

Influence of the sulfidation pressure on the hydrodesulfurization activity of supported CoMo sulfide catalysts

Emiel J.M. Hensen*, A.I. Dugulan and J.A.R. van Veen
Schuit Institute of Catalysis, Eindhoven University of Technology,
5600 MB Eindhoven, The Netherlands
*e.j.m.hensen@tue.nl

Introduction

The development of improved hydrodesulfurization (HDS) catalysts is essential in order to meet the tightening sulfur content of transportation fuels. Mixed CoMo sulfides supported on Al_2O_3 are the most important HDS catalysts. It is widely accepted that the most important factors that determine the catalytic activity of supported Co(Ni)Mo sulfides are the dispersion and morphology of the active phase [1]. Two types of Co-Mo-S phases have been introduced, a Type II in which all Mo–O–Al linkages with the support are completely sulfided with a two times higher activity in gas-phase desulfurization than the not fully sulfided Type I counterpart. The use of complexing agents, which decrease Mo-support interactions, improve Type II Co-Mo-S phase formation [2,3].

Nearly all results in the open literature concern catalysts sulfided at atmospheric pressure. We have now found that an increase of the sulfidation pressure improves catalytic performance considerably, even for catalysts which we would consider to consist of Type II Co-Mo-S. This deserves an explanation which we formulate on the basis of an extensive dataset of well-characterized alumina-supported CoMo and NiMo sulfide catalysts.

Materials and Methods

CoMo and NiMo catalysts were prepared by conventional impregnation techniques on alumina. In some cases, a chelating agent to induce type II active phase formation was used. With the expectation of these catalysts, all materials were calcined. Sulfidation was carried out in $\text{H}_2\text{S}/\text{H}_2$ at atmospheric pressure or at 40 bar. Catalysts were characterized by ^{57}Co Mössbauer spectroscopy (*in situ* sulfidation) and X-ray absorption spectroscopy (quasi *in situ* sulfidation) at Mo and Co K edges. The morphology and dispersion of a set of catalysts was evaluated from representative transmission electron micrographs of sulfided catalysts. Catalytic activity was determined in atmospheric gas-phase thiophene hydrodesulfurization and high-pressure gas-phase dibenzothiophene hydrodesulfurization as a function of sulfidation pressure.

Results and Discussion

Sulfidation at elevated pressure in a mixture of $\text{H}_2\text{S}/\text{H}_2$ leads to a better sulfidation of the active ‘Co-Mo-S’ phase in alumina-supported CoMo catalysts as evidenced by Co and Mo EXAFS and ^{57}Co Mössbauer spectroscopy. For calcined catalysts which typically have a Type I active ‘Co-Mo-S’ phase after sulfidation at atmospheric pressure the HDS activity is increased when the sulfidation pressure is increased. This is due to partial transformation to a more active ‘Co-Mo-S’ phase with an enhanced Type II character. It remains difficult to fully sulfide the active phase and only when Mo-support interactions are minimized in the precursor by the use of a chelating agent is it possible to prepare a pure Type II ‘Co-Mo-S’ phase after high-pressure sulfidation. Atmospheric pressure sulfidation of a CoMo-NTA catalyst leads to

an active ‘Co-Mo-S’ phase somewhere between the Type I and II. A reasonable indicator of the Type I/II character of the active phase appears to be the Mo-S coordination number derived from Mo K-edge X-ray absorption spectroscopy (Figure 1). From a large database of results, we abstract the following points regarding the phase I/II behavior of sulfided CoMo catalysts: (i) there is a continuum of active phase ‘Co-Mo-S’ structures ranging from a less active Type I phase having a strong interaction with the support up to a fully sulfided and possibly well-crystallized Type II ‘Co-Mo-S’ phase with a weak support interaction; (ii) a pure Type II end member is obtained after high-pressure sulfidation of a CoMo-NTA catalyst, whereas the earlier Type II phase resulting from an atmospherically sulfided CoMo-NTA catalyst should now be regarded as having an active phase with some Type I character.

Concomitant with reaching a full sulfidation degree in NTA catalyst, stacking of the MoS_2 slabs occurs. This stacking does not appear to influence gas-phase thiophene HDS much but impedes activity in gas-phase DBT HDS to some extent. The negative effect of stacking on the DBT HDS activity is reproduced for a set of supported NiMo sulfide catalysts. This result could point to some heterogeneity in the distribution of promoter phases on the edges of the slabs in direct contact with the support and the ones on top of that. Thus, the DBT HDS activity of CoMo-NTA catalyst sulfided at high-pressure (pure phase II) with a somewhat stacked MoS_2 morphology may be improved by limiting the stacking of the active phase. The most active catalyst in DBT HDS is a calcined CoMo catalyst and an important explanation seems to be that a large portion of the active phase consists of monolayer slabs. The active phase of this catalyst should be somewhere between a Type I and II ‘Co-Mo-S’ phase and thus further modifications to increase the sulfidation degree whilst keeping the stacking degree low should be the way to improve the activity.

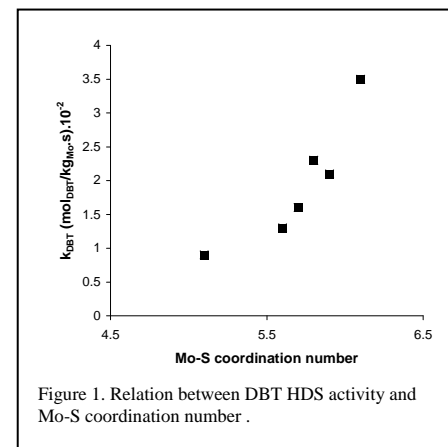


Figure 1. Relation between DBT HDS activity and Mo-S coordination number.

Significance

Optimal hydrodesulfurization catalysts should contain a pure type II Co-Mo-S type phase with a monolayer MoS_2 morphology. The formation of type II Co-Mo-S is very difficult for calcined CoMo/ Al_2O_3 due to the strong metal-support interaction.

References

1. Topsøe, H., Clausen, B.S., Massoth, F.E. “Hydrotreating catalysis”, Springer, Berlin, 1996.
2. Van Veen, J.A.R., Gerkema, E., Van der Kraan, A.M., Knoester, A., *J. Chem. Soc. Chem. Comm.* 1684 (1987).
3. Hensen, E.J.M., De Beer, V.H.J., Van Veen, J.A.R., Van Santen, R.A., *Catal. Lett.* 84, 59 (2002).