Applied Catalysis A: General 425–426 (2012) 1–12

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Activity and surface properties of NiMo/SiO_2–Al_2O_3 catalysts for hydroprocessing of heavy oils

Carolina Leyva[a], Jorge Ancheyta[a,*], Arnaud Travert[b], Françoise Maugé[b], Laurence Mariey[b], Jorge Ramírez[c], Mohan S. Rana[d]

[a] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Mexico City 07730, Mexico
[b] Laboratoire Catalyse et Spectrochimie, CNRS-ENSICAEN, Université de Caen, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France
[c] UNICAT, Departamento de Ingeniería Química, Facultad de Química, UNAM, Cd. Universitaria, Coyoacán, Mexico City 04510, Mexico
[d] Kuwait Institute for Scientific Research, PRD, P.O. Box 24885, Safat 13109, Kuwait

ARTICLE INFO

Article history:
Received 24 August 2011
Received in revised form 2 February 2012
Accepted 10 February 2012
Available online 28 February 2012

Keywords:
NiMo/SiO_2–Al_2O_3 catalysts
FT-IR
CO adsorption
Hydrotreating
Heavy oil

ABSTRACT

NiMo/SiO_2–Al_2O_3 mixed oxide supported catalysts were investigated for hydroprocessing of heavy crude oil at moderate reaction conditions. Hydrodesulfurization (HDS), hydrodemetalization (HDM), hydrodeasphaltenization (HDAs) and hydrodenitrogenation (HDN) reactions were studied as function of time-on-stream (TOS). The results indicated that HDS of crude oil corresponds to the number of active metal sites (sulfide phases) present in the catalyst, HDN is enhanced when the catalyst presents a combination of well dispersed sulfide phases and weak to moderate acidity. HDM presented a complex behavior indicating that it is affected significantly not only by the dispersion of the sulfide phase but also by the porosity and acidity of the catalyst. As expected, for HDAs both acidity and textural properties are important. The stability of the catalyst with time-on-stream was affected by coke and metals deposition. The supports and fresh catalysts were characterized by nitrogen physisorption, SEM-EDX, and FT-IR of CO and pyridine adsorption. The results confirm that NiMo/SiO_2–Al_2O_3 catalysts are a good option for the hydrotreatment of heavy oils and that the method used here for support preparation can tune the formation of meso- or macro-porosity and the type and strength of the catalyst acid sites.

1. Introduction

The interest in heavy crude oils increases to meet the growing worldwide energy demand, additionally, the quality of crude oil is decreasing since petroleum sources are changing into heavy and extra-heavy crude oils [1–7]. These heavy crudes have very high content of bottom of barrel (residua) and their fractionation renders low amounts of distillates with large investment in distillation plants. Hence, it is necessary to upgrade them before distillation [8] in order to convert the large molecules (mainly asphaltenes and metal porphyrins) into low molecular weight fractions, preferably middle distillates and gasoline, while removing at the same time some of the sulfur, nitrogen and metal impurities.

The main problems involved in heavy crude oil hydroprocessing are pore diffusion limitations preventing the access of large molecules to the active sites and the rapid deactivation of the catalyst by coke and metal deposition [9–11]. Tackling these problems requires bifunctional catalysts having a support with (i) sufficient pore diameter to improve metal deposition and pore diffusion [12–15]; (ii) adequate acidity to efficiently crack large molecules while limiting overcracking and coke formation; and (iii) optimum dispersion of active metals. Because of the flexibility of their preparation routes, amorphous SiO_2–Al_2O_3 mixed oxides can be tuned to the required acidic and textural properties [16–18] and appear as good candidates for such processes [19–23].

The combination of properties of silica and alumina oxides could have a positive impact on hydrotreating and make them potentially attractive as supports for heavy oil hydroprocessing catalysts [24]. Many detailed studies have been reported for catalytic hydroprocessing of model molecules or middle distillates [25–33], however, the relationship between the supported sulfide phase and heavy oil hydroprocessing functionalities is not yet totally understood, especially when heavy crude oil with high content of asphaltenes containing high heteroatom concentration is used as feedstock [33]. The aim of the present study is then to investigate the impact of support chemical composition, textural properties, surface acidity, and sulfide phase dispersion on the functionalities of NiMo/SiO_2–Al_2O_3 catalysts for the hydroprocessing of heavy oil. To this aim, a series of NiMo catalysts supported on SiO_2–Al_2O_3 presenting a wide range of acidic and textural properties were prepared, characterized and tested for hydrocracking of heavy Maya crude oil.

---

* Corresponding author. Tel.: +52 55 9175 8429; fax: +52 55 9175 8429.
E-mail address: jancheyt@imp.mx (J. Ancheyta).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.02.033