Hydrogen Storage by Titanium Based Sulfides:
Nanoribbons (TiS₃) and Nanoplates (TiS₂)

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Abstract: Nowadays, finding cheap and non-toxic materials able to reversibly store high amounts of hydrogen is a challenge in the renewable energy field. Metal sulfides seem to be promising candidates to this purpose. Titanium sulfides are reported to be particularly interesting but their ability to store hydrogen remains unclear. In this work, titanium based sulfides TiS₂ and TiS₃ with two-dimensional nanostructures have been synthesized by solid-gas reaction between titanium powder and sulfur at temperatures between 500-600 ºC. The morphology and crystal structure of Ti-sulfides were characterized by SEM (scanning electronic microscopy) equipped with EDX (energy dispersion X-ray) and XRD (X-ray diffraction), respectively. Their thermal stability was examined by TGA (thermal gravimetric analysis). Their hydrogenation properties have been determined by manometric means using a Sieverts system and by DSC-HP (high-pressure differential scanning calorimetric). Ti-sulfides hardly absorb/adsorb hydrogen for hydrogen pressures up to 80 bar and reaction temperatures up to 300 ºC.

Key words: Hydrogen storage, titanium-sulfide, nanoribbons, nanoplates, layer compounds.

1. Introduction

Metal sulfides exhibit very interesting properties in the fields of energy conversion and storage [1-3]. Concerning energy conversion, many of them (FeS₂, TiS₃, MoS₂…) show suitable band gap energy [4-6] and optical properties to be used in photovoltaic systems and photoelectrochemical hydrogen generation [6-8]. Furthermore, they exhibit 2D-layered structures with the possibility to develop peculiar nano-morphologies such as nanotubes, nanoplates and nanoribbons. These materials can be used as nanotransistors because of their optoelectronic properties as well as potential hydrogen stores [9, 10].

Apparently, metal sulfides may store hydrogen with fast H-kinetics because of their S-M-S layered structure which is bounded by Van der Waals interactions. One can reasonably accept that either H atoms or H₂ molecules can be intercalated between the S-M-S layers. Indeed, Chen et al. [11] have reported that TiS₂ nanotubes is able to reversibly store hydrogen up to ~ 2 wt.% at moderate pressures (10 bar) and low temperatures (25 ºC). However, authors did not clarify whether the sorption mechanism entails H₂ physisorption into sulfide layers or H-chemisorption by bonding hydrogen to the elements of the layered structure. Moreover, no further research has been done on titanium sulfides to confirm the reported hydrogenation properties though improved conductivity properties of TiS₂ thin films by hydrogen insertion have been recently reported [12]. The interest of titanium sulfides as potential hydrogen stores additionally relies on the lightness of Ti as well as the cheapness and abundance of both sulfur and titanium. Therefore, the aim of this work is to synthesize and characterize different titanium sulfide compounds (TiS₂ and TiS₃) and to clarify their ability to store...
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2. Experiment

2.1 Synthesis of TiS$_3$ Nanoribbons and TiS$_2$ Powders

Formation of sulfides is accomplished by a solid-gas reaction between titanium powder (~1 g, Goodfellow, 99.5% purity) and sulfur gas produced by heating of sulfur powder (~1.4 g, Merck, 99.99% purity) into vacuum sealed ampoules at 500 °C (S/Ti molar ratio = 3) and 600 °C (S/Ti molar ratio = 2) during 15 days. Temperatures and sulfuration time have been previously optimized [13].

2.2 Structural, Morphological and Thermal Characterization

Titanium sulfides were structurally characterized by X-ray diffraction using an X’Pert PRO Panalytical diffractometer. Morphology and composition was investigated by SEM-EDX (mod. Hitachi S-3000N) coupled with an EDX analyser (mod. INCAx-sight). Thermal gravimetric analysis (mod TGA-Q500 TA) was performed to investigate their thermal stability. Heating rates from 5 to 15 °C/min were used. All measurements were carried out under inert atmosphere (Argon).

2.3 Hydrogen Storage Measurements

The hydrogenation properties of titanium sulfides were determined in a home-made manometric Sieverts apparatus (Fig. 1). Hydrogen pressures up to 80 bar and temperatures between -196 °C to 300 °C were used. The Sieverts’ system comprises several thermalized volumes: a reservoir $V_r$, a sample holder $V_s$, and a connecting volume $V_{cr}$, that includes the volume of the pressure sensor. Depending on the sample amount and the sensitivity of the measurements, either $V_{cr}$ or $V_{cr} + V_r$ were used as initial volume before expansion to $V_s$. The hydrogenation bench is connected to the atmosphere when hydrogen evacuation is needed above 1 bar and also to a rotatory pump for evacuation below 1 bar ($P_{res} \sim 10^{-5}$ bar). The sample-holder can be heated in an electric furnace from RT (room temperature) to 300 °C, or immersed in a liquid nitrogen bath.

In addition, HP-DSC (high pressure differential scanning calorimetry) was used to detect reversible hydrogen sorption through heat flow variations during thermal cycling. In this work, heat flow measurements were carried out in a HP-DSC SENSYS evo DSC instrument from Setaram. Typical sample mass was 10 mg. HP-DSC runs were operated at a heating rate of 5 °C/min and up to 20 bar of hydrogen pressure. The temperature range was fixed between RT and 300 °C.

3. Results and Discussion

3.1 Structural and Morphological Characterization

Figs. 2 and 3 show the XRD patterns of sulfurated titanium at 600 and 500 °C, respectively. All diffraction peaks in Fig. 2 can be indexed in the hexagonal TiS$_2$ phase (Space Group, S.G. $P$-3$m1$), whereas those on Fig. 3 are assigned to the monoclinic
hydrogen as result of their large apparent surface area.

Fig. 4 shows the EDX measurements for the two synthetized samples. Their composition is spatially uniform in agreement with the formation of single phases. The S/Ti stoichiometric ratio is 1.90 ± 0.02 and 2.98 ± 0.01 in samples sulfurated at 600 °C and 500 °C, respectively.

3.2 Hydrogenation Properties

3.2.1 Titanium Disulfide

Hydrogen sorption experiments were performed into the Sieverts system (Fig. 1). Before hydrogenation, TiS2 sample was heated at 150 °C under vacuum during 3 h to remove traces of possible adsorbed gases such as H2O. H-absorption/desorption measurements at different temperatures were performed. Experiments performed at low temperature (-196 °C) under hydrogen pressures up to 12 bars revealed a very low hydrogen storage capacity (< 0.10 ± 0.05 wt.% H2) for a dwelling time of 30 minutes. Experiments at RT under similar pressure and time conditions exhibited a negligible hydrogen capacity.

H-absorption at moderate temperatures was investigated by HP-DSC. To this aim, TiS2 samples were kept under a hydrogen pressure of 10 bars and cycled in temperature from RT to 300 °C. No endo/exothermic events were observed (Fig. 5) suggesting the inability of TiS2 to absorb hydrogen.

Fig. 5 HP-DSC cycle from 50 to 300 °C under 10 bar H2 pressure. Heating rate was 5 °C/min.

phase TiS3 (S.G. P12_1/m1). The XRD pattern of TiS3 sample (Fig. 3) exhibits strong preferential orientation on the (001) plane. The SEM images of TiS2 and TiS3 sample (inset in Fig. 2 and Fig. 3, respectively) show different morphologies: hexagonal plates with thickness smaller than 100 nm are observed for TiS2, whereas ribbons ~ 100 µm in length, 1-5 µm in width, and 50-200 nm in thickness are observed for TiS3. Both morphologies are in principle adequate to readily store
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3.2.1 Titanium Disulfide

Before performing hydrogenation experiments in TiS$_2$, TGA measurements were carried out under argon to determine its thermal stability against decomposition (Fig. 7). TiS$_2$ is stable below 400 °C. At higher temperatures, TiS$_2$ decomposes according to reaction (1).

$$2\text{TiS}_2 + 3\text{O}_2 \rightarrow 2\text{TiS}_2 + \text{Ar} + \text{S}_2 + 3\text{O}_2$$

H-absorption/desorption experiments into the Sieverts system under different pressures and temperatures were performed to elucidate the ability to absorb hydrogen of TiS$_3$. The TiS$_3$ sample was first outgassed by heating at 150 °C under vacuum during 12 h. Next, TiS$_3$ was treated under hydrogen atmosphere of 12 bar during 30 minutes. As for TiS$_2$, no significant hydrogen storage capacity (< 0.05 wt.% H$_2$) was observed, both at low temperature (-196 °C) and at RT.

Concerning high temperature measurements, several TiS$_3$ samples were treated in the Sievert system at 300 °C under different H$_2$ pressures up to 80 bars for 12 h. At low pressure (10 bars) the amount of absorbed hydrogen attained 0.5 ± 0.1 wt.% H$_2$. At high pressure (80 bars), hydrogen absorption increased to 1.1 ± 0.1 wt.% H$_2$. To confirm these results, the H-absorption process was also investigated by HP-DSC-HP under a hydrogen pressure of 20 bars from RT up to 300 °C (Fig. 8). A small exothermic peak appears between 150 and 250 °C that could be related to a hydrogen absorption process.

The sample was extracted from the HP-DSC device after thermal cycling and analyzed by XRD. The recorded XRD pattern is displayed in Fig. 6. The position and relative intensity of all diffraction peaks are the same as for the pristine TiS$_2$ sample. In summary, conversely to previous reports [11], we could not confirm any significant hydrogen sorption in TiS$_2$.

3.2.2 Titanium Trisulfide

Before performing hydrogenation experiments in TiS$_3$, TGA measurements were carried out under argon to determine its thermal stability against decomposition (Fig. 7). TiS$_3$ is stable below 400 °C. At higher temperatures, TiS$_3$ decomposes according to reaction (1).

$$2\text{TiS}_3 + \text{Ar} + 3\text{O}_2 \rightarrow 2\text{TiS}_2 + \text{Ar} + \text{S}_2 + \text{TiO}_2 + 2\text{SO}_2 + \text{S}_2$$

H-absorption/desorption experiments into the Sieverts system under different pressures and temperatures were performed to elucidate the ability to absorb hydrogen of TiS$_3$. The TiS$_3$ sample was first outgassed by heating at 150 °C under vacuum during 12 h. Next, TiS$_3$ was treated under hydrogen atmosphere of 12 bar during 30 minutes. As for TiS$_2$, no significant hydrogen storage capacity (< 0.05 wt.% H$_2$) was observed, both at low temperature (-196 °C) and at RT.

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The sample was extracted from the HP-DSC device after thermal cycling and analyzed by XRD. The corresponding XRD pattern is shown in Fig. 9. It reveals the partial formation of TiS$_2$ phase and therefore
partial decomposition of TiS$_3$. The assigned reaction under hydrogen pressure is:

$$2 \text{TiS}_3(s) + \text{H}_2(g) \rightarrow \text{TiS}_3(s) + \text{TiS}_2(s) + \frac{1}{2} \text{H}_2\text{S}(g) \quad (2)$$

which results on the formation of gaseous H$_2$S(g) as a product of the reaction. This reaction would account for the exothermic signal detected by HP-DSC and the apparent hydrogen sorption reaction detected in the Sieverts system. One should note that for every hydrogen mole acting as a reactant in Eq. 2, only half a mole of H$_2$S is produced, leading to a decrease of the overall pressure in the Sieverts system.

4. Conclusions

TiS$_2$ and TiS$_3$ compounds were successfully prepared by sulfuration of Ti powders and characterized by XRD and SEM-EDX. Their ability to reversibly react with hydrogen was explored in a Sieverts system and by HP-DSC. Contrary to previous reports, we could not confirm that these compounds absorb significant amount of hydrogen under moderate thermodynamic conditions. Moreover, we demonstrate that TiS$_3$ decomposes at 300$^\circ$C and hydrogen pressure up to 80 bars, i.e., lower temperatures than in vacuum, in TiS$_2$ and gaseous products (likely H$_2$S). For future studies in this system, it would be interested in elucidating the reaction mechanisms leading to TiS$_3$ decomposition and to unveil the fundamental reasons of the lack of reactivity of titanium sulfides towards reversible hydrogen sorption. We are currently investigating whether selective doping of titanium sulfides maybe an efficient way to trigger H-reversibility in this system.

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