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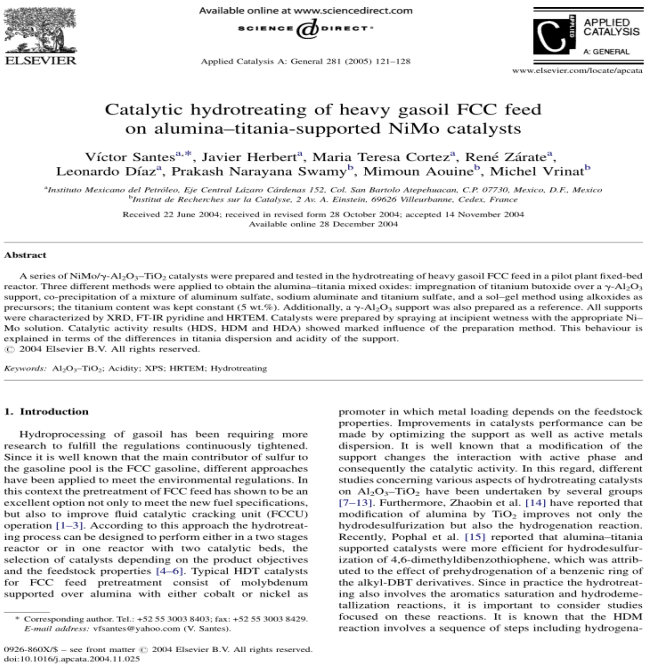

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Catalytic hydrotreating of heavy gasoil FCC feed on alumina–titania-supported NiMo catalysts

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Abstract

A series of NiMo/γ-Al_2O_3–TiO_2 catalysts were prepared and tested in the hydrotreating of heavy gasoil FCC feed in a pilot plant fixed-bed reactor. Three different methods were applied to obtain the alumina–titania mixed oxides: impregnation of titanium butoxide over a γ-Al_2O_3 support, co-precipitation of a mixture of aluminum sulfate, sodium aluminate and titanium sulfate, and a sol–gel method using alkoxides as precursors; the titanium content was kept constant (5 wt.%). Additionally, a γ-Al_2O_3 support was also prepared as a reference. All supports were characterized by XRD, FT-IR pyridine and HRTEM. Catalysts were prepared by spraying at incipient wetness with the appropriate Ni–Mo solution. Catalytic activity results (HDS, HDM and HDA) showed marked influence of the preparation method. This behaviour is explained in terms of the differences in titania dispersion and acidity of the support.

Keywords: Al_2O_3–TiO_2; Acidity; XPS; HRTEM; Hydrotreating

1. Introduction

Hydroprocessing of gasoil has been requiring more research to fulfill the regulations continuously tightened. Since it is well known that the main contributor of sulfur to the gasoline pool is the FCC gasoline, different approaches have been applied to meet the environmental regulations. In this context the pretreatment of FCC feed has shown to be an excellent option not only to meet the new fuel specifications, but also to improve fluid catalytic cracking unit (FCCU) operation [1–3]. According to this approach the hydrotreating process can be designed to perform either in a two stages reactor or in one reactor with two catalytic beds, the selection of catalysts depending on the product objectives and the feedstock properties [4–6]. Typical HDT catalysts for FCC feed pretreatment consist of molybdenum supported over alumina with either cobalt or nickel as promoter in which metal loading depends on the feedstock properties. Improvements in catalysts performance can be made by optimizing the support as well as active metals dispersion. It is well known that a modification of the support changes the interaction with active phase and consequently the catalytic activity. In this regard, different studies concerning various aspects of hydrotreating catalysts on Al_2O_3–TiO_2 have been undertaken by several groups [7–13]. Furthermore, Zhaobin et al. [14] have reported that modification of alumina by TiO_2 improves not only the hydrodesulfurization but also the hydrogenation reaction. Recently, Pophal et al. [15] reported that alumina–titania supported catalysts were more efficient for hydrodesulfurization of 4,6-dimethyldibenzothiophene, which was attributed to the effect of prehydrogenation of a benzenic ring of the alkyl-DBT derivatives. Since in practice the hydrotreating also involves the aromatics saturation and hydrodemetallization reactions, it is important to consider studies focused on these reactions. It is known that the HDM reaction involves a sequence of steps including hydrogena-

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