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Research Note

WS_2 catalysts from tetraalkyl thiotungstate precursors and their concurrent in situ activation during HDS of DBT

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Abstract

The synthesis of tetraalkylammonium thiotungstates $(R_4N)_2WS_4$ {$R_4 =$ tetraheptyl or cetyltrimethyl}, using an aqueous solution method is reported. Tetraheptylammonium thiotungstate and cetyltrimethylammonium thiotungstate were synthesized and characterized using FTIR, UV, and TGA-DTA. These thiosalts precursors were in situ-activated concurrently during hydrodesulfurization (HDS) of dibenzothiophene (DBT), producing WS_2 catalysts. These catalysts were analyzed by X-ray diffraction and surface area. The nature of the alkyl group affects both the surface area and the HDS selectivity. The X-ray diffraction study showed that the catalysts are poorly crystalline, with a very weak intensity of (002).

Keywords: In situ activated; WS_2 catalysts; Tetraalkyl thiometallates

1. Introduction

Ammonium thiometallates (mainly thiomolybdates and thiotungstates) are well-known precursors for Mo and W disulfide catalysts in HDS processes. Understanding their electronic structure toward the nature of these catalytic activities remains unresolved [1]. To this end, extensive theoretical work has been carried out on transition metal sulfide materials [1].

Active sulfide catalysts are conventionally prepared by converting the respective oxides to sulfides with a reductive atmosphere as hydrogen sulfide. Reductive sulfiding of the oxides is usually difficult and does not proceed in a regular manner [2]. Some alternative methods include the thermal decomposition of the corresponding salts [3] and low-temperature precipitation from solution [4]. Materials obtained by these routes have an amorphous or poorly crystalline structure, depending on the temperature of preparation. On the other hand, the decomposition of tetraalkylammonium thiometallates $(NH_4)_2MS_4$ (M = Mo or W) at 673 K and 2 h in a flowing gas mixture of 10% H_2S/90% H_2 yields transition metal catalysts MoS_2 or WS_2 [5]. Alonso et al. [6] recently reported that ammonium thiomolybdate precursors can be decomposed in situ into high activity and high surface area MoS_2 and WS_2 catalysts.

Recently, Alonso et al. [7] have reported a simpler aqueous solution method that significantly improves the yield of tetraalkylammonium compounds compared to previous studies. The aqueous solution method involves a one-step rapid substitution of NH_4^+ ions from ammonium thiomolybdate (ATM) and/or ammonium thiotungstate (ATT) with the respective ions of the desired salts. In this work, the aqueous solution method was used for the preparation of two new catalyst precursors. The two tetraalkylammonium thiotungstates are tetraheptylammonium thiotungstate (THepATT) and cetyltrimethylammonium thiotungstate (CTriMATT). The chemical structures of these catalysts precursors were characterized using the spectroscopic techniques Fourier transform infrared (FTIR) and ultraviolet (UV). Thermal analyses (TGA-DTA) were performed to study the fragmentation of their molecular structures and to determinate their decomposition behavior. The decomposition, as shown by the thermogravimetric analyses, of these thiosalts produces WS_2 catalysts.

Unsupported HDS catalysts have been prepared by different methods, including comaceration [8], homogeneous sulfide precipitation [9], and thiosalt decomposition [10].

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Thiosalt decomposition is an interesting alternative preparation since it provides a simple and reproducible method for obtaining MoS_2 and WS_2 catalysts with controlled stoichiometry. Some patents have reported the use of tetraalkylammonium thiometallates to generate carbon-containing MoS_2 and WS_2 catalysts with high surface area and high catalytic activity [11].

The hydrodesulfurization (HDS) of dibenzothiophene (DBT) has been extensively studied as a model reaction of hydrodesulfurization of petroleum feedstock [12].

The catalysts produced in this study by in situ activation during the HDS of DBT showed poorly crystalline structures as analyzed by X-ray diffraction (XRD).

2. Experimental

2.1. Materials and characterization

The reactants $(heptyl)_4NBr$ of 99% purity and (cetyltrimethyl)NBr (25 wt% in water) were purchased from Aldrich. ATT compounds were prepared following methods reported elsewhere [13]. The tetraalkylammonium precursors are prepared in this work from ATT and were characterized by FTIR spectra using a Nicolet Magna-IR 750 Fourier transform spectrophotometer and electronic (UV-Vis) spectra using a Perkin-Elmer Lambda 10 UV spectrometer, and thermogravimetric analyses (DTA-TGA) were performed on a TA Instrument SDT 2960. WS_2 in situ-prepared catalysts were characterized with a Phillips X Pert MPD diffractometer, equipped with a curved graphite monochromater, using Cu-K_α radiation ($\lambda = 1.54056$ Å) operating at 43 kV and 30 mA. Specific surface area and the BJH method for pore-size distribution determination were made with a Quantachrome AUTOSORB-1 model by nitrogen adsorption at 77 K using BET isotherms. The samples were degassed under flowing argon at 473 K for 2 h before nitrogen adsorption. The mean standard deviation for surface area measurement was about 2%.

2.2. Synthesis of $[(Hep)_4N]_2WS_4$ (THepATT)

$(NH_4)_2WS_4$ (2.0 g, 5.7 mmol) was dissolved in 20 ml of water. A solution of $(Hep)_4NBr$ (5.6 g, 11.4 mmol) in 300 ml of water at 343 K was also prepared. The two solutions were mixed. The resulting solution was stirred at this temperature for 10 min and then kept undisturbed overnight, at room temperature, precipitating yellow crystals of THepATT.

2.3. Synthesis of $[(CTriM)N]_2WS_4$ (CTriMATT)

$(NH_4)_2WS_4$ (2.0 g, 5.7 mmol) was dissolved in 20 ml of water. This solution was added to (cetyltrimethyl)NBr (16.7 ml, 11.4 mmol) at room temperature. The resulting solution was stirred at this temperature for 10 min and then kept undisturbed overnight, at room temperature, precipitating yellow crystals of CTriMATT.

2.4. Catalytic activity and selectivity

The HDS of DBT was carried out in a Parr Model 4522 high-pressure batch reactor. The appropriate amount of tetraalkylammonium precursor to yield 1 g of WS_2 catalysts was placed in the reactor with a reagent (5 vol% of DBT in decaline). Each precursor was prepared in tablet form by uniaxial pressing and was crushed in a mortar before it was placed inside the reactor. The reactor was pressurized to 3.1 MPa with hydrogen and heated to 623 K at a rate of 10 K/min. Sampling for chromatographic analysis was taken during the course of each run to determine conversion versus time dependence. Reaction run time averaged about 5 h. The reaction products were analyzed using a Perkin-Elmer Auto-system chromatograph with a 6 ft long, 1/8-inch packed column containing OV-3 (phenyl methyl dimethyl silicone 10% phenyl) as a separating phase. The main reaction products from the HDS of DBT are biphenyl (BP) and phenylcyclohexane (PCH). Selectivity for the main reaction products (BP, PCH) was determined as the weight percentage of the product in the product mixture. The mean standard deviation for catalytic measurements was about 2.5%. The BP product is from the so-called direct desulfurization pathway (DDS) and the PCH product is from the hydrogenation pathway (HYD). Since these two pathways are parallel [14], the ratio between HYD and DDS can be approximated in terms of the experimental selectivity by means of the equation:

$$\mathrm{HYD/DDS} = (\mathrm{PCH/BP}).$$

3. Results and discussion

The as-synthesized catalytic materials are highly active in several hydrotreating processes such as hydrogenation, hydrodesulfurization, and hydrodenitrogenation [15].

In this work, a high-yield (90–95%) method for the easy preparation of $[(Hep)_4N]_2WS_4$ and $[(CTriM)N]_2WS_4$ is described. This preparation involves the reaction in aqueous solution of $(NH_4)_2WS_4$ with stoichiometric amounts of ammonium salts $(Hep)_4NBr$ and (CTriM)NBr. The reaction involves cation interchange between tetraalkylammonium salts and ammonium, while the water acts as an electrolyte for the reaction. The general relation illustrating the ionic exchange for this process is shown in

$$(NH_4)_2WS_4 + 2(R)_4NBr \rightarrow [(R)_4N]_2WS_4 + 2NH_4Br, \quad (1)$$

where R = the ligands of the salts.

The FTIR and UV results are in agreement with previously reported results by McDonald et al. [16] for other similar tetraethylammonium thiometallates, Pan et al. [17] for molybdenum and tungsten sulfido-complexes, and Müller

et al. [18] for tetrathio-bimetallate compounds. In Infrared spectra, the wavenumber at 449 cm^{-1} is a characteristic important of W–S bonds from tetraalkylammonium thiotungstates. This is because tetraalkylammonium cations change the metal–sulfur bond strength. Indeed, ammonium thiotungstate shows wavenumbers at 458 cm^{-1} [7]. For the case of electronic spectra, it is important to show the three characteristic transitions corresponding to group $WS_4{}^{2-}$. They were found to be in accordance with the reported data on similar compounds [18].

The resulting TGA-DTA for THepATT and CTriMATT were compared to the previous studies made recently by Alonso et al. [6,10] and Brito et al. [19]. In this work, we have proposed the fragmentation of the chemical structures according to the experimental results by thermogravimetric analysis. The fragmentation occurs principally between the sulfur–nitrogen and nitrogen–carbon bonds.

3.1. Precursors characterization

The FTIR spectra for the two tungsten thiosalts THepATT and CTriMATT show the W–S-stretching bands to 449 cm^{-1}. Moreover, the two compounds present complex bands at 2900–3000 cm^{-1} and at 1460–1480 cm^{-1}, assigned respectively to aliphatic C–H and ammonium group N–H bonds, respectively.

The electronic spectra for two precursors were taken in methylene chloride. The two samples exhibited absorptions in both visible and UV spectral regions. There appeared three main transition bands in the case of THepATT and four transition bands in the case of CTriMATT. These transition bands correspond to the tetrahedral groups $WS_4{}^{2-}$. For the THepATT, the transition bands appeared at 483.0, 328.3, and 249.9 nm. The CTriMA complex of W exhibited absorption bands at 396, 336, 283.0, and 251.0.

3.2. Thermal analysis

In this work, according to the thermogravimetric data reported in Table 1, the thermal decomposition of tetraalkylammonium thiometallates in nitrogen follows a pattern different than that reported previously for ATT [6]. In fact, the exothermic peak corresponding to the trisulfide–disulfide transition is not detected. As shown in Table 1, the transitions, as well as the weight losses, of THepATT are consistent with

$$\{[CH_3(CH_2)_6]_4N\}_2WS_4 \rightarrow [CH_3(CH_2)_6]_2S_2 + 2[CH_3(CH_2)]_3N + WS_2. \quad (2)$$

The thermal decompositions of THepATT occur in a single step from 423 to 573 K. It is suggested that during the transition, two molecules of triheptylammine $[(CH_3(CH_2)_6]_3N$ and one molecule of diheptyl disulfide $[CH_3(CH_2)_6]_2S_2$ are directly removed. In this case, the heptyl groups would react with the S^{2-} ions of the $WS_4{}^{2-}$ units to give disulfide compounds.

Table 1
DTA-TGA results for THepATT and CTriMATT precursors in nitrogen atmosphere

	THepATT	CTriMATT
T_1 (K)	423.0	423.0
T_2 (K)	573.0	823.0
Δw_{exp} %wt loss	80.0	70.0
Δw_{theor} %wt loss	76.1	71.8
Assuming loss of:	$[Heptyl]_2S + [heptyl]_6N_2S$	$[(CTriM)N]_2S_2$
$(Final\ product)_{exp}$, %wt remaining	20.0	30.0
$(Final\ product)_{theor}$, %wt remaining	23.9	28.2
Assuming final product WS_2		

Δw is the experimental and theoretical weight losses of sample during the thermal decomposition at the T_1–T_2 temperature range.

Table 1 shows that the transitions and the corresponding weight losses for CTriMATT are consistent with

$$[(CH_3)_3N(CH_2)_{15}CH_3]_2WS_4 \rightarrow [(CH_3)_3N(CH_2)_{15}CH_3]_2S_2 + WS_2. \quad (3)$$

Their thermal decompositions occurring in the range 423–823.0 K suggest the elimination of cetyltrimethylammonium disulfide $[(CH_3)_3N(CH_2)_{15}CH_3]_2S_2$ in one step. This complicated decomposition pattern may involve intramolecular rearrangement and interaction with neighboring units of CTriMA. In all cases, the final products of the thermal decompositions correspond to nearly stoichiometric WS_2.

3.3. WS_2 catalysts characterization

3.3.1. Elemental analysis

The S/W and C/W atomic ratios as determined by EDS are reported in Table 2. A crystalline WS_2 flake was used for calibration of W and S signals. The S/W ratios for all catalysts present a constant stoichiometric value of 2. EDS analysis reveals high C/W ratios (3.0–4.5). The amount of carbon does not present a correlation with the size of the alkyl group in the thiosalt precursors.

3.3.2. Surface area and pore-size distribution

Table 2 also shows the effect of the size of the alkyl precursor on the surface area and total pore volume of WS_2

Table 2
Initial rate constant, selectivity (HYD/DDS ratio), surface area (SA), total pore volume, and elemental analysis (EA) of W, S, and C atomic ratios for in situ prepared tungsten sulfide catalysts

WS_2 catalysts from	SA (m^2/g)	k specific $\times 10^{-7}$ (mol/(g s))	HYD/DDS ratio	Total pore volume (cm^3/g)	EA S/W	EA C/W
THepATT	89	6.1	0.5	0.171	2.1	3.7
CTriMATT	203	5.6	1.4	0.540	2.0	3.0

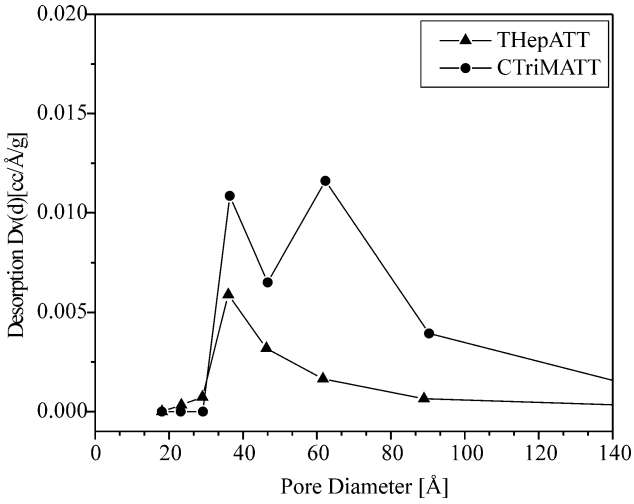

Fig. 1. BJH pore-size distributions of WS_2 catalysts formed by in situ decomposition of thiotungstates precursors.

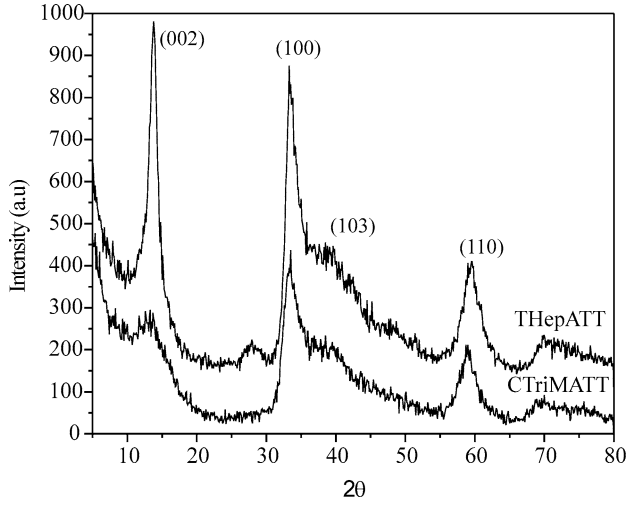

Fig. 2. XRD patterns of WS_2 catalysts formed by in situ decomposition of THepA and TriMA precursors.

catalysts produced. The two catalysts present high surface areas: 89 m^2/g for WS_2 from THepATT and 203 m^2/g for CTriATT. Fig. 1 shows the BJH pore-size distributions. The WS_2 catalysts formed from THepA precursor have pore-size distributions (20 to 50 Å) narrower than catalysts formed from CTriMA precursor (20 to 80 Å).

3.3.3. X-ray diffraction

Fig. 2 shows the XRD patterns of the WS_2 catalysts prepared from THepATT and CTriMATT precursors. The patterns for WS_2 samples show considerable difference. The WS_2 from THepATT shows a more crystalline structure than the WS_2 from CTriMATT. However, two patterns are in agreement with those reported for a poorly crystalline WS_2 structure [20].

3.3.4. Catalytic activity and selectivity

Table 2 summarizes the activity and selectivity values for the two catalysts. As we can see the selectivity depends on the alkyl group in the precursor. The WS_2 from the tetraheptylammonium group present selectivity on BP, that is, a more direct desulfurization with HYD/DDS values of 0.5. In the case of WS_2 catalysts from cetyltrimethylammonium salts the preferred path is the hydrogenation route to CHB, and the HYD/DDS value is 1.4.

The in situ-prepared active sulfide catalysts have high surface areas especially for WS_2 from CTriMATT (203 m^2/g). No clear relationship could be observed relating surface area, alkyl size, and catalytic activity. An interesting effect is observed on the selectivity; in the two catalysts, from the tetraheptylammonium precursor, the preferred path is direct desulfurization and the HYD/DDS ratio is 0.5 for WS_2 while WS_2 from the cetyltrimethylammonium precursors show hydrogenation as the preferred pathway and the HYD/DDS ratio is 1.4. The two catalysts produced have large amounts of excess carbon. The excess carbon could play a negative role in the activity by reducing the number of accessible sites. These catalysts present pore-size distributions between 20 and 80 Å, typical of mesoporous materials. As discussed in a recent work [10], the rim-edge model developed by Daage and Chianelli [21] predicts that selectivity depends on different types of active sites; rim sites are active sites for both hydrogenation and DDS reactions, and edge sites are active sites for DDS reaction. These results indicate that a simple morphological effect is not sufficient to explain the strong changes in the selectivity observed in this study. Consequently, the nature of the sites is probably altered during the in situ activation process. As noted in the paper by Alonso et al. [10], the formation of a sulfocarbide phase would be expected for any catalyst derived from tetraalkylammonium precursors prepared during the course of the HDS of DBT.

Fig. 1 shows two different ranges of mesoporosity: 20 and 50 Å. The WS_2 from THepA-present more DDS with respective values of HYD/DDS = 0.5, while WS_2 from CTriMA present more hydrogenation with respective values of HYD/DDS = 1.4. A relationship between the size of mesoporous structure and the DDS-selective catalytic systems is evidenced: as the pore diameter of the catalysts increases, the selectivity to hydrogenation increases. This may be explained via the prerequisite for hydrogenation being a π-complexation through the aromatic ring. In accord with the rim-edge model, only rim sites present a suitable geometry for adsorbing reactants through the aromatic ring, whereas the C–S bond-breaking mechanism first needs a σ bond between the metal and the sulfur atom.

4. Conclusions

Tungsten thiosalts $(R_4N)_2WS_4$ (where R_4 = tetraheptyl or cetyltrimethyl) can be synthesized by means of a sim-

ple reaction of ammonium thiotungstate with tetraalkylammonium bromides in aqueous solution. For this study, this reaction involves an interchange of cations from the ATT and $(heptyl)_4NBr$ or (CTriM)NBr. Evidence of the molecular structure of these compounds was obtained by FTIR and UV-Vis spectroscopic analyses and by DTA-TGA thermal decomposition.

WS_2 catalysts were prepared by in situ decomposition of tetraalkylammonium thiotungstates precursors (with tetraheptyl and cetyltrimethyl). The final product WS_2 present high surface areas, characteristic type IV isotherms, and narrow pore size-distributions. WS_2 catalysts from THepA-show high selectivity to the direct desulfurization pathway. WS_2 from CTriMA-showed wide pore-size distributions that could explain the preferential hydrogenation due to adsorption of DBT on the edges. The XRD patterns show high dispersion of active phases with low-stacked layers.

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