Support Effects in Hydrodesulfurization: a Combined Synchrotron XRD-Reactivity Approach

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Introduction

Support effects have been recognized for a long time to play a major role in hydrotreating catalysis [1]. However, despite a tremendous effort of research, the "support effect" in catalysis by sulfides is still controversial. This is related to the high degree of complexity of this effect due to the interplay of several parameters: electronic effects of the support, formation of species at the support-catalyst interface (Ti-S-Mo or Al-O-Mo) or influence of the support during the oxide-sulfide activation leading to different degrees of dispersion. Any progress in understanding the support effect must thus be based on catalytic systems for which the different parameters cited above are not interdependent. This can be achieved using a synthetic procedure based on the direct deposition of sulfide species onto the support without using an impregnation step [2]. Such a method avoids the non-reproducible formation of polymeric oxide species and leads to initial equivalent sulfiding conditions among the studied catalysts.

Using this approach, unpromoted and cobalt-promoted MoS_2 catalysts were then deposited on different Al_2O_3, TiO_2, ZrO_2 and SiO_2 supports presenting similar specific surface areas and porous volumes. Various metal loadings (1, 5 and 10 wt% Mo) were used to modify the interaction with the different supports. The different as-synthesized catalysts were then tested in the hydrodesulfurization of thiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) and were characterized using synchrotron(SR) XRD. This technique was successfully developed to provide a complete description of the degree of dispersion of supported MoS_2-based catalysts [3] and was applied here to evaluate the influence of the "support effect" on the morphology-reactivity relationships.

Materials and Methods

The catalysts were synthesized by deposition of ammonium tetrathiomolybdate (ATM) onto the different supports. For example, to prepare the 10 wt% MoS_2/Al_2O_3 catalyst, 0.5 mL of $N_2H_4.H_2O$ was dissolved in 30 mL water and a solution of 0.65 g ATM in 50 mL water was added. Then 2 g of γ-Al_2O_3 was suspended and the mixture was heated at 90°C for 4h. The samples were activated in 15% H_2S/H_2 flow at 550°C for 2h to maximize the active phase-support interaction. The catalysts were tested in the HDS of thiophene (Patm) and 4,6-DMDBT (30 bars H_2) at 340°C and were characterized by SR-XRD, TEM, TPR and LRS.

Results and Discussion

The high signal-to-noise ratio of the synchrotron source allows to observe the diffraction signals of MoS_2 even at very low loading (1 wt %) on strong interacting supports like TiO_2 (Figure 1) showing the interest of the SR-XRD technique for characterizing supported MoS_2-based catalysts. Moreover, application of a full scattering model [3] to evaluate the staking degree of the different samples reveals the formation of mainly single layers whatever the support. The SR-XRD characterization of the different supported catalysts was also performed before and after 4,6-DMDBT HDS test to evaluate the effect of the reaction conditions on the morphology of the different samples. For TiO_2-, SiO_2-, and ZrO_2-supported catalysts, a redispersion effect can be evidenced at low Mo loading (1 wt %) during the HDS test while at high loading (10 wt %), a limited sintering effect is observed. This situation differs from the Al_2O_3 case for which MoS_2 clusters are rather stable in size whatever the Mo loading. Correlations were then established for the different supported catalysts between morphology and activity results in the HDS of 4,6-DMDBT. Results showed that a strong interaction between MoS_2 and TiO_2 (or ZrO_2) at low Mo loading (1 wt %) results in very strong TOF values (resp. 9 and 6.5 times higher than on Al_2O_3) (figure 2). Increasing the metal loading (from 1 to 10 wt % Mo) decreases the support-active phase interaction and leads to lower TOF values for TiO_2- and ZrO_2-supported catalysts. Therefore, a beneficial support effect of titania and zirconia is clearly evidenced. This situation differs once again from the Al_2O_3 case: TOF increases 2.4 times when increasing the Mo loading from 1 to 10 wt% showing a negative influence of alumina on the intrinsic activity of MoS_2. Finally, TOF values hardly change on SiO_2 emphasizing the absence of support effects in this case. Similar results were also acquired for Co-promoted catalysts.
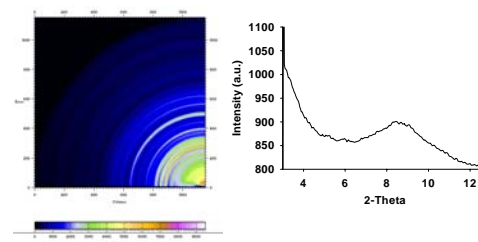

Figure 1. Ewald sphere section (left) and the resulting SR-XRD profile (right) of a 1 wt% MoS_2/TiO_2 catalyst. The (002) diffraction peak is clearly observed.
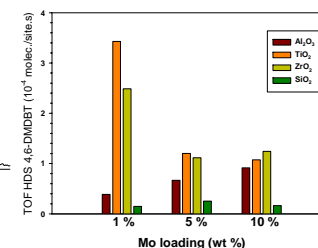
Figure 2. Evolution of the TOF values in the HDS of 4,6-DMDBT for 1, 5, and 10 wt% Al_2O_3-, TiO_2-, ZrO_2-, and SiO_2-supported MoS_2 catalysts.

Significance

A combined synchrotron XRD-activity approach using an all-sulfide route of synthesis allows determining the respective influence of different supports on the intrinsic activity of MoS_2-based catalysts. Beneficial effects of titania or zirconia can be evidenced. This approach can be generalized to study any support effect in hydrotreating catalysis

References

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