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Open flow hot isostatic pressing assisted synthesis of unsupported MoS_2 catalysts

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Abstract

We report the development and application of a new technique for synthesizing highly porous unsupported catalytic materials. The new technique is called open-flow hot isostatic pressing (OFHIP) technique. In this technique, an isostatic pressure is first applied to the catalyst precursor in an open flow fashion, and then heat is applied. Under this condition, as the organic components gradually decompose and leave the material, the voids left behind are immediately filled by the gas (pressure medium) in flow. This substitution warrants the preservation as well as the uniformity of the voids/pores. The result is a very porous material with uniform pore size distribution.

The general goal was to determine the optimal conditions of temperature and pressure for best catalytic activity results. Results indicated that besides temperature and pressure, the catalyst precursor had significant effects, as well.

The unpromoted MoS_2 samples synthesized at 300 °C indicate that as the synthesis pressure increased, both surface area and catalytic activity of the materials produced increased. The catalytic activity *k* value increased by a factor of 2 from 3 to 6×10^{-7} mol/g s that corresponds to increase in pressure from 100 to 800 psi (6.9 to 55.2 bar), respectively. The N_2 gas used as pressure medium resulted in highly porous materials but low activity. H_2 appeared to be the ideal gas for both pressure medium and reducing agent. Co-promoted MoS_2 catalysts synthesized at 1400 psi (96.5 bar) and 300 °C showed catalytic activity as high as 37 mol/g s.

Keywords: Unsupported catalyst synthesis; HDS; Porous materials; Open flow method; Hot isostatic pressure

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1. Introduction

The principal theme in catalysis is the desire to enhance the rate of chemical reactions. It is particularly of crucial importance for the chemical industry. The number of catalysts applied in the industry for catalysis purposes is very large and catalysts come in many different forms, from heterogeneous catalysts in the form of porous solids over homogeneous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes.

The transition metal sulfides (TMS) form a very important group of materials exhibiting a number of interesting properties. One particular chemical property of several of these sulfides is the ability, in the presence of hydrogen, to catalyze sulfur removal from heterocyclic organic molecules, such as thiophene, benzothiophene, and dibenzothiophene (DBT) [1]. The TMS of molybdenum and tungsten, in particular, have been widely used for years in the petroleum industry as hydrodesulfurization (HDS) catalysts [1,2]. The catalytic phase is promoted with a metal, such as Co or Ni and they are collectively but finely distributed in the pores of a supporting material. The supporting material is normally Al_2O_3. Therefore, the general composition of these catalysts contains $Co/MoS_2/Al_2O_3$ or $Ni/MoS_2/Al_2O_3$. The Co or Ni acts as a promoter increasing the hydrotreating activity. The concentrations of these metals and Mo in the catalyst body are typically in the ranges of 3–5 and 10–20 wt%, respectively. The balance is the Al_2O_3 support.

The unsupported HDS catalysts, on the other hand, do not have the support material in their composition. This allows the entire structure to be composed of the catalytic material. Consequently, the catalytic activity per unit mass of unsupported catalysts would be the maximum it can be. Perhaps that is why ExxonMobil claims that its unsupported catalyst NEBULA [3] is the world's most active hydrotreating catalyst demonstrated in many hydroprocessing applications.

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1.1. Unsupported catalyst synthesis techniques

The decomposition of thiosalts has been widely used for synthesizing MoS_2 and WS_2 catalysts. The catalytic properties of MoS_2 and WS_2 catalysts obtained from the thiosalt decomposition are reported to depend strongly on the processing atmosphere, as well as the heating conditions [4]. Large variations in surface area have been observed for these catalysts, from a few to several hundred square meters per gram, depending on the decomposition conditions [5,6]. Metal-promoted unsupported catalysts prepared from decomposition of thiosalts have shown higher catalytic activities than catalysts prepared from other precursors [7].

The different techniques for synthesizing catalysts involving thiosalt decomposition have been under intense investigation. These techniques may be categorized into three classes:

(a) ex situ;
(b) in situ;
(c) hydrothermal.

1.1.1. Ex situ technique

In this technique, the catalyst precursor is heated in a reductive environment at ambient pressure. Conventionally, active sulfide catalysts have been prepared by converting the respective oxides to sulfides in a reductive atmosphere, such as H_2/H_2S. Reductive sulfiding of the oxides is usually difficult and does not proceed in a regular manner [8]. Some alternative methods include the thermal decomposition of the corresponding salts [9] and low temperature precipitation from solution [10]. Materials obtained by these routes have an amorphous or poorly crystalline structure, depending on the temperature of preparation.

Another approach involves the decomposition of tetraalkylammonium thiometallates $(NH_4)_2MS_4$ (M = Mo or W) at 350 °C and 2 h in a flowing gas mixture of 10% H_2S/H_2 yielding transition metal catalysts MoS_2 or WS_2 [11]. Thiosalt decomposition is interesting as a method for obtaining better catalysts; the thiosalts have sulfur already bound to the metal atoms in a tetrahedral coordination, and their decomposition has been reported to undergo a topotactic reaction, where the *c*-axis of sulfide remains the same as in the precursor [12].

1.1.2. In situ technique

This technique, a variation of the hydrothermal technique, involves heating (350 °C) the catalyst precursor and the reaction mixture containing dibenzothiophene in a closed pressurized (450 psi, 31 bar) reactor. Reaction samplings at 1 h intervals are withdrawn during the 5 h process for chromatographic analysis. One interesting feature of this process is the simultaneous catalyst synthesis and catalyst activity measurement. There are many reports [13–15] on in situ decomposition of ammonium thiomolybdate (ATM) precursors into high activity and high surface area unsupported MoS_2 and WS_2 catalysts. Their X-ray diffraction (XRD) studies describe poorly crystalline structures.

1.1.3. Hydrothermal technique

In spite of the fact that the hydrothermal technique has made tremendous progress, there is no unanimity about its definition. A survey of the literature indicates that "hydrothermal technique" is a generic term encompassing such terms as hydrothermal reaction, hydrothermal growth, hydrothermal synthesis, hot isostatic pressing (HIP), and hydrothermal hot pressing. Moreover, the common features in the hydrothermal technique are described by the definition: "any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above room temperature and at pressure greater than 1 atm in a closed system" [16–22]. From this definition, it is evident that there is "isostatic pressure" acting on the material under investigation at high temperatures in a *closed* system.

1.2. A new technique for unsupported catalyst synthesis

In this study, we introduce a new technique for synthesizing unsupported MoS_2 catalysts. It is called open-flow hot isostatic pressing (OFHIP) technique. By applying OFHIP technique, the catalyst may be produced directly from the desired precursor in an *open-flow* system with a *gas* as both the reducing agent and pressure medium. While in most processes using HIP, heating normally precedes pressurization, in OFHIP technique, however, the isostatic pressure is first applied, via a pressure medium in flow, to the starting material/catalyst precursor, and then heat is applied. Under this condition, as the organic components gradually decompose and leave the material, the voids left behind are immediately filled by the gas (pressure medium) in flow. This substitution warrants the preservation as well as the uniformity of the voids/pores. This process, taking place in the absence of any solvent, would produce *clean* porous catalysts devoid of any undesirable residues. Furthermore, the process is simpler and less costly than the previous processes, rendering a viable technique for mass-producing porous materials/catalysts. The resulting materials are termed "amorphous sulfide sieves" to reflect their unique properties that include high surface area, narrow pore size distribution, and high activity. The catalysts are applicable to all petroleum and petroleum chemical companies for a wide variety of environmental and product improvement purposes.

2. Experimental

2.1. Materials and characterization

The reactants tetrapentylammonium bromide $(Pen)_4NBr$ of 99% purity and cobalt chloride $CoCl_2$ were purchased from Aldrich. The ammonium thiomolybdate $(NH_4)_2MoS_4$ compound was prepared following methods reported elsewhere [23,24]. One of the methods for ATM preparation involves bubbling H_2S into an aqueous solution (30 ml distilled water) of 10 g ammonium heptamolybdate and 100 ml NH_4OH for about 2 h.

Characterization of the catalysts was performed on samples obtained after the catalytic tests. The samples were separated from the reaction mixture by filtration, washed with