

Under Graduate Project (UGP) Report Different Silica Supports Catalyst Synthesis For Hydrodesulfurization

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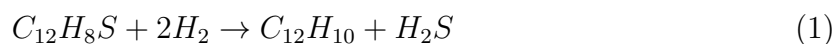
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1. Introduction to Hydrodesulfurization (HDS)

Hydrodesulfurization (HDS) is an essential catalytic chemical process employed in the petroleum refining industry to remove sulfur-containing compounds from hydrocarbon streams. The process involves the reaction of sulfur compounds present in petroleum fractions with hydrogen gas in the presence of a catalyst, typically based on metals such as molybdenum or cobalt supported on alumina. Through this reaction, sulfur atoms are effectively cleaved from the organic molecules and subsequently converted into hydrogen sulfide (H_2S), which can be easily separated from the hydrocarbon mixture.

A representative example of the HDS process is the desulfurization of dibenzothiophene (DBT), a refractory sulfur compound commonly found in petroleum. During this reaction, dibenzothiophene undergoes hydrogenation and sulfur removal to form biphenyl and hydrogen sulfide, as depicted in the following chemical equation:



Here, the DBT molecule reacts with molecular hydrogen under catalytic conditions to yield biphenyl ($C_{12}H_{10}$)—a sulfur-free aromatic hydrocarbon—and hydrogen sulfide gas, which is subsequently removed. This reaction highlights the fundamental mechanism of HDS.

1.1 Importance of HDS

- Hydrodesulfurization (HDS) plays a critical role in significantly reducing sulfur emissions from fuels, thereby minimizing environmental pollution and mitigating the formation of acid rain, which can have severe ecological and infrastructural consequences.
- HDS is essential for preventing catalyst poisoning in downstream refining processes, as the presence of sulfur compounds can deactivate precious metal catalysts and compromise the efficiency, longevity, and overall economics of refinery operations.

- By effectively removing sulfur and related impurities, HDS ensures that fuels comply with stringent international fuel quality standards and regulations, thereby promoting cleaner combustion, enhancing engine performance, and protecting public health

2. Challenges in DBT Hydrodesulfurization

- **Steric Hindrance:** The rigid, fused-ring structure of DBT reduces catalyst accessibility.
- **Low Reactivity:** DBT has strong C–S bonds, requiring high temperatures (300–400°C) and severe hydrogenation conditions.
- **Catalyst Deactivation:** Sulfur compounds and coke formation poison the catalyst, reducing its lifespan and efficiency.
- **High Hydrogen Demand:** Large hydrogen requirements increase operational costs and complexity.

3. Catalyst Synthesis Procedures

3.1 Pelletization and Sieving

- **Pelletization:** It is the process of forming small, uniform pellets from a mixture of catalyst components. This is typically done by mixing the active metal components with a binder and then pressing the mixture into pellets. The pellets are then dried and calcined to harden them. Pelletization ensures that the catalyst has a consistent shape and size, which is important for even distribution and efficient use in the reactor.
- **Sieving:** It is the process of separating particles based on size by passing them through a sieve or mesh. In catalyst synthesis, it is used to ensure uniform particle size distribution. This is important because uniform particle size helps in achieving consistent catalytic activity and prevents clogging or uneven flow in the reactor.

3.2 Reactor Filling Process

The reactor filling involves:

- **Catalyst Preparation:** Pelletized and sieved for uniform size.
- **Barrier Layer:** Coswool is used for cushioning to prevent damage; direct handling causes skin irritation.
- **Layering Sequence:** Coswool → Gamma Al_2O_3 (support) → Catalyst → Coswool → Gamma Al_2O_3 .
- **Filling Method:** Small portions filled with vibration techniques to minimize void spaces.
- **Sealing:** Tighten bolts and perform a helium leakage test and soap bubble test for the verification.

4. Synthesis of Amorphous Alumina

4.1 Solution Preparation

3.679 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to a 3-neck flask containing 15 ml of oleylamine (OAM).

4.2 Addition of Reducing Agents

0.5 ml each of oleic acid and tri-octyl phosphate (TOP) were added as reducing agents.

4.3 Thermal Decomposition

The mixture was heated from 30°C to 250°C at a rate of $1.5\text{--}2^\circ\text{C}/\text{min}$ in an oil bath and then cooled to room temperature.

4.4 Purification: Washing Procedure

- **Step 1 : Dissolution** - Dissolved the overnight dried sample in 20–25 ml of toluene or hexane and transferred to a clean tarson (let say Tarson A).
- **Step 2 : Weight Balancing** - Added distilled water to another tarson (let say Tarson B) to balance the weight of Tarson A within an error margin of less than 0.005 g.
- **Step 3 : Centrifugation** - In centrifugation machine, set the controls at 10000 rpm for 2 minutes and then discarded the supernatant from Tarson A to the disposal bottle.
- **Step 4 : Acetone Treatment** - Added 40 ml of acetone to the precipitate and subjected to intense vibration using shakers and sonicator devices to form a homogeneous mixture.
- **Step 5 : Repeating** - Repeat the process from step 2 three times to ensure purity.

5. Preparation of Support Material

5.1 Amorphous Alumina + Normal Silica Support

- **Step 1 : Mixing** - Measured amounts of amorphous alumina [$\text{am-Al}_2\text{O}_3$ (87%)] and silica [SiO_2 (13%)] are mixed via attrition mixing using a mortar-pestle for about 20-30 minutes so that both gets mixed properly.
- **Step 2 : Drying** - Transferred the mixture to a small Tarson and covered it with aluminum foil with small holes. Dried at 120°C in a heater overnight to remove moisture. Finally we will get the desired support material.

5.2 Amorphous Alumina + Varieties of Silica Support

- **Step 1 : Mixing** - Measured amounts of amorphous alumina [$\text{am-Al}_2\text{O}_3$ (87%)] and silica [SiO_2 (13%)] from MCM-41 source, KIT-6 source and SBA-15 source are mixed one by one separately via attrition mixing using a mortar-pestle for about 20-30 minutes so that both gets mixed properly and three mixtures are ready.
- **Step 2 : Drying** - Transferred the all three mixtures to a three separate fresh small Tarsons and covered all tarsons with aluminum foil with small holes. Dried at 120°C in a heater overnight to remove moisture. Finally we will get the desired support materials using varieties of Silica (MCM-41, SBA-15 and KIT-6).

6. Catalyst Preparation

- **Step 1 : Measuring Components** - Measured the amount of support formed and then calculated and weighted the relevant amounts of nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and ammonium molybdate tetrahydrate [$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$].
- **Step 2 : Mixing Solution** - The raw materials were mixed in a tarson in the presence of 0.5 - 1 ml citric acid, forming a homogeneous solution.
- **Step 3 : Impregnation** - The mixed solution of salts was added dropwise onto the support ($\text{am-Al}_2\text{O}_3 + 13\% \text{SiO}_2$).
- **Step 4 : Final Mixing and Calcination** - Finally, the solution was kept for overnight mixing, ensuring wet impregnation of active materials [Nickel(Ni) and Molybdenum(Mo)] onto the support before calcination at 550°C with a $2^\circ\text{C}/\text{min}$ ramp rate

7. Calculations and Results of Support and Catalysts

7.1 Overview

I developed a MATLAB code to calculate the support and active material required to achieve a specific catalyst composition. The code is clearly commented, making it easy to modify for different catalyst weights.

7.2 Key Features

- Well-commented for easy understanding.
- Dynamic and adaptable for any catalyst weight and concentrations.
- Provides clear numerical results.

7.3 Download the MATLAB Code

For detailed MATLAB calculations, click the link below: [Download MATLAB Code](#)

8. Status of the Work Done in Project

- Gained a comprehensive understanding of Hydrodesulfurization (HDS) reactions and the need for efficient catalysts in the process.
- Learned the catalyst loading procedure for reactor systems.
- Synthesized five catalysts with varying active material concentrations:
 - 15%, 20%, 30%, 35%, and 50%
- Prepared seven batches of amorphous alumina with the following weights: 0.8318 g, 0.8017 g, 0.6976 g, 0.4314 g, 0.8346 g, 0.8325 g, and 0.5250 g.
- Synthesized catalysts using three different varieties of silica : MCM-41, SBA-15, and KIT-6—with a fixed active material concentration of 20%.
- Successfully completed all project tasks assigned to me.

9. Reflections on the Project

9.1 Learning Experience

- This project deepened my understanding of catalysis, particularly the practical aspects of catalyst synthesis, bridging theoretical knowledge with hands-on experimentation.

9.2 Experimental Exposure

- Conducting experiments firsthand exposed me to high-level research, enhancing my appreciation for the precision and rigor required in scientific methodologies.

9.3 Gratitude

- I sincerely thank Dhyananand Sir for his unwavering guidance and Professor Sri Sivakumar for providing this invaluable opportunity and mentorship.