Designing MoS_2 nanocatalysts with high exposure of active edge sites for anthracene hydrogenation reaction

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Abstract: Designing MoS_2 nanocatalysts with rich active edge sites by engineering of nanostructures is an effective strategy to enhance their catalytic activity. MoS_2 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 MoS_2 nanoflowers are respectively 3.2 times and 31.2 times as high as those of commercial MoS_2.

Keywords: MoS_2, 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.[1] Various MoS_2 nanostructures have been achieved by various methods, exhibiting exotic physical and chemical properties distinct from the bulk state.[2] These studies inspire us to design MoS_2 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 MoS_2 catalysts.[3]

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. MoS_2 samples were harvested, and named as MoS_2-DW and MoS_2-EG. MoS_2 -EG sample was annealed at 400℃ for 4 h in N_2 and H_2, and denoted as MoS_2-CN and MoS_2-CH. For comparison, commercial MoS_2 was used and denoted as MoS_2-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.

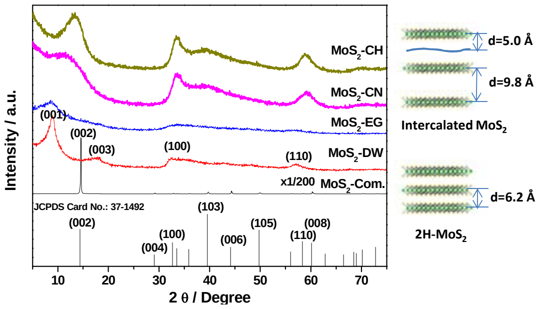

Figure 1. XRD patterns of commercial and synthesized MoS_2 samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of commercial and synthesized MoS_2 samples. The (002) diffraction peak of MoS_2-Com. is located at 14.4° (JCPDS card:37-1492). But for MoS_2-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 AHx 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_4), octahydroanthracene (AH_8), and perhydroanthracene (AH_{14}) 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.

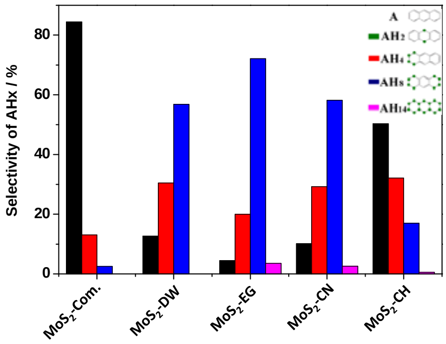

Figure 2. The selectivity and hydrogenation percentage of catalytic anthracene hydrogenation to AH_x on MoS_2 catalysts. Reaction conditions: catalyst, 0.075 g, anathracene, 3.0 g, solvent, tridecane, 30 g, P= 11 MPa, T= 623 K, t = 4 h.

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.

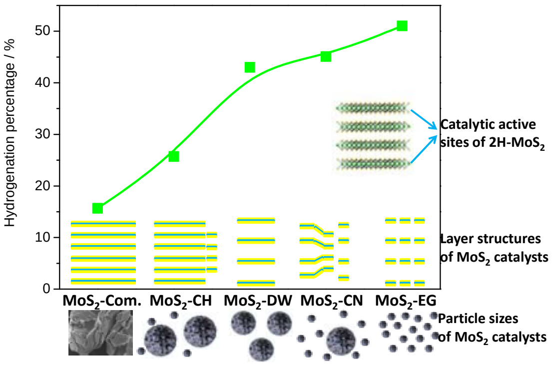

Figure 3. The schematic diagram for structure-activity relationship of MoS_2 catalyst in catalytic A

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.

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