



Tungsten disulfide catalysts from tetraalkylammonium thiotungstates by ex situ activation, their properties and HDS activity

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ARTICLE INFO

Article history:

Received 29 February 2012

Received in revised form 7 May 2012

Accepted 9 May 2012

Available online 17 May 2012

Keywords:

Hydrodesulfurization

WS₂

Tetraalkylammonium

Carbon

Activation

ABSTRACT

The role of carbon coming from tetraalkylammonium thiotungstate precursors during the ex situ activation of WS₂ catalysts was herein studied through the comparison of two different thiosalts, ammonium tetrathiotungstate (ATT, without carbon) and cetyltrimethylammonium tetrathiotungstate (CTATT, with carbon). The influence on the resulting WS₂ catalysts, of a N₂ vs a H₂S/H₂ (20% H₂S) atmosphere during ex situ activation was also evaluated. Freshly obtained catalysts were characterized by N₂ adsorption–desorption isotherms, X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX), while their catalytic properties were evaluated in the hydrodesulfurization of dibenzothiophene at 3.1 MPa and 623 K. No significant difference was found in the textural and morphological properties of the final WS₂ catalysts derived from thermal decomposition of ATT under N₂ flow, compared to 20% H₂S/H₂ flow. In contrast, the textural, morphological and catalytic properties of WS₂ catalysts derived from CTATT were strongly influenced by the nature of the atmosphere. Samples of WS₂ derived from ATT showed an absence of porosity, while WS₂ catalysts formed from CTATT presented a mesoporous organization characterized by type IV N₂ isotherms. XRD and TEM showed that the use of CTATT induces a strong destacking of the WS₂ particles and the excessive formation of amorphous carbon, thus yielding less active WS₂ catalysts which confirm the negative role of carbon-containing tetraalkylammonium precursors in the activation of WS₂ catalysts, as opposed to their positive influence in the activation of MoS₂ catalysts. The very high activity of the WS₂ catalyst obtained from ATT is attributed to an optimized incorporation of structural carbon inside the WS₂ structure. Finally, selectivity results show the depleted hydrogenating character of the WS₂ catalysts formed from CTATT.

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1. Introduction

Hydrotreating catalysts based on transition metal sulfides were developed in the 1930s in order to reduce the presence of oil fractions containing heteroatoms, which hindered the refining process and yielded pollutants upon combustion. Depending on the heteroatom, hydrotreating reactions include hydrodesulfurization (HDS), hydrodenitrogenation, hydrodeoxygenation, and hydrogenation [1–4].

Preparation of molybdenum or tungsten sulfide catalysts, with surface areas in the order of 5–50 m²/g have been achieved by several methods in the past 40 years, most noticeably by sulfidation

of co-precipitated oxides [5,6], comaceration [7,8], homogeneous sulfide precipitation [9,10], ceramic method [11], and impregnated thiosalt decomposition [12–15].

An alternative to improving catalytic activity by increasing the surface area of molybdenum or tungsten sulfide, is to use precursors containing both sulfur and carbon. In this respect, tetraalkylammonium thiometalates have been initially synthesized by the metathesis reaction between ammonium tetrathiomolybdate, (NH₄)₂MoS₄ (ATM) with tetraalkylammonium chlorides [16] or tetraalkylammonium hydroxides using acetonitrile as solvent [17]. More recently, Alonso et al. [18,19] have improved this synthesis technique by preparing, in high yield and in aqueous solution, the same kind of transition metal sulfide precursors (NR₄)₂MS₄, where R = H, CH₃, or C₄H₉ (butyl) and M = Mo or W through the reaction between ammonium tetrathiomolybdate and the corresponding tetraalkylammonium bromide. The as-obtained precursors are

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