Understanding selectivity changes during hydrodesulfurization of dibenzothiophene on Mo₂C/carbon catalysts

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Introduction

Mo₂C, a novel catalyst that has attracted attention due to its Pt-like behavior [1], has potential as an effective catalyst for S removal from crude oils. However, the stability of Mo₂C in the presence of S is not well established [2, 3]. In the present study, we report on the stability of β-Mo₂C catalysts supported on a high surface area activated petcoke (APC), during the hydrodesulfurization (HDS) of dibenzothiophene (DBT). The transformation of the Mo₂C during the HDS reaction is reported as a function of the Mo₂C particle size. Also, the dynamic transition of Mo₂C with time-on-stream is investigated. The effect of S on Mo₂C catalyst surface has been determined experimentally by several characterization methods (BET, XRD, XPS, and HRTEM). Furthermore, a density functional theory (DFT) calculation was applied to illustrate the impact of S on the binding energy of the DBT to the Mo₂C catalyst surface.

Materials and Methods

Activated petcoke (APC) was prepared by chemical activation to obtain a high surface area activated carbon (ca. 2000 m²/g) [4]. The prepared APC was impregnated with ammonium heptamolybdate (AHM). After solvent evaporation under vacuum, the impregnated sample was dried overnight at 110 ℃ to yield the precursor. Samples were prepared with different loadings of Mo. Carbothermal hydrogen reduction (CHR) was then applied with a ramp rate of 1 ℃/min, holding at the final temperature of 600~700 ℃ for 90 min prior to quenching to room temperature, to yield the APC supported β-Mo₂C (Mo₂C/APC). All the catalysts were passivated in 1%O₂/N₂ following synthesis.

The catalyst performance was assessed in a down-flow packed bed reactor (hot zone: 30 cm) using 314 ppm S from dibenzothiophene (DBT, 0.2 wt% in decalin) as reactant. Prior to the reaction, the passivation layer of the Mo₂C/APC was removed by reduction in H₂ at 400 ℃ for 2 h. The experiments were operated at 350 ℃ with a constant pressure of 4.1 MPa under H₂/feed of 600 and LHSV of 4 h⁻¹. The liquid products collected periodically were analyzed by GC-MS. Fresh and used catalysts were characterized using BET, XRD, XPS and HRTEM-EDX. A theoretical study by DFT calculation was performed to elucidate the influence of S on the surface of Mo₂C catalyst.

Results and Discussion

β-Mo₂C formation was confirmed by XRD, XPS and TEM. TEM results showed that the particle size of the Mo₂C increased with increased Mo loading from 2% to 10 wt%. The deconvolution of the Mo 3d XPS spectra indicated that the ratio of Mo₂C plus oxycarbide to Mo-oxide species was similar (~ 65:35) for all Mo loadings.
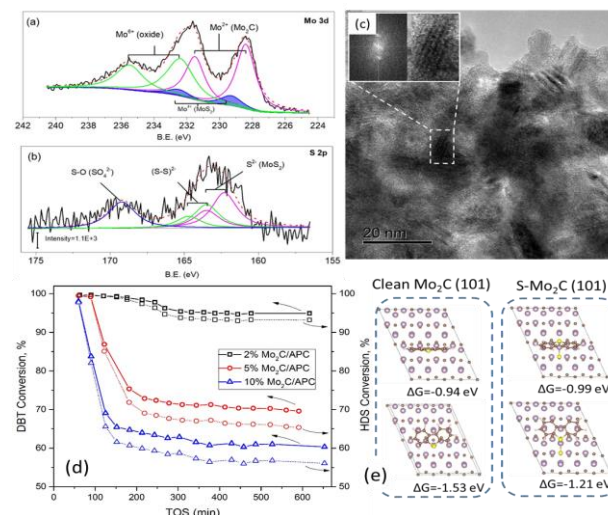
Figure 1. (a, b) XPS analysis of 5Mo₂C/APC catalyst after HDS; (c) TEM analysis of used 10Mo₂C/APC catalyst; (d) DBT conversion of Mo₂C/APC catalysts with different particle sizes; (e) DFT calculation of DBT adsorption energy on clean and s-adsorbed Mo₂C catalyst surface.

Experiments were conducted for ~500 min time-on-steam (TOS) in order to investigate catalyst stability in the presence of the S. After 600 min TOS and stabilized selectivity and conversion, MoS₂ formation was confirmed by multiple characterization methods as shown in Figure 1(a-c). Figure 1(d) shows that the conversion of DBT decreased and the product selectivity changed with reaction time before stabilizing. Since the catalyst characterization confirmed that S can change the Mo₂C structure and form MoS₂ species, S replacement of the carbon of Mo₂C must occur. Hence, DFT calculations to assess DBT adsorption on the Mo₂C (101) surface with different degrees of S replacement were completed (Figure 1(e)).

Significance

The present study demonstrates the mechanism of Mo₂C deactivation during HDS reaction. A MoS₂ overlayer is formed on the Mo₂C, resulting in irreversible deactivation and change in product selectivity.

References

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