

Application of clay and silica-alumina supported metal catalyst for hydrogenation and hydrotreatment reaction

A Thesis submitted by
Unnati Gupta

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Indian Institute of Technology Jodhpur
Department of Chemistry
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Conclusions

6.1 Summary

The main study of the thesis is centered around the synthesis of metal-based catalysts upon sustainable clay-based support systems (Natural clay and Synthetic clay i.e. Silica alumina) via facile synthesis methods. With the goal of developing a natural-clay-based catalytic system that is eco-friendly and cost-effective, an impregnation method using dilute nitric acid was used to intercalate Pd into natural clay. The ultimate goal is to improve conversion rates and product yields by improving catalyst composition and design an efficient heterogeneous catalytic system for hydrogenation of imine to value-added product amine. Further, a series of mono- and bimetallic catalysts containing non-noble metals such as Cobalt, Nickel, and Iron were prepared, and the activities of the catalysts in hydroprocessing were tested. The catalyst synthesis procedure involved hydrothermal synthesis of support and metal inclusion through a wet-impregnation process. These catalysts are employed for the production of diesel-grade hydrocarbons using model compounds and vegetable oils. The research aims to enhance biomass conversion into biofuels, addressing worldwide energy demand, by catalytic upgrading of non-edible biomass resources.

The significant findings of the thesis are as follows:

1. Natural clay catalyst system are inexpensive and environmentally friendly materials that can be easily modified with metal cations or organic compounds, enhancing selectivity in product structure and yield. A sustainable natural clay-supported palladium catalytic system is developed using a simple wet-impregnation approach. Pd/Clay catalyst exhibited remarkable efficiency for hydrogenating 3-diphenyl prop-2-en-1-imine under mild reaction conditions. Excellent reusability over five cycles was observed, unveils novel opportunities concerning the large-scale manufacture of amines.
 2. Highly dispersed non-noble metal-based (Co and Fe-Ni doped $\text{SiO}_2\text{-Al}_2\text{O}_3$) heterogeneous catalytic system is developed to efficiently convert Methyl oleate and vegetable oil into diesel grade hydrocarbons, overcoming the deactivation of sulfided metal catalysts due to oxygenates and moisture.
 3. Incorporation of cobalt into a $\text{SiO}_2\text{-Al}_2\text{O}_3$ supported catalytic system on the conversion and selectivity for conversion of methyl oleate into diesel-grade hydrocarbons is investigated. A significant correlation was found between the conversion and selectivity and the formation of a Co_3O_4 phase over CoO/Co , the amount of Co loading, reaction time, temperature, and H_2 pressure.
 4. Fe-Ni-doped $\text{SiO}_2\text{-Al}_2\text{O}_3$ displayed excellent conversion and selectivity using methyl oleate and FAME of different oils (linseed, rapeseed, neem, and tung oils) under optimised reaction conditions. The significance of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion ratio in the catalytic conversion, as well as the C17-C18 selectivity of the HDO reaction, was evaluated.
- The current investigation offers an intriguing approach to develop an efficient HDO catalyst. The non-noble metal-based incorporated $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is capable of being envisioned as an upcoming cost-effective green catalyst for large-scale production of diesel-grade hydrocarbons.

6.2 Future scope

The synthesized catalyst and process show promise in filling gaps in the process, leading to new strategies for creating "designer catalysts" from layered clay minerals. Further, multidisciplinary expertise and collaboration are crucial for breakthroughs in clay-based catalyst design and preparation. A large scale production of fuel-grade hydrocarbons from biomass-

derived substrates can be produced using fixed bed and fluidized bed reactors. To match the performance of fossil fuel, testing, and modifications and/or additives of the thus produced biofuel can be performed. Hydrogen gas is evitable for the deoxygenation of glycerides but use of hydrogen gas can be minimized by mixing with nitrogen gas, reducing processing costs. This strategy can be explored for fuel-grade hydrocarbon production from various substrates like non-edible oil, vegetable oil, and animal fat. Additionally, research focusing on low cost, stability, reusability, and environmental friendliness can open new avenues of research for discovery of solid heterogeneous catalysts for various industrial-scale processes. Furthermore, it is possible to design catalysts that can achieve more cracking during the treatment of non-edible oils and algae oils in order to produce jet fuel grade hydrocarbons. Also, catalysts can be designed to promote the selective isomerization of hydrocracked substances in order to obtain high-octane-rated renewable gasoline fuels.

6.3 Real world application of developed catalytic system.

As environmental regulations and safety concerns increase, these catalysts are increasingly sought after due to their higher acidity and superior mechanical properties. Their low-cost nature and commercial availability offer potential for scale-up, replacing fossil feedstock with biomass for diverse product applications. The developed catalyst and process can lead to industrial-scale catalyst development owing to the unique structure-property relationships in clays and silica alumina catalyst. Amorphous silica-alumina is a key catalyst in petrochemical industries, enhancing process efficiency, improving product yields, and meeting the evolving demands of the refining and petrochemical sectors. The growing global demand for transportation fuels has led to the use of amorphous silica-alumina in FCC catalyst formulations. Advancements in catalyst technology improve selectivity, stability, cause resistance to deactivation and optimizes production processes by converting heavy hydrocarbons into lighter, more valuable products.

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