Intrinsic potential of supports for HDT revealed and assessed by clean CoMo preparation methods

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Introduction

In many countries, 2009 is the year of the 10 ppm sulfur in automotive fuels. To satisfy this strengthened regulation and to further reach the "zero sulfur" in transportation fuels, hydrotreating catalysts must always be improved. Low pressure hydrodesulfurization (HDS) catalysts usually consist of sulfided molybdenum slabs promoted by cobalt and supported over γ-alumina. The active phase is known to be the "CoMoS" phase, with Co decorating the edges of MoS_2 particles [1], and the formation of additional refractory phases, such as $CoMoO_4$ must be avoided or at least minimized. The CoMoS nanoparticles are composed of slabs, having a more or less hexagonal shape with two kinds of edges [2]. The promoter to molybdenum ratio in the slabs and the M edge to S edge repartition, which may be responsible for the activity and the selectivity of the promoted catalysts, might depend on the interaction between the active phase and the support.

One way to develop new catalysts is thus to tune support and active phase interactions by investigating the use of new supports such as silica, titania or aluminas with different textural and/or structural properties. However, it is well known that conventional preparation techniques, including pore volume impregnation, lead to catalysts with poor activity with respect to their γ-alumina-supported counterparts: by such techniques the active phase may be poorly dispersed or evenly promoted. This is the reason why, to control the formation of the active phase "CoMoS", new and clean preparation methods of promoted molybdenum-based catalysts, such as the CVD-technique have been developed [3].

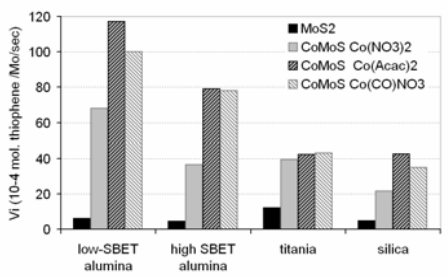
In this work, easy and clean preparation methods have been used to properly prepare promoted catalysts, and thus compare the intrinsic potential of the different supports for HDT purposes. It consists in an impregnation of the sulfided unpromoted catalysts by various Co precursors including Co(Acac) complexes decomposing on the MoS_2 edges. The supports chosen for this study are titania, silica as well as a low and a high surface area alumina. In the first part of this study, the preparation method was used for titania and γ-alumina (high surface alumina) to compare with earlier literature results. Results obtained were also compared with CVD technique using $Co(CO)_3NO$. Then those clean preparation methods were extended to silica and a low surface area alumina to assess their potential as new supports for HDT catalysts.

Materials and Methods

Molybenum has been impregnated on the different supports by using ammonium heptamolybdate (AHM). Since these supports have different textural properties, in particular very different specific surface area (100-280 m^2/g), the amount of molybdenum introduced was chosen in order to have the same surface density of molybdenum atoms on each support. The catalysts were further dried, calcined, and sulfided at 450°C. After sulfidation, the Co precursor was added by either classical $Co(NO_3)_2$ impregnation or using a complex such as $Co(acac)_2$.

All catalysts were evaluated in thiophene or 4,6-dimethyldibenzothiophene HDS. That last molecule also provided information on the catalysts selectivity since it reacts via two main routes (desulfurization (DDS) or hydrogenation (HYD)). The differences observed in activities and selectivities were rationalized using a thorough characterization of the catalysts including TEM, XPS and Infrared spectroscopy coupled with CO adsorption.

Results and Discussion



Results obtained for thiophene HDS are reported on the left hand side for all supports and all preparation methods. First, when focusing on the comparison of titania with γ-alumina supported catalysts it may be noticed that the unpromoted MoS_2/TiO_2 catalyst is the most active in HDS [4], and that the promoted catalysts supported on titania never reach the intrinsic activity level of their high surface area alumina counterparts, whatever the promoting method used. This is in accordance with the epitaxial relation between the MoS_2 particle and TiO_2 which has been reported in the literature [5]. Indeed, as a result of this epitaxial relation, unpromoted catalysts have a higher M-edge/S-edge ratio, which is not favorable for promotion on a CoMo catalyst [2]. On silica, high or low surface area aluminas, the choice of a clean promotion ("CVD" or "Acac" *Vs* "NO_3") method allowed a dramatic increase in HDS intrinsic activity, in accordance with XPS or IR(CO) indicating a better quality of promotion. The most interesting result is the catalytic behavior obtained for low-surface area alumina with clean preparation techniques. Here, properties of the support seem to play a key role, since we observe an M-edge to S-edge ratio favoring CoMo promotion with respect to γ-Al_2O_3. As a matter of fact, the low surface area Al_2O_3 also demonstrated a higher DDS/HYD selectivity.

Significance

In this work a new preparation technique was used to obtain clean promoted catalysts on silica, titania, high and low surface area aluminas. We checked that results obtained with this technique are consistent with earlier results published in the literature (titania *Vs* alumina, CVD). Catalytic results were rationalized by in depth characterization of the catalysts and show that low-surface area alumina is the most promising support due to a higher S-edge/Mo-edge, which allows a better promotion of the CoMo catalysts.

References

1. Topsøe, H., Candia, R., Topsøe, N.Y., Clausen, B.S., *Bull. Soc. Chim. Belg*. 93, 763 (1984)
2. Krebs, E., Silvi, B., Raybaud, P., *Catalysis Today* 130, 160 (2008)
3. Okamoto, Y., Ochiai, K., Kawano, M., Kobayashi, K., Kubota, T., *Appl. Cat. A: General* 226, 115 (2002)
4. Vrinat, M., Letourneur, D., Bacaud, R., Harlé, V., Leclercq, C., in "Hydrotreatment and hydrocracking of oil Fractions" p153 Elsevier ,Amsterdam, 1999
5. Costa, D., Arrouvel, C., Breysse, M., Toulhoat, H., Raybaud, P. *J. Catal* 246, 325 (2007)