2@SiO_2$ was found to have higher turnover frequency (TOF) than bulk MoS_2 or MoS_2 nanoparticles (with no mesoporous silica shell). Furthermore, $MoS_2@SiO_2$ was stable up to at least 38 h (55% H_2S conversion at 800°C) and showed less sintering and loss of active sites compared to bulk or nanoparticle MoS_2. Solid sulfur could be collected at the outlet of the reactor tube (Figure 1, bottom right). Doping with Ni or Co improved the catalytic performance further (long-term H_2S conversion: 57%).

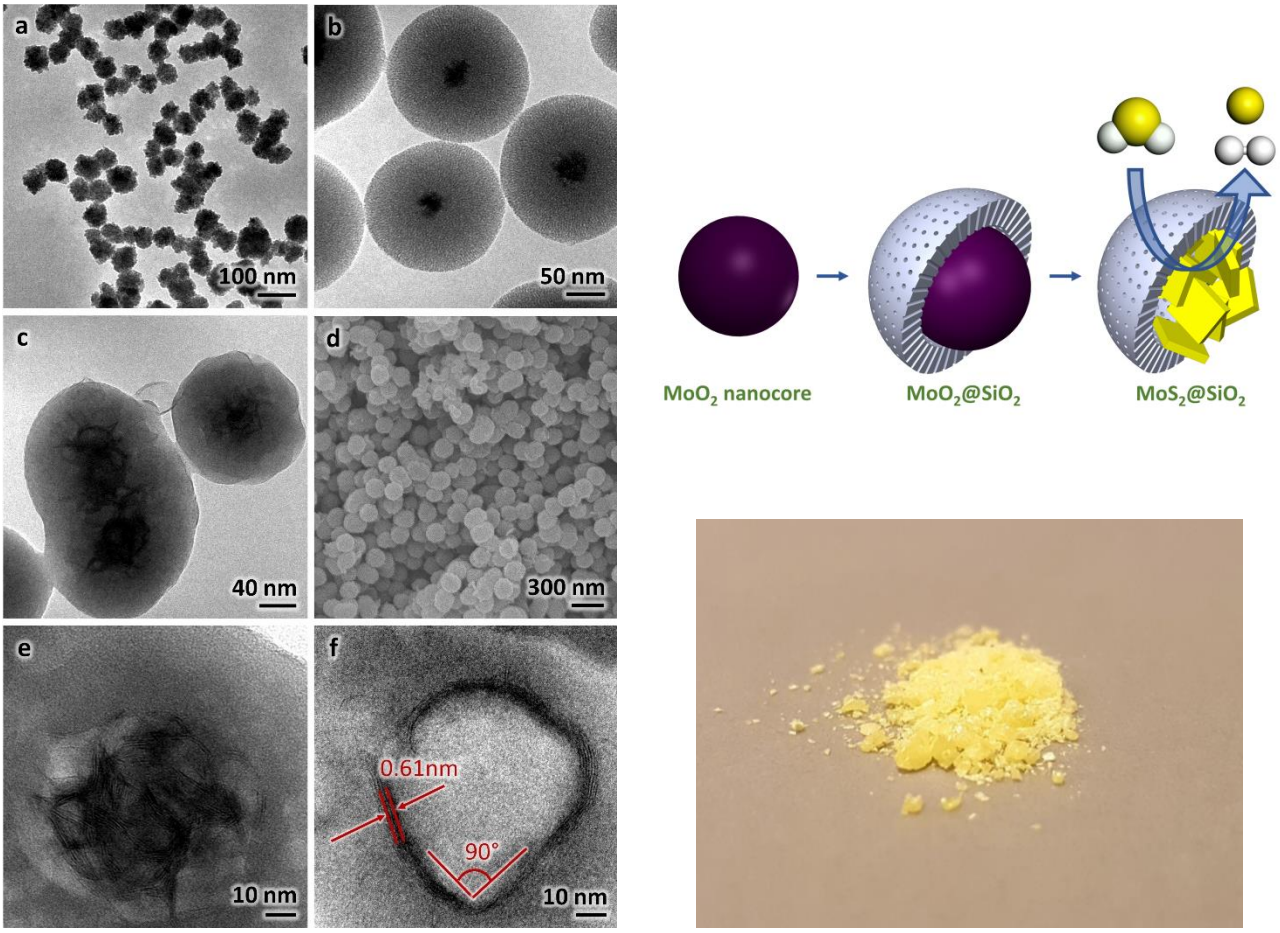

Figure 1. Left: TEM and SEM images of (a) MoO_2 nanocores, (b) $MoO_2@SiO_2$, (c-f) $MoS_2@SiO_2$; Top right: Synthesis route of $MoS_2@SiO_2$; Bottom right: solid sulfur collected after H_2S decomposition reaction.[4]

4. Conclusions

We have synthesized $MoS_2@SiO_2$ core-shell catalyst with highly-curved few-layered MoS_2 nanosheets constrained within a mesoporous shell. The catalyst has high turnover frequency and long-term stability for H_2S decomposition to H_2 and S. While currently H_2S is treated using the Claus process to yield water and sulfur, using the $MoS_2@SiO_2$ catalyst we can instead decompose H_2S to produce hydrogen as a clean energy source or as a recycle feed for hydrodesulfurization.[5]

References

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