Designing MoS2 nanocatalysts with high exposure of active edge sites for anthracene hydrogenation reaction

Donge Wang*, Yuxia Jiang, Jiahe Li, Min Li, Zhendong Pan, Huaijun Ma, Guang Lv, Wei Qu, Lin Wang, Zhijian Tian

Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
*Corresponding author:, dewang@dicp.ac.cn

Abstract: Designing MoS2 nanocatalysts with rich active edge sites by engineering of nanostructures is an effective strategy to enhance their catalytic activity. MoS2 nanoflowers with short slab of 5-10 nm, 3-5 stacking layers and expanded basal spacing of 0.98 nm were synthesized via a one-pot solvothermal synthesis method using high boiling point and viscosity ethylene glycol as solvent, and maximized the exposure of active edge sites. For the catalytic anthracene hydrogenation reaction in slurry-phase reactor, the hydrogenation percentage and selectivity to deep hydrogenation product of the MoS2 nanoflowers are respectively 3.2 times and 31.2 times as high as those of commercial MoS2.

Keywords: MoS2, anathracene hydrogenation, active sites.

1. Introduction

Layered transition metal dichalcogenides are generally considered as a significant kind of material for application in environmental and energy technology, displaying excellent properties in catalysis and many other fields. Various MoS2 nanostructures have been achieved by various methods, exhibiting exotic physical and chemical properties distinct from the bulk state. These studies inspire us to design MoS2 nanostructures with preferential exposure of active edge sites. To achieve this goal, we put forward that nano-scaled engineering may benefit the structural design to expose specific crystal planes. Thus, engineering nano-structure on the basal planes can be expected to increase the exposure of active edge sites by reducing the surfaces of the nanosheets, which may dramatically improve the catalytic hydrogenation performance. The polycyclic aromatics anthracene has been used as model compounds of heavy oil hydrogenation to research the structure-activity relationship of MoS2 catalysts.

2. Experimental

Ammonium heptamolybdate and elemental sulfur were dissolved in deionized water (DW) or ethylene glycol (EG) to form the suspension solution under constant stirring. And then hydrazine monohydrate (80%) was put in the above solution. The solution was transferred to a Teflon-lined stainless steel autoclave of capacity 100 mL, and heated o 180 °C for 24 h. MoS2 samples were harvested, and named as MoS2-DW and MoS2-EG. MoS2 -EG sample was annealed at 400 °C for 4 h in N2 and H2, and denoted as MoS2-CN and MoS2-CH. For comparison, commercial MoS2 was used and denoted as MoS2-Com..

Catalytic activity for polycyclic aromatic anthracene (A) hydrogenation was measured in a 100 mL slurry-bed Parr high pressure reactor. The reaction reactor was pressurized to 80 bar with hydrogen, thus heated to 623 K, and maintained at 623 K for 4 h under constant stirring with the stirring speed of 300 r.p.m.

3. Results and discussion

Fig. 1 shows the XRD patterns of commercial and synthesized MoS2 samples. The (002) diffraction peak of MoS2-Com. is located at 14.4° (JCPDS card:37-1492). But for MoS2-DW and EG, the splitting of the typical peak of (002), leads to two separated diffraction peaks located at 9.0° and 17.8°, respectively. The splitting can be attributed to the expansion of interlayers induced.
by the intercalation species. Calculated by the Bragg equation, the basal spacing of MoS$_2$-DW and EG is enlarged to 9.8 Å. The value of increasing basal spacing, 3.6 Å, matches well with the size of the NH$_4^+$ ion, 3.5 Å. Combined the results of element analysis and TG and EDX, the intercalation species can be NH$_4^+$ ion. Interestingly, it can be found that the diffraction peak of intercalated MoS$_2$ shifts from 9.0° to the high angle of 10.8° for MoS$_2$-CN, corresponding to basal spacing of 8.2 Å. For MoS$_2$-CH sample, the (002) peak in the XRD patterns appeared and located at 13.7°, corresponding to the basal spacing of 6.5 Å. Therefore, all the synthesized MoS$_2$ samples possess similar hexagonal 2H structure, but different basal spacings, which may be caused by the amounts of intercalated species.

Fig. 2 shows the catalytic hydrogenation selectivity to AH$_x$ with synthesized and commercial MoS$_2$ samples as the catalysts. Conversion of anthracene (A) to 9,10-dihydroanthracene (AH$_2$) can be easily achieved even under a low catalytic activity, but further conversion to tetrahydroanthracene (AH$_3$), octahydroanthracene (AH$_4$), and perhydroanthracene (AH$_8$) depend on the activity of catalysts. The selectivity of AH$_8$ increases from 2.5% for MoS$_2$-Com. catalyst to maximum 72.1% for MoS$_2$-EG, and then decreased to 17.0% for MoS$_2$-CH catalyst. Furthermore, for MoS$_2$-EG catalyst, the selectivity of AH$_{14}$ can reach 3.5%. For the A hydrogenation in slurry-phase reactor, nano-scaled MoS$_2$ catalysts demonstrate much higher selectivity to deep hydrogenation products (AH$_8$ and AH$_{14}$), especially, the selectivity to AH$_8$ of MoS$_2$-EG catalyst reached 31.2 times that of MoS$_2$-Com. catalyst.

The structure-activity relationship of MoS$_2$ catalysts was summarized in Fig. 3. The catalytic activity of AN hydrogenation with MoS$_2$ catalysts showed the same order with the expectation of active edge sites: MoS$_2$-EG > MoS$_2$-CN ~ MoS$_2$-DW > MoS$_2$-CH > MoS$_2$-Com.. It can be observed that micro-scaled bulk MoS$_2$ catalyst with larger stacking layer number exhibits very low HP, which means quite low catalytic activity of A hydrogenation. As the slab length and stacking layer number of MoS$_2$ catalysts decreased, the catalytic activity of A hydrogenation is enhanced dramatically. Overall, the catalytic hydrogenation activity of A hydrogenation for MoS$_2$ catalysts mainly depends on its exposure of active edge sites, which are decided by their nanostructures.

4. Conclusions

MoS$_2$-EG nanoflowers with maximum active edge sites were synthesized by one-pot solvothermal method with high boiling point and viscosity ethylene glycol as solvents. The nano-scaled MoS$_2$-EG nanosheets possess short slab length, few stacking layer and expanded basal spacing, which favor the exposure of active edge sites. For the catalytic A hydrogenation in slurry-phase reactor, hydrogenation percentage and selectivity to deep hydrogenation product of MoS$_2$-EG nanoflowers are respectively 3.2 times and 31.2 times as high as those of bulk MoS$_2$-Com. catalyst. The structure-activity relationship of MoS$_2$ catalysts suggest that adjusting the particle size and layer structures by engineering of nanostructures is a strategic direction for developing high active hydrogenation catalysts.

References