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ScienceDirect
Catalysis Today 130 (2008) 327–336
CATALYSIS TODAY
www.elsevier.com/locate/cattod

CoMo/MgO–Al_2O_3 supported catalysts: An alternative approach to prepare HDS catalysts

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Available online 3 December 2007

Abstract

Three different supports were prepared with distinct magnesia–alumina ratio $x = MgO/(MgO + Al_2O_3) = 0.01$, 0.1 and 0.5. Synthesized supports were impregnated with Co and Mo salts by the incipient wetness method along with 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) as chelating agent. Catalysts were characterized by BET surface area, Raman spectroscopy, SEM-EDX and HRTEM (STEM) spectroscopy techniques. The catalysts were evaluated for the thiophene hydrodesulfurization reaction and its activity results are discussed in terms of using chelating agent during the preparation of catalyst. A comparison of the activity between uncalcined and calcined catalysts was made and a higher activity was obtained with calcined MgO–Al_2O_3 supported catalysts. Two different MgO containing calcined catalysts were tested at micro-plant with industrial feedstocks of heavy Maya crude oil. The effect of support composition was observed for hydrodesulfurization (HDS), hydrodemetallization (HDM), hydrodeasphaltenization (HDAs) and hydrodenitrogenation (HDN) reactions, which were reported at temperature of 380 °C, pressure of 7 MPa and space-velocity of 1.0 h^{-1} during 204 h of time-on-stream (TOS).
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Keywords: Chelating agent; Al_2O_3–MgO supported catalysts; Maya crude hydrotreating

1. Introduction

Environmental regulations are focusing in reducing the level of pollutants by diminishing at lower level of sulfur, nitrogen and metals (particularly Ni and V) contents in commercial fuels. For this reason, refiners need to decrease the concentration of contaminants such as sulfur in petroleum fractions particularly gasoline and middle distillates. Hydrodesulfurization is an important hydrotreating process (HDT) by which this target can be reached by modifying the support properties of the catalysts or by increasing the severity of the reaction. Among them, the modification of the support particularly mixed oxides and catalyst properties is more suitable and less expensive [1,2]. The use of mixed oxides is not new, which assessed the catalytic functionalities of sulfided CoMo catalysts, and their dependence on the nature of the support and incorporation of additives. Common supports for hydrodesulfurization of petroleum are alumina-based [3]. The incorporation of MgO, SiO_2, TiO_2 and ZrO_2 with Al_2O_3 modifies the nature of active phase interactions on the support surface [4]. Therefore, these oxides play a structural promoting role to the support contribution and its interaction towards the active metal [5].

Particularly MgO–Al_2O_3, recently [6–10] showed that the support basicity might be favorable increasing the interaction between support and acidic molybdenum species (MoO_3). Therefore, the use of MgO–Al_2O_3 as a basic support can present a wide range of textural properties making it useful as a support for HDT catalysts. Apart from the support composition, remarkable improvements in HDS activity of CoMo and NiMo catalysts can be achieved by the addition of chelating agent during the preparation of catalysts [11–18]. These complexing agents have been found to be very effective in the formation of highly active CoMoS sites with extremely high selectivity by suppressing Mo-support interactions. According to Cattaneo et al. [13] the role of the chelating ligand is believed to change the sulfiding mechanism of Ni by complexing with Ni, which subsequently leads to a higher dispersion of the promoter on the edges of the MoS_2 slabs. The chelating ability of the described ligands is closely related to the pH of the impregnation solution. The metal ion/chelate ratio in the complex depends on the overall metal ion/chelate ratio in solution, the presence of other ligands or metal ions and the pH. It is seen that sulfidation of the

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doi:10.1016/j.cattod.2007.10.105