Journal of Molecular Catalysis A: Chemical 363–364 (2012) 311–321

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Hydrodesulfurization of sulfur refractory compounds: Effect of gallium as an additive in NiWS/γ-Al_2O_3 catalysts

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ARTICLE INFO

Article history:
Received 21 May 2012
Received in revised form 4 July 2012
Accepted 8 July 2012
Available online 20 July 2012

Keywords:
Hydrodesulfurization
NiW
Gallium
4,6-Dimethyldibenzothiophene
TPR
XPS
Raman spectroscopy
HRTEM

ABSTRACT

The effect of gallium over the NiW/γ-Al_2O_3 catalyst was investigated in the hydrodesulfurization (HDS) of 4,6-dimethyl-dibenzothiophene (4,6-DMDBT). The alumina carrier was modified with gallium by the addition of an aqueous solution of $Ga(NO_3)_3 \cdot H_2O$ in order to obtain supports with a nominal composition between 0.0 and 3.0 wt.% of Ga. The Ni–W catalysts were prepared with respectively 2.8 W atoms and 1.9 Ni atoms per nm^2 of initial surface area for the alumina support. The catalysts were characterized by different techniques such as temperature-programmed reduction, X-ray diffraction, UV–vis, Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy and they were evaluated in the HDS of 4,6-DMDBT. The highest HDS activity for NiW catalysts was observed when the amount of gallium was 2.4 wt.%, improving the value by ca. 90% as compared with that for the NiW gallium-free catalyst. This result was correlated to the effect of Ga over the dispersion of W and Ni entities. Indeed, the amount of WO_x particles calculated by the Raman (O═W═O + W═O)/W—O—W band intensities ratio was the highest for NiW/Ga(2.4)-γ-catalyst and HRTEM examination on the sulfided catalysts showed a decrease for the average stacking number and for the average length of WS_2 particles with the gallium content. Moreover, change of the promoter (Ni^{2+}) interaction with the support was induced by the affinity of gallium (at low loadings) to the tetrahedral sites of alumina, inducing an increase of the octahedral species of Ni in the oxidic state of the catalysts as evidenced from UV–vis and to a higher amount of the NiWS mixed phase in the sulfided samples as deduced from XPS analysis.

1. Introduction

The high demand for diesel fuels with less than 10 wppm of sulfur implies to achieve high conversions in hydrotreatment (HDT) units [1,2]. Therefore, the challenge in deep hydrodesulfurization (HDS) is to convert the most refractory sulfur species such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) [3,4]. Moreover, the presence of nitrogen-containing and aromatic compounds must be considered due to their inhibiting effect on the HDS reaction [5,6]. In this line, the nickel–tungsten–alumina (NiW/γ-Al_2O_3) catalysts are particularly relevant owing to their outstanding catalytic actions in hydrogenation (HYD) and hydrodenitrogenation (HDN) reactions.

Commercial NiW/γ-Al_2O_3 catalysts are mostly prepared by impregnation of nickel and tungsten solutions over γ-Al_2O_3. The polytungstate anions adsorb electrostatically on the alumina surface [7] and they react with the hydroxyl groups, producing a strong metal–support interaction after calcination. However, a recent paper [8] proposed that several phases coexist in the NiW oxide samples and that their relative concentrations depend on the Ni/(Ni + W) atomic ratio and on the W loading. From characterization for WO_3 and NiO–WO_3 catalysts supported on alumina by X-ray diffraction (XRD) [9], X-ray photoelectron spectroscopy (XPS) [7] and Raman spectroscopy [10–12] it is now well established that W species are generally highly dispersed and thus, the anchor Al—O—W is highly stable. Due to this interaction, the surface species formed on NiO–WO_3/γ-Al_2O_3 catalysts are difficult to sulfide as previously evidenced by temperature-programmed sulfiding (TPS) [13], infrared Fourier transform spectroscopy of adsorbed NO (FT-IR(NO)) and by quasi in situ XPS [14] experiments. Therefore, the role of the support is fundamental in order to synthesize highly active NiWS catalysts. One way to obtain that could be to modify the surface properties of the alumina in order to decrease the tungsten–alumina interaction, since easier sulfidable species could be synthesized. Studies by FT-IR(NO) [14], TPS, XPS [15], quick extended X-ray absorption fine structure (QEXAFS), X-ray absorption near-edge structure spectroscopy (XANES) [16] and nuclear magnetic resonance (NMR) [17] have shown that fluorination of alumina modified the interaction of tungsten with the

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http://dx.doi.org/10.1016/j.molcata.2012.07.006

support increasing the sulfidation of this metal. Also, it has been published that, at low concentrations, gallium decreased the interaction of Ni [18] with γ-Al_2O_3, due to the high affinity of Ga^{3+} to the tetrahedral sites of alumina, modifying the ratio of $Ni^{2+}_{tet}/Ni^{2+}_{oct}$ species. Furthermore, it has been found that gallium induced relevant changes in the interaction of NiMo with γ-Al_2O_3 [19–21] and it increased their activity in the HDS of dibenzothiophene (DBT) and 4,6-DMDBT [19,21].

In a previous work some of us reported that gallium addition on a commercial alumina carrier affected significantly its surface [22]. The presence of at least two gallium species was proposed, $GaAl_2O_4$ species decreasing the isoelectric point (IEP) at low gallium content and the formation of Ga_2O_3 at high contents, increasing the IEP. The highest amount of irregular WO_x particles, calculated from the Raman (O=W=O + W=O)/W—O—W band intensities ratio, was observed for the catalyst leading to the higher activity in the dibenzothiophene hydrodesulfurization reaction. As a continuation of the previous work we decided to explore the gallium effect on the NiW system supported on alumina. This effect was studied on a series of nickel–tungsten catalysts supported on alumina with a gallium content ranging from 0 to 3% wt. These catalysts were tested on the HDS of DBT in a batch reactor and on the HDS of 4,6-DMDBT in a continuous flow reactor. These results are discussed considering the characterization by Raman spectroscopy, UV–vis, TPR, XPS and HRTEM.

2. Experimental

2.1. Catalyst preparation

The supports were prepared by pore filling impregnation at equilibrium pH of a commercial γ-Al_2O_3 [high purity, BET surface area 260 $m^2\,g^{-1}$, pore volume (V_p) 0.66 $cm^3\,g^{-1}$ and particle size 80–120 μm] with appropriate aqueous solutions of $Ga(NO_3)_3 \cdot xH_2O$ (Aldrich Chemical, 99.9%) to obtain supports with 0, 0.6, 0.9, 1.2, 1.8, 2.4 and 3.0 wt.% of Ga. After 12 h, the obtained solids were dried at 393 K for 12 h and calcined at 723 K for 4 h under a flow of air (5.16×10^{-3} mol min^{-1}) with a heating rate of 1 K min^{-1}.

NiW catalysts were prepared by successive impregnation of the calcined Ga/γ-Al_2O_3 supports using the pore filling method with aqueous solutions of ammonium metatungstate (AMTW) ($(NH_4)_6W_{12}O_{39} \cdot xH_2O$, Aldrich Chemical, 99.99%) and nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Aldrich Chemical, 99.99%). Ammonium metatungstate impregnation was performed at pH = 3.7 (natural solution) and impregnation of nickel was performed with the solution of nickel nitrate at pH = 4.4. For tungsten and nickel 2.8 and 1.9 atoms per nm^2 of initial surface area of alumina were respectively added, leading to an atomic ratio r = Ni/(Ni + W) equal to 0.41. In a typical preparation, the solution of AMTW was first impregnated on the support, left for maceration for 12 h, and then the solid was dried under a stream of air (5.16×10^{-3} mol min^{-1}) at 393 K for 12 h, with a heating rate of 3 K min^{-1}. Then Ni was impregnated under the same conditions and the final solid was calcined at 723 K for 4 h under a flow of air (5.16×10^{-3} mol min^{-1}) with a heating rate of 1 K min^{-1}. The catalysts will be denoted as NiW/Ga(x)-γ-Al_2O_3, x being the weight percent of gallium introduced.

A series of Ni/Ga(x)-γ-Al_2O_3 materials was also prepared by the pore filling method on the calcined Ga/γ-Al_2O_3 supports with the corresponding aqueous solution. Loading of the metal was the same than that present in the NiW catalysts. Solids were dried at 393 K for 12 h and calcined at 723 K for 4 h under a flow of air (5.16×10^{-3} mol min^{-1}) with a heating rate of 1 K min^{-1}. The samples will be denoted as Ni/Ga(x)-γ-Al_2O_3.

2.2. Characterization techniques

After calcination, the metal contents were determined by plasma coupled atomic emission spectroscopy (AES-ICP) after appropriate dissolution of the solid samples.

Raman spectra were obtained at room temperature on a T64000 triple monochromator (Jobin-Yvon-Horiba) using the 514.5 nm line of an Ar^+ laser (Lexel Laser). All the spectra were obtained at a power of 10 mW at the laser head, in the range 10–1600 cm^{-1}, using an Olympus microscope with a ×100 objective and 10 accumulations of 60 s each. The spectrum resolution was 1 cm^{-1}. Gaussian decomposition of spectra was carried out with appropriate commercial software.

The oxide catalysts were sulfided at 673 K for 2 h with a mixture of H_2S/H_2 (10% H_2S) by using a total flow rate of 2.97×10^{-3} mol min^{-1} and a heating rate of 5 K min^{-1}. After this step, the catalysts were cooled to room temperature and flushed with N_2 for about half an hour and kept in sealed bottles under argon.

For the XPS measurements the sulfided samples were transferred into a glove box without air exposure and under the presence of argon to avoid the contact with air. The samples were pressed on an indium foil attached to the sample holder and transported into the preparation chamber of the XPS machine. The XPS spectra were recorded on a VG Instrument type ESCALAB 200R system. The sample excitation was done by Al Kα X-rays (1486.6 eV). Peak shifts due to charging of the samples were corrected by taking the Al 2p line of Al_2O_3 at 74.0 eV as a reference.

High resolution transmission electron microscopy (HRTEM) examinations were performed with a JEOL 2010 (200 kV) instrument equipped with a Link ISIS micro-analysis system. Its resolution was 0.195 nm. Freshly sulfided catalyst samples were ultrasonically dispersed in an ethanol solution at room temperature and the suspensions were collected on a carbon-coated copper grid. In the sulfided state, alumina-supported W catalysts exhibit WS_2 slabs building a layered structure. The average number of layers per stack and the average stack length were calculated from examination of more than 800 particles, the statistical studies were made according to Eqs. (1) and (2) [23–25] respectively:

$$\bar{N} = \frac{\sum_{i=1}^{n} n_i N_i}{\sum_{i=1}^{n} n_i} \qquad (1)$$

$$\bar{L} = \frac{\sum_{i=1}^{n} n_i l_i}{\sum_{i=1}^{n} n_i} \qquad (2)$$

where l_i is the length of slab-particle i, n_i the number of particles with a l_i length or N_i layers, and N_i the number of layers in the particle i.

2.3. Catalytic activity measurements

The HDS of DBT (Aldrich Chemical, 98%) was performed in a 500 mL batch reactor, magnetically stirred (1200 rpm) (Parr Instrument Co.) equipped with four baffles on the wall to prevent vortex formation. The conditions of the tests were as follows: temperature of 593 K under an hydrogen atmosphere of 5 MPa, using 250 mg of sulfided catalyst and 1.22×10^{-3} mol of DBT dissolved in 100 mL hexadecane (Aldrich Chemical, 99%). The reactor was flushed with nitrogen and heated under stirring to reach the reaction temperature, hydrogen was then introduced (P_{tot} = 5 MPa). The reaction time was counted from this moment. The total pressure was controlled constantly during the course of the reaction by adding hydrogen to compensate for its consumption. Samples were periodically collected and analyzed quantitatively by gas chromatography. The catalytic activity was expressed by the initial