

**OPEN FLOW HOT ISOSTATIC PRESSING ASSISTED SYNTHESIS OF
HIGHLY POROUS MATERIALS AND CATALYSTS**

MOHAMMAD HOSSEIN SIADATI

The Materials Research Institute

APPROVED:

Dr. Russell R. Chianelli, Chair

Dr. Roy Arrowood

Dr. William Durrer

Dr. Abbas Ghassemi

Dean of the Graduate School

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HIGHLY POROUS MATERIALS AND CATALYSTS**

By

MOHAMMAD HOSSEIN SIADATI, B.S., M.S.

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ABSTRACT

Open-flow hot isostatic pressing (OFHIP) technique is applied for synthesizing molecular sieves and highly porous catalytic materials. First, the isostatic pressure is applied 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/replaced 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 very uniform pore size distribution.

Another advantage is the production of the catalyst directly from the precursor, in the absence of solvent (neat), rendering the process simpler and less costly than previous processes. The entire process takes place under flow of the gas that is used as medium to develop the isostatic pressure. Consequently, the entire process, as well as the final product produced, is devoid of any undesirable residues.

This endeavor also introduces 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 potentially licensable to all petroleum and petroleum chemical companies for a wide variety of environmental and product improvement purposes.

The results obtained on unpromoted samples synthesized at 300 °C indicate that as the synthesis pressure is increased, both surface area and catalytic activity of the materials produced increase. The increase in activity k value from 3 to 6 x 10⁻⁷ mol/g.s

corresponds to increase in pressure from 100 to 800 psi, respectively. The N₂ gas used as pressure medium results in highly porous materials but low activity. H₂ seems to be the ideal gas for both pressure medium and reducing agent.

Co-promoted catalysts synthesized at 1400 psi and 300 °C show catalytic activity as high as 47 mol/g.s. Based on the activity values obtained at all pressures tested, the projected activity values if tested at 2000 psi by polynomial and exponential curve fittings would be 98×10^{-7} mol/g.s, and 142×10^{-7} , respectively.

This manuscript contains two parts. Part One consists of eight chapters. Chapters 1 and 2 review supported/unsupported catalysts and the importance of catalysis. Chapters 3-8 provide an exhaustive overview of the existing industrial techniques for the precursor preparation and catalyst synthesis. Part Two of this manuscript covers the OFHIP technique. A separate chapter (Chapter 11) is dedicated to reviewing the Small Angle X-ray Scattering (SAXS) technique for its importance and relevance to this work.

OBJECTIVE

The objective of this work was to synthesize catalyst(s) from the desired precursor(s) using a minimum number of processing steps. Attempts were made to transform the desired catalyst precursor to the final catalytic material in one single step. By minimizing the number of processing steps, the cost of catalyst production would be minimized, rendering a process for mass-producing catalysts desirable for industrial applications. To achieve this objective, open-flow hot isostatic pressing (OFHIP) method has been applied to transform the desired precursor(s) to the final catalyst(s). The objective set forth was

achieved for catalysts with activity as high as 47 mol/g.s. has been produced by this newly developed technique.

PREVIEW

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PART ONE

Chapter 1 Introduction

Two constituents of all petroleum crude materials are sulfur and nitrogen. They retain in the liquid-transportation and heating fuels produced from the petroleum crude materials. Upon combustion in transportation vehicles, sulfur and nitrogen react with oxygen and two byproducts SO_x and NO_x are generated. These are both polluting to the environment and hazardous to the human health. Removing the sulfur and nitrogen from the fuels during the refining process of the petroleum crude materials can minimize the generation of these two byproducts. This is accomplished at the refinery in a process known as hydrotreating: hydrodesulfurization (HDS) for sulfur removal and hydrodenitrogenation (HDN) for nitrogen removal. In this process, the petroleum feedstock (crude oil or refined product) is passed through a reactor at elevated temperature and in an atmosphere of H_2 gas at high pressure. The removal of sulfur and nitrogen under these conditions requires the presence of a material known as catalyst. The fuel comes in contact with the catalyst housed in the reactor. The level to which the sulfur and nitrogen are removed from the fuel in the refining process defines the effectiveness or catalytic activity of the catalyst involved.

Hydrotreating is one of the most important catalytic processes in the petroleum industry. Catalysts used for this purpose account for 10% of the annual sales of the total market of catalysts. For example, petroleum refining catalyst sales were \$2.16 billion in 1998. Although various hydrotreating processes have been in service since the 1930's, the technology remains the target of vigorous research to lower costs and meet

increasingly stringent specifications for sulfur content of fuels. For example, the new regulations by the Environmental Protection Agency (EPA) require that most refiners and importers meet a corporate average gasoline sulfur standard of 120 ppm and a cap of 300 ppm beginning in 2004, and by the year 2006 the cap will be reduced to 80 ppm [1] at an estimated cost of four to five cents per gallon [2].

A catalyst is a substance that alters the rate of a chemical reaction, and itself is not consumed in the reaction. A more specific usage applies the term catalyst to a substance that increases the rate of a chemical reaction versus the term inhibitor referred to a substance that retards the rate of a chemical reaction. Catalysts speed the reaction by lowering the activation energy of the reaction. However, they do not change the thermodynamics of the reaction nor the equilibrium composition.

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 [3]. The TMS of molybdenum and tungsten, in particular, have been widely used for years in the petroleum industry as hydrodesulfurization (HDS) catalysts [3, 4].

1.1 Supported Catalysts

For hydrotreating processes, the conventional catalysts currently being used are transition metal sulfide materials based on MoS_2 or WS_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 $\text{Co/MoS}_2/\text{Al}_2\text{O}_3$ or $\text{Ni/MoS}_2/\text{Al}_2\text{O}_3$. 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 wt% and 10-20 wt%, respectively. The balance is the Al_2O_3 support. In recent years, the catalyst manufacturers have been increasing the amount of Mo in these catalysts to enhance their catalytic activity. This has been undertaken with the sole purpose of meeting the ever more stringent government regulations for sulfur and nitrogen removal.

Regulations in the United States continue to lower the levels of sulfur and nitrogen that is permitted to remain in the fuels. This is also true in Europe and other parts of the world. The increasingly strict regulations governing sulfur and nitrogen reduction from fuels have rendered the current hydrotreating capability of supported catalysts inadequate.

1.2 Unsupported Catalysts - Higher Performance

The obvious and simplest way to increase the overall catalytic performance in any given reactor beyond the current levels would be by increasing the amount of the active phase, MoS_2 or WS_2 , in the reactor. Since the reactor volume is fixed, the increase in the amount of active phase can only be accomplished by the elimination of the Al_2O_3 support, while maintaining the high surface area and structural integrity of the catalysts.

Unsupported HDS catalysts have been prepared by different methods, including comaceration [5], homogeneous sulfide precipitation [6], and thiosalt decomposition [7]. The thiosalt decomposition method has been widely used in the preparation of molybdenum and tungsten sulfide catalysts for hydrotreating processes [7]. The catalytic properties of MoS_2 and WS_2 obtained by these methods are reported to depend strongly on the processing atmosphere, as well as heating conditions [5, 7]. Large variations in surface area have been observed for MoS_2 and WS_2 catalysts, from a few to several hundred square meters per gram, depending on the decomposition conditions [8, 9]. Metal-promoted unsupported catalysts prepared from decomposition of thiosalts have shown higher catalytic activities than catalysts prepared by other techniques [10]. Some newly synthesized catalysts have surface areas that equal or exceed those of current commercial catalysts and they exhibit corresponding improvements in hydrotreating activity. In addition, these catalysts have unusual pore size distributions. For example, catalysts produced by these techniques have narrow pore size distributions with all pores lying in the region of 20-40Å [11, 12].

1.3 Choice of Catalyst Precursor

The ideal catalyst should possess sufficiently high surface area to render the highest catalytic activity possible. Most often, surface area and catalytic activity are directly proportional in any given system, i.e., the higher the surface area, the higher the catalytic activity. Studies have shown that the catalyst precursor plays a major role in obtaining a final catalyst that would show the most suitable catalytic properties. It is well

known that the catalyst precursor's physical and chemical nature/state determine the physical and catalytic properties of the final catalyst. It has been discovered that the template formulation surrounding the metal sulfide in any given precursor would determine the final catalytic properties of the resulting catalyst [11, 12].

The decomposition of thiosalt precursors has been shown to be very effective as a method for obtaining better catalysts because the thiosalt precursors have sulfur already bound to the metal atoms in a tetrahedral coordination, and their decomposition involves a topotactic reaction, whereby the *c*-axis of sulfide remains the same as in the precursor [13]. In a series of studies on thiosalt decomposition, Alonso *et al.* [12] have shown that TPenATM stands out as the best catalyst precursor to be used in this study for synthesizing highly porous materials/catalysts.

1.4 Porous Materials and Molecular Sieves

Molecular sieves serve the petroleum refining, petrochemical, and chemical process industries as selective catalysts, adsorbents, and ion exchangers. They have made possible cheaper and lead-free gasoline, higher performance and lower-cost synthetic fibers and plastics, and many improvements in process efficiency and quality and in performance.

Molecular sieves are microporous or mesoporous materials with pores of a well-defined, substantially uniform diameter in the range of 20 Å (microporous) and between 20 and 500 Å (mesoporous). Most molecules, whether in the gas or liquid phase, both inorganic and organic, have dimensions that fall within either of these ranges for their

operating environments. Selecting a molecular sieve with a suitable pore size therefore allows separation of a molecule from a mixture through selective adsorption, hence the term "molecular sieve".

Applications in purification processes, too, use the ability of molecular sieves to exclude molecules too large to enter the pores and admit smaller ones. Similarly, shape-selective catalysis takes advantage of the ability of the pores to favor the admission of smaller reactant molecules, the release of smaller reaction product molecules, or the restriction of the size of transition-state complexes inside the micropores of the molecular sieve [14].

Molecular sieves have improved many technological fields. Their large internal pore volumes, molecular-size pores, regularity of crystal structures, and the diverse framework chemical compositions allow "tailoring" of structure and properties. In the field of porous materials fabrication, the aim is to control the size, shape and uniformity of the porous space and the atoms and molecules that define it. In recent years there have been significant advances in the ability to fabricate new porous solids with ordered structures from a wide range of different materials. This has resulted in materials with unusual properties and broadened their application range beyond the traditional use as catalysts and adsorbents. In fact, porous materials now seem set to contribute to developments in areas ranging from microelectronics to medical diagnosis.

1.5 New Technique for Unsupported Catalyst Synthesis

In this study, a new approach is undertaken in synthesizing catalysts. By applying hot isostatic pressing technique, the catalyst may be produced directly from the desired precursor in an *open-flow* system with H_2 as both the reducing agent and pressure medium. First the isostatic pressure is applied to the starting material/catalyst precursor, and then the heat is applied. Under this condition, as the organic components gradually decompose and leave the material, the voids left behind are immediately filled/replaced 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 potentially licensable to all petroleum and petroleum chemical companies for a wide variety of environmental and product improvement purposes.

Chapter 2 Importance of Catalysis

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.

In the petroleum industry, the challenge has been to process petroleum residues because of the large sizes and structural complexity of their molecules, high boiling point range, and high contents of sulfur, nitrogen and metals. At the same time, it has become clear that crude oils in many existing reserves are heavier and higher in sulfur contents than those already recovered [15]. As a consequence, there is a growing interest in research and development for converting heavy feedstock (petroleum residues and heavy oils) into lower boiling products of high quality and lower sulfur content. Therefore, hydrodesulfurization (HDS) of heavy petroleum feedstock to produce distillate fuels, particularly diesel fuels and gasoline (either directly or via subsequent fluid catalytic cracking) has become an important research subject.

Earlier research has shown that certain sulfur compounds are easier to convert and the reactivities of the 1- to 3-ring sulfur compounds decrease in the order of thiophene>benzothiophene>dibenzothiophene [16, 17]. It has also been shown that under mild conditions, conventional catalysts are not effective for converting bulky organo-sulfur compounds, particularly 4-methyl and 4,6-dimethyl substituted

benzothiophenes [17, 18]. Hence, it has become necessary to develop catalysts for converting bulky sulfur compounds in order to produce environmentally friendly transportation fuels.

2.1 Heterogeneous Catalysis

Catalysts that operate on reactions taking place on surfaces, heterogeneous catalysts, are of great importance in chemical industry and in living organisms. In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by a physical attraction called *adsorption* while the reaction takes place. Adsorption may be relatively weak (physical adsorption) or may have a strength comparable to the strengths of chemical bonds (chemisorption). In either case adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called *active sites*.

2.2 Heterogeneous Catalytic Activity and Rate Law

Considering the following reaction that occurs in a constant volume batch reactor:



Mole Balance:

$$\frac{dN_A}{dt} = r_A V$$

Rate Law:

$$-r_A = kC_A^\alpha$$

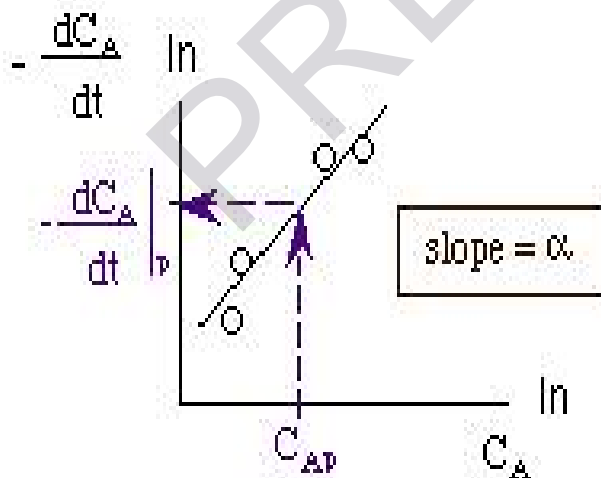
Stoichiometry:

$$V = V_0$$

Combine:

$$-\frac{dC_A}{dt} = kC_A^\alpha$$

The reaction order can be found from a ln-ln plot of:



$$k = \frac{-\frac{dC_A}{dt}|_p}{C_{Ap}^\alpha}$$