



The nature of the sulfur tolerance of amorphous silica-alumina supported NiMo(W) sulfide and Pt hydrogenation catalysts

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ABSTRACT

Amorphous silica-aluminas (ASA) based NiMo and NiW sulfide and Pt hydrogenation catalysts were prepared and compared in toluene hydrogenation in the presence of H₂S to alumina- and silica-supported reference catalysts with the aim to elucidate the influence of (strong) Brønsted acidity of the support on the sulfur tolerance. Despite precautions to prepare NiMo sulfide catalysts with equal morphology, the stacking degree of the MoS₂ phase was found to decrease with alumina content of the ASA. Similar but more pronounced differences of the stacking degree were observed among the NiW sulfide catalysts. This variation in the stacking degree had a substantial effect on the catalytic activity of dibenzothiophene hydrodesulfurization. ASA-based catalysts show higher activity and improved sulfur tolerance in toluene hydrogenation compared to their alumina- and silica-based counterparts. However, the sulfur tolerance does not correlate with the number of strong Brønsted acid sites, nor, indeed, with total Brønsted acidity. Instead, it decreases with increasing Al content of the ASA support. The sulfur tolerance of the active metal sulfide phase is related to the electronegativity of the support. That silica itself does not follow this trend is surmised to be due to its lack of Lewis acid sites, necessary for introducing the active phase-support effect.

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1. Introduction

Amorphous silica-aluminas (ASA) are technologically important acid catalysts, which are extensively used in the oil refining and petrochemical industry [1–3]. Although ASA are less acidic than zeolites, present-day composite hydrocracking catalysts often contain ASA next to steam stabilized Y zeolite. ASA are the main acid component in diesel-selective hydrocracking catalysts [3]. In hydrocracking catalysts, an additional purpose of ASA is to disperse the hydrogenation function, which nearly always consists of the mixed metal sulfides of Ni and Mo or Ni and W. The use of noble metals such as Pt and PtPd has also been explored [4], specifically for two-stage hydrocracking processes [2] and for deep hydrogenation of aromatics [5]. Mixed sulfide combinations of NiMo, CoMo and NiW are also the essential ingredients of hydrotreating catalysts extensively used to remove hetero-atoms from organosulfur and organonitrogen compounds in distillate streams in oil refineries [6–8].

The resistance of hydrogenation catalysts against sulfur poisons is a critical issue in refinery practice because of the high sulfur content in crude oil feedstock. Noble metals such as Pt exhibit a lower sulfur tolerance than mixed metal sulfides [4]. The acidity of the

support has long been known to enhance the tolerance of noble metal catalysts towards poisons. This beneficial effect is more substantial for zeolites than for less acidic amorphous silica-aluminas [9,10]. A similar influence of the support acidity on the sulfur tolerance has been reported for CoMo and NiMo sulfide catalysts [11–14].

Despite considerable efforts the mechanism of sulfur poisoning of hydrogenation catalysts has not been unequivocally determined. An explanation that is well accepted for the combination of acidic zeolite-noble metal is a change in the metal-sulfur bond strength due to enhanced electron deficiency of the metal particles [15–18]. It has been argued that very small noble metal particles interact with strong Brønsted acid sites. An alternative is the direct involvement of the acidic sites at the perimeter of the metal nanoparticles in the catalytic action [10,19–26].

The role of acidity on amorphous silica-alumina based hydrogenation catalysts is less well-explored. Lercher and co-workers have shown that the aromatics hydrogenation activity of Pt/ASA varies with the intermediate electronegativity of the support containing Lewis acid sites [27]. The role of Lewis acid sites interacting with the metal particles was stressed. More recently, the same group attributed the higher sulfur tolerance of Pt/ASA compared to Pt/Al₂O₃ to reactant adsorption on Brønsted acid sites close to the metal particles in case the metal surface is covered by sulfur-containing compounds [21]. Hensen et al. [28] have discussed the increased sulfur tolerance of sulfided Co(Ni)Mo/ASA in terms of a

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