



Improving the selectivity to HDS in the HDT of synthetic FCC naphtha using sodium doped amorphous aluminosilicates as support of CoMo catalysts

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ABSTRACT

CoMo catalysts supported on sodium-doped amorphous aluminosilicates (ASA) with different Si/(Si + Al) ratios were prepared. The catalytic performance of these catalysts in the HDT of synthetic FCC naphtha was compared with the one of a CoMo catalyst supported on pure alumina, as well as with another one supported on sodium-modified alumina. The catalysts results were also compared with the ones of CoMo catalyst supported on ASA without sodium. The catalysts were characterized by XRF, XRD, Raman, as well as their textural and acid properties. The sodium introduction simultaneously with the variation of the Si/(Si + Al) ratio conducts to obtain a catalyst (15% Si/(Si + Al), 3 wt.% Na) with, on the one hand, an Mo oxide species distribution with an important participation of β -CoMoO₄ crystalline species and, on the other hand, a selective formation of weak Brønsted acid sites. As a consequence of this especial balance between the acid properties and the oxidic Mo-surface-species distribution, this catalyst presented an activity similar to the one of the CoMo/Al₂O₃, but with improvements in the selectivity to HDS. Additionally, it was also encountered that when CoMo catalysts supported on materials of predominantly acidic nature are used, the linear olefins inhibit more the HDS activity than the branched ones, whereas the contrary effect was encountered when supports of a predominantly basic nature are used.

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1. Introduction

The challenge with the deep hydrotreatment (HDT) of the fluid catalytic cracking (FCC) naphtha constitutes to remove the maximum of sulfur impurities avoiding olefin saturation [1]. Thus, it is imperative to search for catalysts that are more selective to the hydrodesulfurization (HDS) than the conventional CoMo/Al₂O₃ [1]. Support modification appears as one of the variables explored in literature, either by modifying the classical alumina or by using completely different materials [1–9]. Many works claim that an increment in the hydrodesulfurization/hydrogenation of olefin (HDS/HYDO) selectivity can be observed using less acidic carriers than classical γ -alumina [5,9,10]. However, improvements of the HDS/HYDO selectivity can be found using more acidic catalysts [6,9,11]. Thus, there is not a clear position about the effect of support in the HDS/HYDO selectivity and, specifically, about the involvement of its acid–base properties.

In a previous article [12], CoMo catalysts supported on amorphous aluminosilicates with different Si/(Si + Al) ratios were essayed in the HDT of a synthetic naphtha. It was encountered that the Brønsted acidity of these catalysts increased with the Si/(Si + Al) ratio, producing acid-type reactions, such as cracking and isomerization of olefins and the alkylation of 2-methylthiophene (2-MT) with olefins [12]. These acid-type reactions competed with the HDS and the HYDO, and in the case of the catalysts with the highest Si content, even inhibiting them completely [12]. From the analysis of the product distribution of these reactions, it was concluded that a way to inhibit olefin saturation was by achieving an acid–properties balance such that the double-bond and skeletal isomerization reactions are promoted, but cracking is avoided. As a consequence, the HYDO could be inhibited by a double effect. On the one hand, olefins that are more difficult to hydrogenate are produced by double-bond isomerization [1,5,8,13]. On the other hand, there is competition for the adsorption of olefins between the acid sites and the HYDO ones [12]. However, it was concluded that the variation of the Si/(Si + Al) ratio only was not enough to finely control the acid properties [12].

Some authors have succeeded in finely controlling the acid–base properties of their catalysts by combining one modification that conducts to improve the acidity with another that conduct to reduce it [4,9]. For instance, La Parola et al. [4] showed that

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