



Effect of modification of the alumina acidity on the properties of supported Mo and CoMo sulfide catalysts

Wenbin Chen^{a,b}, Françoise Maugé^{a,*}, Jacob van Gestel^a, Hong Nie^b, Dadong Li^b, Xiangyun Long^b

^a Laboratoire de Catalyse et Spectrochimie, ENSICAEN – Université de Caen – CNRS, 6 bd Maréchal Juin, 14050 Caen, France

^b Research Institute of Petroleum Processing, SINOPEC, 18 Xue Yuan Road, 100083 Beijing, PR China

ARTICLE INFO

Article history:

Received 7 December 2012

Revised 4 March 2013

Accepted 6 March 2013

Available online 10 May 2013

Keywords:

Hydrotreatment

HDS

Sulfide catalyst

Acidity

Boron on alumina

IR spectroscopy

Water

Brønsted acidity

ABSTRACT

Aluminas with different boron loadings were prepared by impregnation with H_3BO_3 solutions and then used to prepare pure Mo and CoMo catalysts. According to infrared (IR) spectroscopy of 2,6-dimethylpyridine, the acid properties of the alumina have been finely tuned by boron addition. The effect of alumina acidity change on the properties of sulfided Mo and CoMo has been characterized using transmission electron microscope, X-ray photoelectron spectroscopy, and IR spectroscopy of CO-adsorption as well as model compound reactions as thiophene hydrodesulfurization (HDS), 4,6-dimethylbenzothiophene (4,6-DMDBT) HDS and 2,6-dimethylaniline (DMA) hydrodenitrogenation (HDN). The acidity change of alumina has a direct influence on the electronic properties of MoS_2 and CoMoS sites but not substantially modifies the morphology and dispersion of the sulfide phase. The results point out a relationship between the Brønsted acidity of the support and the electronic properties of the MoS_2 and CoMoS phase. The change of the electronic properties of the active sites has a marked positive influence on the hydrogenation activity of the active phase. The performances of the Mo and CoMo catalysts in the reactions of HDS of thiophene and 4,6-DMDBT and HDN of DMA have been related to the variations of the structural and electronic properties resulted from boron addition.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Hydrotreating (HDT) catalysts have been of worldwide interest from applied and fundamental points of views for several decades due to their important applications in crude oil fraction upgrading [1–11]. The catalytic properties of the current hydrotreatment catalysts need to be enhanced to meet the requirements of the ever-increasing stringent environmental regulations in the near future [12–15]. The industrial hydrotreating catalysts are commonly composed of sulfides of Mo(W) as active components and Co(Ni) promoters supported on γ -alumina. Accordingly, the strategies to improve the performances of catalysts are mainly focused on the aspects of the preparation methods, the active phase genesis, and the support characteristics [7,16–20]. With respect to the supports, many materials have been attempted to substitute pure alumina support in several HDT processes, as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrocracking (HC) [7,19,21–25]. The development of acidic supports represents one of the attractive directions. Tuning the support acidity is usually realized by introducing additives into the γ -alumina, such as boron, fluorine, phosphorus, silicon, zeolites [7,21–23,26,27]. It is generally

shown that the presence of acidic species in alumina has a beneficial effect on the catalytic properties of the catalysts [7,22].

Hence, a control of both the acidic properties of the support and the active sites of the sulfide phase is a key point to design optimal catalysts. The effect generated by modifying the acidic sites of the support could have several origins such as a change of dispersion and morphology of the sulfide phase, adjustment of the sulfide-support interactions, modification of the catalytic functions by a synergetic effect between the acidic species and the active components of the catalyst or by the direct involvement of acidic sites of the support [28–32].

Hédoire et al. [33] studied the role of acidity of the support on the hydrogenation properties of a series of Mo/ β -zeolite catalysts by means of infrared (IR) spectroscopy of adsorbed CO at low temperature. The results showed that the enhancement of activity in hydrogenation was related to the electron deficient character of the sulfide phase in the acidic zeolite. Another study by Maugé et al. [34] concerning sulfided NiW catalysts supported on amorphous silica alumina (ASA) with various Si/Al ratios pointed out a good relationship between hydrogenation activity and the electronic properties of the sulfide phase which was modified by the support acidity. Mey et al. [35] used potassium to decrease the acidity of a commercial CoMo/ Al_2O_3 catalyst and revealed that a lower acidity of the support increased the electron density of the

* Corresponding author. Fax: +33 231 45 28 22.

E-mail address: francoise.mauge@ensicaen.fr (F. Maugé).

sulfide phase. The modification of the electronic properties was also related to variation of the catalyst selectivity in the transformation of a synthetic FCC gasoline [35]. Another study by Rocha et al. [36] concerning Mo sulfide catalysts supported on Al_2O_3 , Nb_2O_5 , and $\text{Nb}_2\text{O}_5\text{-Al}_2\text{O}_3$ revealed that the modification of the electronic properties was related to an interaction Mo–Nb either through the formation of a mixed Mo–Nb sulfide phase or through the interaction between MoS_2 slabs and the support. As for the effect of acidity, it was also mentioned by Vissenberg et al. [37] that the protons themselves might possibly play an active role in the HDS reaction or act as a structural promoter by, e.g., increasing the electron deficient character of the metal sulfide. However, recently, a study of Hensen et al. [38] showed that, on the contrary, the Brønsted acidic groups negatively affect the catalytic performance of amorphous–silica–alumina (ASA)-supported CoMo and NiMo sulfides in thiophene hydrodesulfurization.

In the above-mentioned cases, the increase in the support acidity is mainly related to the presence of strong Brønsted acidity. However, alumina, i.e. the widely used hydrotreating catalyst support, possesses weak Brønsted acid sites (BAS) in addition to Lewis acid sites (LAS), and several reports showed that it can be interesting to modulate its acidic properties. The acidity of alumina can be somewhat increased by deposition of additives as boron. Several studies reported that boron addition affected the alumina properties and modifies hydrotreating catalyst performances. DeCanio and Weissman [39] revealed that the Brønsted acid site density increased with increasing boron content up to a loading of 1.0 wt% and then decreased slightly. Sato et al. [40] reported that the Brønsted acid sites of alumina–boria catalysts were related to the BO_4 species, and the highest acid strength was attained for a boria content of 10 wt%. However, other studies showed different results on the acidity caused by the addition of boron. Flego and O'Neil Parker [41] indicated, using pyridine adsorption, that no Brønsted acidity was evidenced on calcined alumina–boria, and they related this result to the low boron loading (1.9 wt%). They also revealed that the higher acidity of alumina–boria was not due to a larger number of total acid sites, but rather to an increase in acid strength. Generally, the strong Brønsted acidity can be produced by boron addition at high loading [40,41]. Hence, it appears that most of the papers report an increase in Brønsted acidity with boron, even if some disagreements appear in the amount of boron necessary to generate Brønsted acidity and in the strength of these sites.

The effect of boron addition on the properties and performance of hydrotreating catalysts has been studied and interpreted from various aspects. Flego observed that the thiophene HDS activity of CoMo catalysts was influenced by the density of acid sites on boron-modified alumina [42]. Lewandowski and Sarbak reported that the increased HDN activity of boron-modified NiMo/ Al_2O_3 catalysts was due to the change of acid properties of alumina, whereas the HDS activity was practically not affected [43]. Likewise, Ferdous et al. indicated that the increase in the HDN activity of NiMo/ Al_2O_3 catalysts by boron addition was due to the formation of new strong acid sites on the catalyst surface [44–46]. Moreover, it was reported that the increased Brønsted acidity of the support by boron addition can enhance the conversion of 4,6-dimethyldibenzothiophene (4,6-DMDBT) via isomerization and demethylation reactions [47,48]. The effect of boron on the dispersion of the catalysts has been mentioned in many works. Ramírez et al. pointed out that the addition of boron into Co–Mo catalyst changed the distribution and reducibility of the oxidic species, which coincided with the catalytic activity variation in thiophene HDS [49]. Li et al. studied the dispersion of active phases by several techniques and found that the basal dispersion of Ni and Mo species increased markedly when introducing a small amount of boron and decreased with further addition of boron [50]. The change of the dispersion could explain the hydrogenation activity

variation of the catalysts as well as other catalytic functions, like hydrocracking, and hydrodesulfurization [50,51]. The concentration of the active sites is also claimed to change with the addition of boron. DeCanio and Weissman revealed by NO adsorption that the incorporation of boron caused an increase and ultimately a decrease in the number of MoS_2 edge sites in NiMo/ Al_2O_3 catalyst, in agreement with sulfur removal variation [39]. Saih and Segawa indicated that the higher HDS activity for DBT and 4,6-DMDBT could be attributed to the stronger interaction of Co-species with the B-modified alumina generating a more active CoMoS phase after sulfidation [52]. Regarding the morphology, Ferdous et al. pointed out that the increased activity was related to the decrease in average slab length and an increase in dispersion of MoS_2 edge and corner atoms [46]. Usman et al. suggested that boron addition weakened the metal support interaction between the CoMoS phase and the Al_2O_3 surface and thus increased the formation of CoMoS Type II phase [53]. Greater stacking of sulfided phase on NiMo catalyst was also noticed in the presence of boron [54].

From the above, most of the work concerning boron addition was focused on the aspects of acid–base properties, reducibility, and dispersion of the catalyst. Little information is available concerning the modification of the electronic properties of the active phase. From the literature, the addition of boron at low loading appears as an appropriate choice to modify in a controlled manner the weak Brønsted acidity of alumina. Therefore, the objective of the present work is to study the effect of changing weak Brønsted acidity of alumina by low content of boron on the dispersion, structure and electronic properties of sulfide Mo and CoMo phases and to relate these modifications to catalytic performances in thiophene HDS, 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS and 2,6-dimethylaniline (DMA) HDN model reactions. This paper will also develop a model to explain the relationship between the weak Brønsted acidity of alumina and the electronic properties of sulfide phases in order to establish the origin of such affect.

2. Experimental

2.1. Supports and catalysts preparation

Commercial $\gamma\text{-Al}_2\text{O}_3$ (from RIPP) was impregnated by pore volume method with an aqueous H_3BO_3 solution to prepare the supports with different boron loadings. The supports, denoted as $\text{Al}_2\text{O}_3\text{B}(x)$, where x is the weight percentage of boron determined by elemental analysis, were dried at 393 K for 3 h and then calcined at 773 K for 4 h. The as-synthesised supports were used to prepare Mo catalysts by pore volume impregnation. The molybdenum was added onto the supports using a solution of ammonium heptamolybdate with the same targeted MoO_3 (15.5 wt%) content. The samples were dried at 393 K for 3 h and then calcined at 723 K for 4 h. The CoMo catalysts were prepared by impregnation of the Mo samples with a solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in order to obtain a Co/(Co + Mo) atomic ratio of 0.3. The impregnated samples were dried and calcined using the same conditions as for Mo catalysts. The prepared catalysts were denoted as (Co)Mo/ $\text{Al}_2\text{O}_3\text{B}(x)$. The compositions of all the catalysts are the same as the targeted contents (less than 2% error).

X-ray diffraction (XRD) patterns of all the supports and catalysts showed the characteristics of $\gamma\text{-Al}_2\text{O}_3$ phase without any other crystalline phase indicating the good dispersion of boron, Mo and CoMo phases. The textural properties of the supports and the calcined catalysts are gathered in Table 1.

2.2. IR characterization of the supports and catalysts

Samples were pressed into self-supported disks of mass of ~10 mg (precisely weighted) and area of 2 cm². The disk was

Download English Version:

<https://daneshyari.com/en/article/61222>

Download Persian Version:

<https://daneshyari.com/article/61222>

[Daneshyari.com](https://daneshyari.com)