

# Solution synthesis of unsupported Ni–W–S hydrotreating catalysts

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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  $\text{WO}_2\text{S}_2^{2-}$  core reacted with  $\text{Ni}^{2+}$  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.

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**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 market, which contain very high amount of sulfide and can be considered as unsupported systems (i.e. NEBULA, a registered 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  $\text{MoS}_2$  and  $\text{WS}_2$  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  $(\text{NH}_4)_2\text{WO}_2\text{S}_2$ .

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## 2. Experimental

### 2.1. Preparation of $(\text{NH}_4)_2\text{WO}_2\text{S}_2$ oxothiotungstate (OTT) precursor

Ammonium metatungstate (20 g, ca 0.1 mol W) was dissolved in 50 ml of concentrated  $\text{NH}_4\text{OH}$  and 40 ml  $\text{H}_2\text{O}$  and stirred for 1 h. Then 100 ml of  $(\text{NH}_4)_2\text{S}$  (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  $\text{Ni}^{2+}$ , 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  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . 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.%  $\text{H}_2\text{S}/\text{H}_2$  at 400 °C for 4 h.

### 2.3. Characterizations

The X-ray diffraction patterns were obtained on a BRUKER diffractometer with  $\text{Cu K}\alpha$  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 ( $\sigma^2$ ), and energy shifts ( $\Delta E_0$ ) 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  $1 \times 10^5$  Pa of hydrogen (thiophene pressure: 2.4 kPa; total mass flow: 6  $\text{L h}^{-1}$ ). 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  $\text{WS}_2$  and  $-138.5$  kJ/mol for  $\text{MoS}_2$  [37], whereas for oxides the difference has an opposite sign ( $-668.1$  for  $\text{MoO}_3$  and  $-763.8$  kJ/mol for  $\text{WO}_3$ ) [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  $\text{WS}_2$ . The same concerns the synthesis of thiosalt precursor. Thus,  $(\text{NH}_4)_2\text{MoS}_4$  can be routinely obtained by adding of  $(\text{NH}_4)_2\text{S}$  to the heptamolybdate solution, whereas the  $(\text{NH}_4)_2\text{WS}_4$  preparation is a delicate procedure including  $\text{H}_2\text{S}$  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  $\text{WS}_2$  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	$S$ ( $\text{m}^2/\text{g}$ )	$V$ ( $\text{cm}^3/\text{g}$ )	HDS rate ( $10^{-8}$ mol/(gs))		
			573 K	593 K	613 K
NiW-L	83	0.18	176	274	364
$\text{MoS}_2$	65	–	12	21	39
$\text{WS}_2$	41	–	9	17	33
$\text{NiW}/\text{Al}_2\text{O}_3$	200	0.35	180	389	577

moted molybdenum and tungsten sulfides, though somewhat lower than the industrial reference (NiW sulfide, 20%W, 3%Ni on alumina).

Worth noting that the molar amounts of the precursors introduced in the reaction mixture ( $r^1 = \text{Ni}/(\text{Ni} + \text{W}) = 0.4$ ) and the ratio of the elements in the resulting precipitate, ( $r^2 = \text{Ni}/(\text{Ni} + \text{W}) = 0.7$ ) were substantially different. While the yield was quantitative relative to the nickel salt introduced to the reaction mixture, the extra tungsten species remained in the solution as fully oxygenated soluble tungstate species. In the case of NiW-L solids the reaction of precipitation is therefore different from that of thiomolybdates [34] where quantitative reaction between cobalt or nickel cations and thioanions was observed. The sulfidation of nickel ions by tetrathiotungstate and the concomitant loss of sulfur coordination by W have been reported earlier in the supported catalysts [38]. In any case the precipitate obtained at own pH seems to have inverted Ni to W ratio as compared to the known bis(tetrathiotungstate)nickelate(II) ion, described by Müller and Diekmann [39]. In the sulfided NiW-L solid some residual carbon was observed (1.68 wt.%) which might be due to the retained solvent and surfactant from the reaction solution. XRD pattern (not shown) demonstrated that the pre-catalyst was amorphous, whereas further sulfidation yielded very broad peaks of WS<sub>2</sub> and NiS crystalline phases. Residual carbon amount in the sulfided catalyst was rather low (1.6 wt.%).

The TEM images of the sulfided NiW-L catalyst showed only the presence of randomly packed WS<sub>2</sub> layer stacks (Fig. 1). Nickel sulfide even if present according to the XRD, was difficult to find in the sample by TEM technique probably due to its low content.

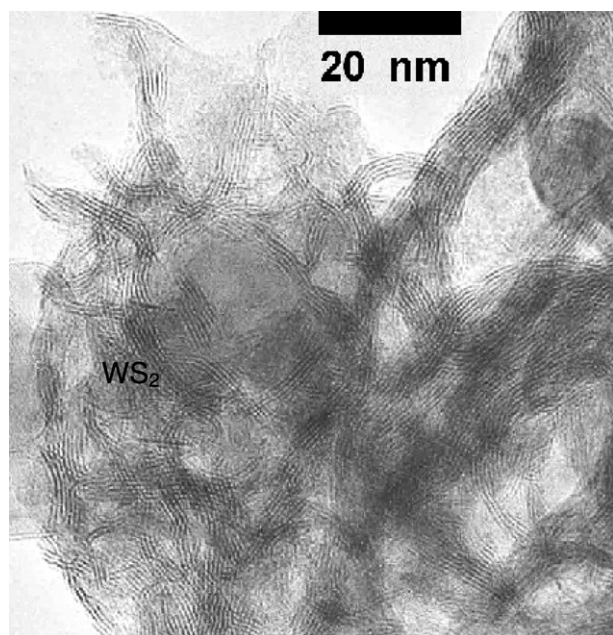


Fig. 1. TEM image of the sulfided NiW-L solid.

### 3.2. EXAFS study

To understand better the evolution of the transition metals species during the precipitation, and during further sulfidation, we undertaken an EXAFS study. If in the sulfided catalyst the state of metals could already be inferred from the XRD and TEM data, the amorphous could not be studied by these techniques but only by EXAFS.

Ni K and W L3 edge spectra of NiW-L pre-catalyst are presented in Fig. 2. Already the inspection of XANES part of spectra provides valuable information about the differences of the Ni and W state in these preparations. **Indeed, white line is virtually absent in the Ni K spectrum and is rather intense for the W L3 one, suggesting the presence of oxygen in the coordination sphere of tungsten, whereas nickel seems to be fully sulfided.**

In agreement with XANES, the EXAFS fit of Ni K spectrum of the pre-catalyst demonstrated all-sulfur coordination of Ni atoms. The imaginary part of FT was symmetric and pointed to the top of FT modulus peak suggesting a unique neighbor. Fitting of the filtered data provided high fidelity fit with approximately one W neighbor ( $R$ -factor 7.7%,  $\chi^2$  test value 9%; Fig. 3). The fitting parameters are summarized in Table 2.

For the W L3 spectrum of NiW-L pre-catalyst, EXAFS fitting in the  $R$  and  $k$  spaces requires introduction of two light and one heavy neighbors. The results of fit show that W atoms remain partially sulfided after reaction with nickel salt (Table 3). However their sulfur coordination increases as compared to the tetrahedral WO<sub>2</sub>S<sub>2</sub><sup>2-</sup> ions in the solution, probably due to the polymerization in the solid, but also due to the disproportionation of tungsten species mentioned above. After sulfidation the spectrum was transformed to the well known spectra of tungsten sulfide (not shown).

### 3.3. Optimization of the preparation technique

After establishing the general approach to the synthesis of Ni–W–S solids, we proceeded to a more detailed study

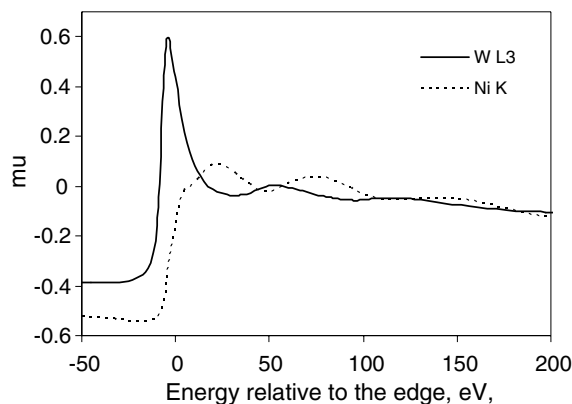


Fig. 2. Edge regions of the XAS spectra of NiW-L pre-catalyst measured at Ni K and W L3 edges.

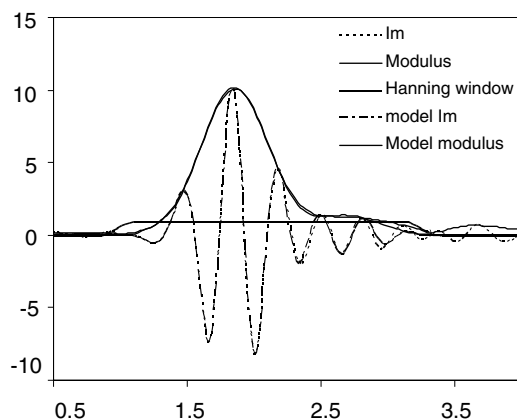


Fig. 3. *R*-space Ni K edge EXAFS fit for the NiW-L pre-catalyst. Hanning window used for BFT is also indicated.

Table 2  
EXAFS fitting results; Ni K edge

Atom	<i>R</i> (Å)	N	$\sigma$ (Å <sup>2</sup> )	$\Delta E$ (eV)
<i>NiW-L pre-catalyst</i>				
S	2.20	3.77	0.006	−2.5
W	2.75	0.8	0.006	4
Ni	3.02	0.3	0.007	1.6
<i>NiW-L sulfided catalyst</i>				
S	2.33	3.99	0.009	−1
W	2.78	0.8	0.008	−1.2

Table 3  
EXAFS fitting results for NiW-L pre-catalyst; W L3 edge

Atom	<i>R</i> (Å)	N	$\sigma$ (Å <sup>2</sup> )	$\Delta E$ (eV)
O	1.94	1.5	0.005	5
S	2.42	4.5	0.006	6
W	2.78	1.4	0.01	11

of the influence of synthesis conditions. Numerous parameters could be varied in these preparations, such as the nature of the solvent, the surfactant, the Ni/W mole ratio, pH value and nickel precursors, drying and sulfidation conditions and so on.

We observed that the composition of the solvent plays crucial role for the NiW-L preparation, probably since it determines the nucleation and growth parameters of the precipitate particles. For different solvent compositions, only the catalyst obtained from the mixed solvent–surfac-

tant water-EG–Triton system had good surface area properties. It seems that such ternary solvent is a convenient precipitation medium, more or less independently on the nature of the precipitating species. Indeed, recently Yang et al used a similar ternary solvent to obtain high surface area phosphides [40]. For the same type of NiW-L preparations, three different non-ionic surfactants were tried in the reactant solution, belonging to the same alkyl aryl-polyethylene glycol family. The variations in the HDS activity and texture properties as a function of the surfactant used were minor.

The influence of the Ni/W mole ratio in the reaction solution was also studied. It was observed that at the own reaction mixture pH near to 6, the precipitates stoichiometry was close to two nickel per one tungsten atom whatever the metals ratio in the solution. However when the input ratio  $r^1$  in the reactant solution increased the textural properties of the sulfide solids worsened. The thiophene HDS rate of catalyst with  $r^1 = 0.2$  was five times higher than that with  $r^1 = 0.6$  (Fig. 4).

The influence of base/acid adding appeared to be crucial. We carried out the precipitations under basic or acidic conditions, adding respectively aqueous NH<sub>3</sub> and 1 M HCl (Table 4). No systematic study at different pH was carried out but just a brief comparison of the specimens obtained at pH 11 and pH 3, instead of the own pH of the reaction

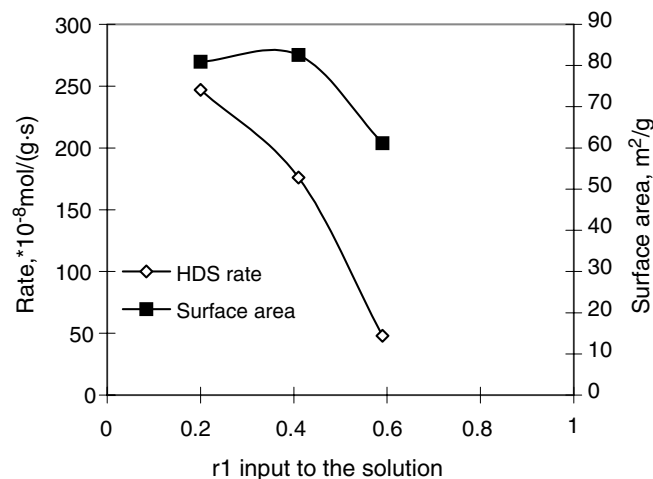


Fig. 4. Specific surface area and thiophene HDS rate at 573 K as a function of Ni/(Ni + W) mole ratio ( $r^1$ ) in the reaction solution (NiW-L catalyst).

Table 4  
Properties of the solids prepared with base/acid adding

Catalysts	pH	$r^1$ Solution	$r^2$ Solid	<i>S</i> (m <sup>2</sup> g <sup>−1</sup> )	<i>V</i> (cm <sup>3</sup> g <sup>−1</sup> )	Rate (10 <sup>−8</sup> mol/(g s))		
						573 K	593 K	613 K
NiW-L	6 (own)	0.41	0.71	83	0.18	176	274	364
NiW-L-OH	11 (NH <sub>4</sub> OH)	0.41	0.50	51	0.1	277	463	638
NiW-L-H	3 (HCl)	0.41	0.45	27	0.05	118	180	245

$r^1$  = Ni/(Ni + W) mole ratio input to the reaction solution.

$r^2$  = Ni/(Ni + W) mole ratio in the sulfide solid.

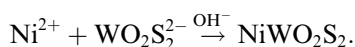
Table 5  
Properties of the solids prepared using different nickel precursors

Catalyst designation	Ni precursors	$r^1$ Solution	$r^2$ Solid	$S$ (m <sup>2</sup> g <sup>-1</sup> )	$V$ (cm <sup>3</sup> g <sup>-1</sup> )	Rate (10 <sup>-8</sup> mol/(g s))		
						573 K	593 K	613 K
NiW-L-ac	Nickel acetate	0.41	0.71	83	0.18	176	274	364
NiW-L-co	Nickel basic carbonate	0.67	0.80	38	0.10	149	257	385
NiW-L-aa	Nickel acetylacetonate	0.67		42	0.18	164	261	362
NiW-L-nit	Nickel nitrate	0.41	0.65	108	0.20	340	508	621

$r^1$  = Ni/(Ni + W) mole ratio input to the reaction solution.

$r^2$  = Ni/(Ni + W) mole ratio in the sulfide solid.

mixture. We found that addition of base can greatly improve the HDS activity whereas acidification worsened it. Due to base addition, the Ni/W ratio in the solid was significantly decreased, and the precipitation became almost stoichiometric, occurring seemingly according to the equation:



Obviously, conditions of hydrolysis and (poly) condensation of both aqueous Ni cations and W oxothioanions were changed while varying pH. Clarifying this question would require an independent study. Here we only establish the conditions which led to the precipitates of optimal composition.

The association between Ni and W moieties could also be affected by the nature of Ni precursor. Four kinds of nickel precursors were used which are acetate, basic carbonate, acetylacetonate and nitrate. Among four catalysts studied, the catalyst prepared with nickel nitrate had the highest specific surface area, pore volume and thiophene HDS activity (Table 5).

Summarizing the results of this section, we showed that the preparation route can be optimized by changing conditions such as solvent, Ni/Ni + W ratio, pH value and the nature of nickel precursor. Whatever the remaining optimization possibilities, we prepared the catalysts having twice as higher mass activity, compared to the supported commercial Ni–W sulfide reference.

#### 4. Conclusion

A simple solution technique was developed to prepare Ni–W–S unsupported catalysts with high HDS activity. The reaction of  $\text{WO}_2\text{S}_2^{2-}$  core with nickel salts in mixed solutions produced amorphous solids with Ni/Ni + W ratio depending on the conditions and nickel precursors. Optimization of the promoted unsupported NiW system allowed us to obtain catalysts with very high activity in the thiophene HDS reaction. EXAFS study revealed that the precipitates (pre-catalysts) contain fully sulfided Ni and partially sulfided W ones. Further sulfidation at 400 °C transformed these pre-catalysts into the highly dispersed sulfides  $\text{WS}_2$  and eventually some NiS. Strong difference was noted of the behavior between Mo and W in the solution reactions including sulfide species.

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