Mechanistic consequences of Ni-promotion on the hydrogenation of phenanthrene over (Ni)MoS$_2$/Al$_2$O$_3$

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Introduction

Transition metal sulfides, particularly MoS$_2$ promoted with Ni, have been extensively studied as hydrotreating catalysts. Especially for hydrodesulfurization, detailed reaction pathways and models for active sites exist [1]. Hydrogenation of polyaromatic hydrocarbons has been less investigated despite its growing relevance for heavy oil conversion. The present contribution investigates the hydrogenation of phenanthrene as a model aromatic compound aiming at a deeper insight into the hydrogenation mechanisms on (Ni)MoS$_2$/Al$_2$O$_3$.

Materials and Methods

Ni-MoS$_2$/γ-Al$_2$O$_3$ was prepared by impregnation and thermal treatment in H$_2$/H$_2$S and characterized by a series of standard and advanced techniques as reported elsewhere [2]. The catalytic activity was explored in the hydrogenation of phenanthrene (Phe), or dihydronaphthalene (DiHPhe) at differential and integral conditions in a trickle-bed reactor at 60 bar, 553-583 K, and in the presence of H$_2$S.

The energetics of adsorption of the hydrocarbon on MoS$_2$ and Ni-MoS$_2$ were determined by density functional theory calculations using the QUANTUM ESPRESSO code employing ultrasoft pseudo-potentials to represent the core electrons. The BEEF-vdW [3] exchange correlation functional was used throughout.

Results and Discussion

MoS$_2$/Al$_2$O$_3$ and Ni-MoS$_2$/Al$_2$O$_3$ with similar Mo content, the bimetallic catalyst having a molar Ni/(Mo+Ni) ratio of 0.3, were studied. The Phe hydrogenation network given in Figure 1A was derived from experiments at integral conditions with Phe and DiHPhe as reactants. The mechanism is identical for MoS$_2$/Al$_2$O$_3$ and Ni-MoS$_2$/γ-Al$_2$O$_3$. However, the contribution of the deep-hydrogenation pathway ($k_2$, $k_4$, $k_6$) is significant only in the presence of Ni, which also increases the Phe and DiHPhe consumption rates by a factor of 2.2.

The reaction order in Phe (see Fig. 1B), around -0.65, was not influenced by the presence of Ni while the H$_2$ reaction order (see Fig. 1C) increased from 0.68 for MoS$_2$/Al$_2$O$_3$ to 1.2 for Ni-MoS$_2$/γ-Al$_2$O$_3$. Interestingly, the presence of Ni had no effect on the reaction over MoS$_2$/Al$_2$O$_3$ (zero order in H$_2$S) whereas it has a negative impact over Ni-MoS$_2$/Al$_2$O$_3$ (reaction order of -0.2). Combining the kinetic analysis and characterization of SH groups at the sulfide surface by IR-spectroscopy (which evidenced an acid character), allows to conclude that the hydrogenation of Phe occurs via stepwise proton addition and electron transfer in concerted mode. The rate determining steps are the first and second addition of hydrogen pairs for DiHPhe and tetrahydrophenanthrene (TetHPhe), respectively.

Combined IR and isotopic H-D exchange experiments showed that the concentration of active surface hydrogen increased by 30% in presence of Ni. This may explain the increased rate of DiHPhe formation. However, it does not account for the dramatic increase of TetHPhe production rates and the concomitant change in rds. Deep hydrogenation is concluded to occur on the Ni-decorated MoS$_2$ edges (characterized by IR-spectroscopy of CO) where DiHPhe and TetHPhe are formed at comparable rates.

In line with this proposal, DFT calculations indicate that Phe adsorbs strongly on the basal planes of MoS$_2$ where it may undergo hydrogenation without the participation of exposed cations. In contrast, the restructured Ni-decorated MoS$_2$ edges offer adsorption modes that lead to the activation and multiple hydrogenation of the terminal rings of Phe.

Figure 1. (A) Reaction network for the hydrogenation of phenanthrene. The blue arrows denote steps occurring on MoS$_2$/Al$_2$O$_3$ and Ni-MoS$_2$/Al$_2$O$_3$ while red arrows denote steps occurring only on the latter. (B) Reaction order in H$_2$ and; (C) reaction order in phenanthrene during the hydrogenation of phenanthrene on MoS$_2$/Al$_2$O$_3$ (●) and Ni-MoS$_2$/Al$_2$O$_3$ (○) at 573 K and 60 bar.

Significance

This study sheds light on the reaction pathways, active sites, and surface reactions involved in the conversion of aromatic hydrocarbons on sulfide catalysts. Special emphasis is put on understanding the effect of Ni on the hydrogenation functionality of MoS$_2$/Al$_2$O$_3$. Thus, the present results help to achieve more efficient conversion of heavy oils with the state-of-the-art hydrotreating technology.

References

