Available online at www.sciencedirect.com

ScienceDirect

Catalysis Communications 8 (2007) 2232–2237

CATALYSIS
COMMUNICATIONS

www.elsevier.com/locate/catcom

Solution synthesis of unsupported Ni–W–S hydrotreating catalysts

Le Zhang [a], Pavel Afanasiev [b], Dadong Li [a], Xiangyun Long [a], Michel Vrinat [b,*]

[a] Research Institute of Petroleum Processing, SINOPEC, 18 Xue Yuan Road, 100083 Beijing, PR China
[b] Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS/Université Lyon 1, 2 Av. A. Einstein, 69626, Villeurbanne, Cédex, France

Received 22 February 2007; received in revised form 25 April 2007; accepted 1 May 2007
Available online 10 May 2007

Abstract

Solution synthesis of unsupported Ni–W–S hydrotreating catalysts was studied, in which $WO_2S_2^{2-}$ core reacted with Ni^{2+} ions, eventually in the presence of organic surfactant. The products were characterized by X-ray powder diffraction, low-temperature nitrogen adsorption, transmission electron microscopy and extended X-ray absorption fine structure spectroscopy. Catalytic activity of Ni–W–S systems was evaluated in thiophene hydrodesulfurization (HDS) reaction. It has been shown that highly active unsupported sulfides can be obtained by this method. The influence of preparation conditions on the activity and physico-chemical properties of the solids was discussed.

Keywords: Nickel; Tungsten; Unsupported catalyst; Hydrotreating; Thiosalt; EXAFS

1. Introduction

Environmental concerns lead to increasingly drastic regulations on sulfur, nitrogen and aromatics content in fuels. Utilizing of more active catalysts for hydrotreating and particularly hydrodesulfurization (HDS) would be the less costly and the most effective way for the refineries, because it would allow avoiding modifications for the plant installations. Usually the HDS catalysts contain molybdenum sulfide promoted with cobalt or nickel and supported on a high surface area alumina. Currently, new catalysts appeared at the marked, which contain very high amount of sulfide and can be considered as unsupported systems (i.e NEBULA, a registred trademark of the Exxon Mobil Company). The development of such unsupported systems bearing very high density of active sites and high specific activity per volume unit seems to be a promising research direction.

Earlier, unsupported hydrotreating catalysts were prepared by different methods including comaceration [1], homogeneous sulfide precipitation [2–6], thiosalt decomposition [7–9], hydrothermal and solvothermal processes [10–14] and solution reactions [15,16]. Thus prepared molybdenum sulfide can be further promoted by cobalt or nickel [17–19].

Thiometallates are used for many applications spreading from biological systems [20–23], to catalyst precursors [24–29]. Several works have reported the use of the thiometallates to generate MoS_2 and WS_2 catalysts with high surface area and high catalytic activity [30–32]. Among the four combinations of transition metal sulfides Ni(Co)–Mo(W), NiW system displays the highest hydrogenation and deep desulfurization properties. Compared to the Co(Ni)–Mo systems, Ni-promoted W unsupported catalysts are less studied. The goal of this work was to find simple and reproducible techniques to prepare highly active unsupported Ni–W sulfides. In this study, unsupported Ni–W–S catalysts were prepared by the solution route using as the precursor ammonium oxothiotungstate $(NH_4)_2WO_2S_2$.

---

[*] Corresponding author. Tel.: +33 4 72 44 53 23; fax: +33 4 72 44 53 99.
E-mail address: michel.vrinat@ircelyon.univ-lyon1.fr (M. Vrinat).

1566-7367/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2007.05.001

2. Experimental

2.1. Preparation of $(NH_4)_2WO_2S_2$ oxothiotungstate (OTT) precursor

Ammonium metatungstate (20 g, ca 0.1 mol W) was dissolved in 50 ml of concentrated NH_4OH and 40 ml H_2O and stirred for 1 h. Then 100 ml of $(NH_4)_2S$ (50 wt.%) was rapidly added to the solution at ambient temperature. Yellow precipitate was formed which was isolated by filtration and dried under nitrogen flow. It was identified as OTT by XRD and chemical analysis.

2.2. Preparation of the Ni–W–S catalysts

Unsupported Ni–W pre-catalysts were prepared by solution reaction between OTT and aqueous Ni^{2+}, eventually in the presence of ethylene glycol and organic surfactant. In a typical preparation, to a solution of 2 g (about 0.003 mol) of OTT in 100 ml of distilled water, 100 ml of ethylene glycol, and 30 ml of non ionic surfactant Triton X114, was added 50 ml of aqueous solution containing 1 g (0.003 mol) of $Ni(NO_3)_2 \cdot 6H_2O$. The resulting dark precipitate (pre-catalyst) was separated by three centrifugation/water washing cycles and dried overnight under vacuum at 80 °C. The black solids produced by solution reaction were sulfidized under 15 vol.% H_2S/H_2 at 400 °C for 4 h.

2.3. Characterizations

The X-ray diffraction patterns were obtained on a BRUKER diffractometer with Cu Kα radiation. Standard JCPDS files were employed to identify the phases. Chemical analyses were realized using the atomic emission method with a flamespectrometer ICPD device. The surface areas and pore volumes were determined by low-temperature nitrogen adsorption using respectively the BET and the BJH equations. High-resolution transmission electron microscopy (HREM) and energy-dispersive X-ray analysis (EDX) were done on a JEOL 2010 device. The EXAFS studies were performed at the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France), on the XAS 13 spectrometer using a Ge(400) monochromator. The measurements were carried out in the transmission mode at the W L3 edge (10207 eV) and Ni K edge (8333 eV) at ambient temperature. The sample thickness (BN pellet) was chosen to give an absorption edge step of about 1.0 near the edge region. Phase shifts and backscattering amplitudes were obtained from FEFF [35] calculations. The EXAFS data were treated with the VIPER program [36]. Curve fitting was done alternatively in R and k spaces to get simultaneous convergence. Coordination numbers (N), interatomic distances (R), Debye-Waller parameters (σ^2), and energy shifts (ΔE_0) were used as fitting variables.

2.4. Catalytic test

Thiophene HDS was carried out in the vapor phase in a fixed bed micro reactor operated in the dynamic mode at 1×10^5 Pa of hydrogen (thiophene pressure: 2.4 kPa; total mass flow: 6 L h^{-1}). A catalyst charge of about 0.07 g was employed. The reaction specific rate was measured in the steady state after 16 h on stream. The reaction products were analyzed chromatographically.

3. Results and discussion

Earlier, we reported on the solution preparations of highly loaded or unsupported Mo-based catalysts [33,34], using thiomolybdates. The present paper describes preparations which are somewhat similar by general idea. However the precursor used here is not fully sulfided thiotungstate, but thiooxosalt. The reason is that W oxygenated species are more difficult to transform to sulfide state. Indeed, the free energy of formation per sulfur atom is −119.9 kJ/mol for WS_2 and −138.5 kJ/mol for MoS_2 [37], whereas for oxides the difference has an opposite sign (−668.1 for MoO_3 and −763.8 kJ/Mol for WO_3) [7]. Therefore many reactions which end up with the fully sulfided Mo compounds fail to do that for W. Thus, we tried several techniques of earlier successful Mo-based preparations [13–16] but no one of them gave dispersed WS_2. The same concerns the synthesis of thiosalt precursor. Thus, $(NH_4)_2MoS_4$ can be routinely obtained by adding of $(NH_4)_2S$ to the heptamolybdate solution, whereas the $(NH_4)_2WS_4$ preparation is a delicate procedure including H_2S bubbling through a solution with thorough control of temperature. Being concerned about simplicity of the techniques developed, we replaced all-sulfur thiotungstate by easily available oxothiotungstate, which contains two sulfur atoms per tungsten, sufficient to produce WS_2 in the following reactions.

3.1. HDS activity and properties of the NiW-L catalyst

The preparation conditions and the most important properties of the sulfide catalyst as compared with references are listed in Table 1. The unsupported NiW-L catalyst prepared from OTT and acetate of nickel in the mixed solvent containing EG and Triton 114, possessed thiophene HDS activity much higher than the non-pro-

Table 1
Properties of sulfided NiW-L catalyst compared to the reference sulfide catalysts

Sulfide catalyst	S (m^2/g)	V (cm^3/g)	HDS rate (10^{-8} mol/(gs))		
			573 K	593 K	613 K
NiW-L	83	0.18	176	274	364
MoS_2	65	–	12	21	39
WS2	41	–	9	17	33
NiW/Al_2O_3	200	0.35	180	389	577