

### 2.1 Clay as a support- a brief literature review.

Clay has recently emerged as a common support material due to its lamellar structure and mechanical/thermal stability (Pinnavaia, 1983). Clay with its low-cost, ordered layer structure, unique swelling, intercalation, and high ion exchange properties can be used as a catalyst precursor, promoter, and support (Hayakawa et al., 2016). Clay has the unique property of allowing H<sub>2</sub>O and other organic/inorganic entities to enter between unit layers, causing the lattice to expand in the c-direction (Manikandan et al., 2007). These layers are functionalized through cation exchange via isomorphous substitution, which results in charge imbalance. Hydratory cations such as Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> counterbalance this by introducing catalytically active materials to the interlayers (Qiu et al., 2019). The acid treatment with dilute acids like HNO<sub>3</sub> also results in the relocation of Al to the interlayer spacing, thus modifying the acidic centers (Luna et al., 2018).

Various clay minerals have been used as robust supports for palladium to perform important organic transformations in recent years due to their low cost, simple preparation method, and remarkable reusability (Zheng et al., 2020). A palladium-based bifunctional metal-acid catalyst supported on K-10 acidic clay has been employed to convert Hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (2,5-DMF), (Gawade et al., 2016) while Sreekumar et al. used a clay-supported Pd catalyst to carry out regioselective arylation of 3,4-ethylenedioxythiophene (Sreekumar et al., 2020). Pd catalyzed furfural hydrogenation with montmorillonite clay yields 1,2-pentanediol (1,2-PeDO) with 66% selectivity (Date et al., 2018). A Pd-supported halloysite nano clay (PdM@Hal) was also reported for the efficient oxidation of methane. The applicability of clay for the palladium-based catalyst can be understood from its extensive use in a variety of coupling reactions coupling reaction such as Suzuki-Miyaura coupling, (Boruah et al., 2018) (Vellayan et al., 2018), Sonogashira Reaction (Loganathan et al., 2017), Heck–Mizoroki reactions (Martínez et al., 2015).

The efficacy of Pd NPs and Ni/Co intercalated montmorillonite clay has been investigated as green catalysts for the chemo-selective hydrogenation of squalene into squalane and the conversion of microalgae oil to diesel-grade hydrocarbons (Soni and Sharma, 2016, Soni et al., 2017). Organophilic montmorillonite Pd-M samples showed catalytic activities and stereoselectivities in 1-phenyl-1-butyne hydrogenation, with representative sample Pd-M2 being less active but more stereoselective for cis-alkene stereoisomer production (Mastalir et al., 2000, Wang et al., 2009). The researchers investigated the catalytic efficiency of Pd-nanoparticle catalysts for the selective hydrogenation of alkynes under mild conditions. Pd/Al<sub>2</sub>O<sub>3</sub>-Mg was the most effective catalyst for purifying 1-pentene, with 94% selectivity, while Pd/CaCO<sub>3</sub> showed similar activity and selectivity to the Lindlar catalyst (Cordoba et al., 2019). In continuation, a new catalyst with 1,3-diaminopropane diamine for immobilizing Pd nanoparticles, demonstrated high activity in the hydrogenation of PAOs and high catalyst recyclability, allowing multiple reaction runs without loss of catalytic activity (Asadi et al., 2022). Pd catalyst supported on gamma alumina was synthesized for selective hydrogenation of phenyl acetylene regulated with high-energy facets. The catalyst demonstrated higher activity and selectivity due to well-dispersed Pd and strong metal-support interaction (Lv et al., 2023).

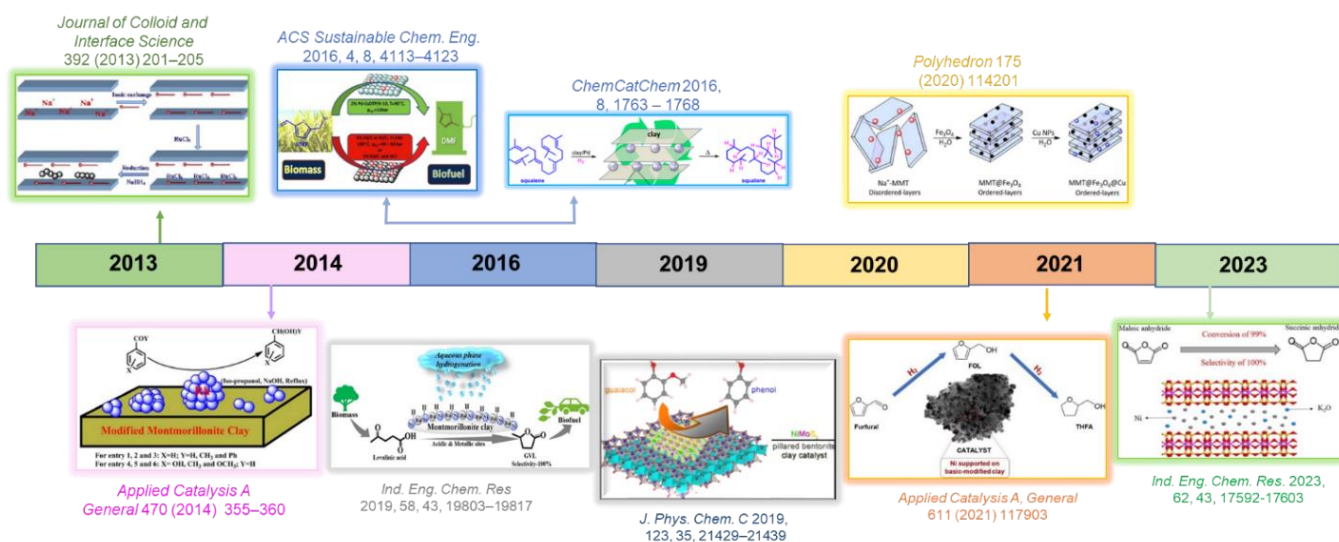


Figure 2.1 A brief timeline using clay minerals as catalysts.

## 2.2 The use of non-noble and noble metals.

Non-noble metals have been explored in various hydrogenation reactions, considering their cost-effectiveness. Several metal-based heterogeneous catalysts for hydrogenation reactions have been employed, including first-row transition metals, platinum group metals (PGM), alkali and alkaline earth metals. Considering environmental concerns and costs, designing catalysts that utilize first-row transition metals, as they are more common less toxic, and inexpensive than noble metals, is a desirable task (Garduño and García, 2020). First-row transition metals are preferred due to their low cost, but they require an extremely high H<sub>2</sub> pressure and an elevated reaction temperature to break the metal-hydrogen (M-H) bond. Furthermore, the 3d metals' tendency to show radical reactions renders them a less attractive choice. Further, the absence of a vacant d orbital in alkali metals leads to severe activation of the substrate and limited product selectivity (Bauer et al., 2018). Palladium, a noble metal, offers an intriguing solution owing to its weak Pd-H bond strength, availability of unoccupied d orbitals, and its ability to dissolve a substantial amount of hydrogen in its crystal lattice (Chen et al., 2013). Nevertheless, considering its high cost and agglomeration affinity, there is a growing demand for palladium catalysts with minimal loading, high turnover number (TON), and great recyclability. To accomplish this, the prospect of immobilizing Pd nanoparticles (NPs) on suitable support is being thoroughly considered (Das et al., 2016).

## 2.3 Imine hydrogenation- a brief literature review.

There were a few investigations on imine reduction in the late 1950s and early 1960s, primarily by Billman and workers (Billman and Tai, 1958). Borch and coworkers (Borch et al., 1971) reported on the reductive amination of aldehydes and ketones with NaBH<sub>3</sub>CN in 1971, which signaled the start of important advancements in the reduction of imines with metal hydrides. This significant development changed the environment, propelling C-N compound reduction onto the center of hydride reduction activity. Based on the realization of the importance of this reaction on amine synthesis, further efforts were made toward further development of imine reduction. Billman and workers reported some of the earliest studies of imine reductions with metal hydrides, where they synthesized several types of imines and examined their reductions with hydrides resulting in secondary amines. Stable metal hydride, LiAlH<sub>4</sub>, reacts with polar C=O bonds in aldehydes, ketones, and carboxylic acids, and showed potential to reduce C=N bonds in imines under elevated temperature. LiAlH<sub>4</sub> can be used in catalytic imine hydrogenation under mild conditions, avoiding hazardous aqueous work-up and Li/Al salts as side-products in a highly economical and environmentally friendly non-stoichiometric route. LiAlH<sub>4</sub> is effective in imine hydrogenation catalysis, but its homologues like NaAlH<sub>4</sub> and NaBH<sub>4</sub> are less active (Elsen et al., 2021). Imine reactions mediated by main group metals are crucial in

industry. Solid-state reductive amination of carbonyl compounds was examined using different inorganic solid supports such as alumina, clay, silica, and others, and clay displayed the best results. The ability of NaBH<sub>4</sub>-wet clay to reduce in situ-generated Schiff's bases has been investigated. Clay not only works as an acid but also provides water from its interlayers, accelerating the NaBH<sub>4</sub>'s reducing ability. The entire process consists of combining in situ-produced imines, with 10% NaBH<sub>4</sub>-wet clay and irradiating the resulting mixture in an unmodified domestic microwave oven (Varma and Dahiya, 1998).

## 2.4 Metal supported Natural clay for hydrogenation

A study reported the use of cobalt and natural clay for selective hydrogenation processes to valorize fatty acids and esters from agro-food industry waste by selective hydrogenation processes. Under optimized conditions, zero-valent cobalt nanoparticles immobilized on pristine halloysite and ammonium-functionalized clay exhibit high conversions and chemoselectivity, leading to the exclusive formation of saturated fatty acids (Serrano-Maldonado et al., 2023). Ni-supported Si-pillared montmorillonite systems were studied as catalysts for benzene hydrogenation. The systems were characterized by their structure, surface area, volume, and density. Reactivity was evaluated at 70-150 °C under atmospheric pressure and compared to other Ni catalysts. The study also examined the effects of internal and external mass transfer limitations on particle sizes and their dependence on process temperature and porosity (Manikandan et al., 2012). Further, Ni/montmorillonite (MMT) catalyst was prepared using Cetyltrimethylammonium bromide (CTAB)-pillared MMT and characterized using various methods. The catalyst showed high naphthalene conversion (88.2%) in the hydrogenation reaction, surpassing those of pristine MMT, Al<sub>2</sub>O<sub>3</sub>-pillared MMT, and SBA-15. The CTAB pillars played a role in the catalyst's thermal decomposition during impregnation, suggesting a mechanism for promoting catalytic activity (Ren et al., 2014b).

**Table 2.1** Literature survey concerning metal based catalysts for imine hydrogenation.

| Catalyst                                                                                                            | Amount of catalyst | Substrate                    | Time   | Temperature | H <sub>2</sub> Pressure                      | Solvent                                     | Conversion/Selectivity            | References                     |
|---------------------------------------------------------------------------------------------------------------------|--------------------|------------------------------|--------|-------------|----------------------------------------------|---------------------------------------------|-----------------------------------|--------------------------------|
| [Ir(COD)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> X <sup>-</sup> (1) (X = PF <sub>6</sub> , BF <sub>4</sub> ) | -                  | N-benzylidene                | 3 h    | 40 °C       | 5 atm                                        | CH <sub>2</sub> Cl <sub>2</sub> /MeOH (1:1) | >97% conversion                   | (Margalef-Català et al., 1999) |
| Pd-montmorillonite                                                                                                  | 10 mg              | 1-Phenyl-1-butyne            | 60 min | 298 K       | 10 <sup>5</sup> Pa                           | Hexane                                      | 86–88% stereoselectivity          | (Mastalir et al., 2000)        |
| Pd/organoclay                                                                                                       | 0.2 wt. %          | NMP (N-methyl-2-pyrrolidone) | 60 min | 100 °C      | O <sub>2</sub> flow, 25 mL min <sup>-1</sup> | -                                           | 66% Conversion/ 91% benzaldehyde  | (Wang et al., 2009)            |
| Pd-MCM                                                                                                              | S: Pd = 2000       | 3-Butyn-1-ol                 | 80 min | 298 K       | 105 Pa                                       | Toluene                                     | 91.8% Conversion/ 100 Salkene (%) | (Papp et al., 2005)            |

|                                           |             |                         |        |        |                 |                 |                                    |                                         |
|-------------------------------------------|-------------|-------------------------|--------|--------|-----------------|-----------------|------------------------------------|-----------------------------------------|
| 1%Pd/HMS                                  | R:P = 2500. | 1-phenyl-1-hexyne       | 90 min | 298 K  | 1 bar           | Tetrahydrofuran | 96 styrene b (%)                   | (Marín-Astorga et al., 2006)            |
| Pd/ Al <sub>2</sub> O <sub>3</sub> -Mg    | 0.4 wt. %   | 1-pentyne               | 50 min | 303 K  | 150 kPa         | Toluene         | 100% Conversion/1-pentene (94%)    | (Cordoba et al., 2019)                  |
| Pd/ (111)γ-Al <sub>2</sub> O <sub>3</sub> | 0.5 wt. %   | Phenylacetylene         | 20 min | 40 °C  | 1 MPa.          | -               | 100% Conversion                    | (Lv et al., 2023)                       |
| Pd/HNT-Lhalloysite                        | 5 wt. %     | Polyalphaolefins (PAOs) | 8 h    | 130 °C | 7 bar           | -               | 98% Conversion                     | Asadi et al, 2022                       |
| Co/halloysite-                            | 2.5 mol %   | Oleic Acid              | 6 h    | 120 °C | 20 bar          | -               | 90% Conversion                     | (Serrano-Maldonado et al., 2023)        |
| Ni/Si-pillared clay                       | 16.4 wt. %  | Benzene                 | 25 min | 90 °C  | 1 atm           | -               | 100% Conversion                    | (Louloudi and Papayannakos, 2016)       |
| Ni/clay                                   | 5 wt. %     | Furfural                | 2 h    | 140 °C | 3 MPa           | Ethanol         | 100% Conversion / 100% THFA        | (Tian et al., 2021)                     |
| Ni(o)-K10                                 | 2.84 wt. %  | Styrene                 | 8 h    | 70 °C  | 0.2ml Hydrazine | Ethanol         | 100% ethyl benzene                 | (Dhakshinamoorthy and Pitchumani, 2008) |
| Ni/MMT-CTAB                               | 10.0 wt. %  | Naphthalene             | 2.0 h  | 300 °C | 5.0 MPa         | n-dodecane      | 88.2% conversion/ 99.4 Tetralin    | (Ren et al., 2014b)                     |
| NiNPs on unfunctionalized halloysite      | 1 mol %     | Diphenylacetylene       | 7 h    | 25 °C  | 3 bar           | Ethanol         | >99 Conversion 1,2-diphenyl ethene | (Pérez Alonso et al., 2022)             |
| Co/CL-10                                  | 7% wt. %    | Acetylene               | 60 min | 140 °C | -               | -               | 95% Conversion/97% ethylene        | (Aitugan et al., 2021)                  |
| Ru(o)-hectorite                           | 3.2 wt. %   | Benzene                 | 2 h    | 50 °C  | 50 bar          | -               | 38% Conversion                     | (Süss-Fink et al., 2009)                |

|               |          |              |        |       |         |   |                 |                                 |
|---------------|----------|--------------|--------|-------|---------|---|-----------------|---------------------------------|
| Ru-MMT        | 2.5 wt.% | Allylbenzene | 1 h    | 80 °C | 10 bar  | - | 87% Yield       | (Upadhyay and Srivastava, 2015) |
| Ir-NPs        | -        | Arenes       | 6 h    | 75 °C | 5 bar   | - | 100% Conversion | (Das et al., 2016)              |
| Ru/MCM-41/HNT | 0.74%    | Benzene      | 75 min | 80 °C | 3.0 MPa | - | 100% Conversion | (Glotov et al., 2020)           |

## 2.5 Hydrodeoxygenation (HDO)

Deoxygenation (DO) and hydrodeoxygenation (HDO) procedures of vegetable oil employing appropriate catalysts have been effectively demonstrated as a feasible upgrading process for dealing with engine instability and compatibility difficulties with the advantage of having high cetane numbers (Soni and Sharma, 2016). Different kinds of catalysts, including noble metals (Pt, Pd, Rh, and Ru) and hydrodesulfurization (HDS) catalysts (sulfided CoMo and NiMo), have been investigated for the DO reactions of vegetable oils and their model compounds (Galadima and Muraza, 2015, Kubička and Kaluža, 2010, Mora-Vergara et al., 2018). In most instances, these heterogeneous catalysts exhibit low to moderate selectivity for HDO over DCO<sub>2</sub>/DCO. Sulfur-free catalytic transformation of microalgae and vegetable oil into hydrocarbons has shown good to high selectivity toward CN alkanes in recent research (Hachemi et al., 2016, Gosselink et al., 2013b, Song et al., 2013, Gosselink et al., 2013a). Pt-based catalysts (Murata et al., 2010), and molybdenum carbides (Han et al., 2011) supported on carbon demonstrated significant activity and selectivity for HDO of fatty acids/esters. Bitter and co-workers (Gosselink et al., 2013b, Hollak et al., 2013) conducted extensive research on the catalytic conversion of vegetable oil along with comparable substrates. Transition metal carbides (Mo<sub>2</sub>C and W<sub>2</sub>C) supported by various carbon structures like activated carbon, graphene, carbon nanotubes, and others have recently been reported as promising catalytic materials for the DO of vegetable oils (Kim et al., 2015, Pang et al., 2019). HDO of Ni/HBeta and Ni/ZrO<sub>2</sub> catalysts tested on stearic acid produced octadecane and n-heptadecane, respectively (Ma and Zhao, 2015). Lercher and colleagues (Peng et al., 2012a, Peng et al., 2013, Song et al., 2013) have conducted substantial studies on the hydroprocessing of microalgae oil. For instance, Peng et al. studied the HDO of palmitic acid in a semi-batch reactor at 260 °C and 12 bar of H<sub>2</sub> over 5 wt.% Ni supported on ZrO<sub>2</sub>, H-BETA and H-ZSM-5, and 5 wt.% Pd/C in previous study. The results showed that Ni catalysts with small cluster sizes exhibited high activity, achieving 100% conversion after 6 hours, while Pd catalysts produced only 20% conversion (Peng et al., 2013). Further by utilizing Ni/HBeta catalyst, stearic acid and microalgae oil were converted into alkanes with exceptional HDO selectivity (Peng et al., 2012a, Lee et al., 2014).

Recent advances in noble (Hollak et al., 2014, Shao et al., 2015, Zhang and Zhao, 2016, Ouyang et al., 2019) and non-noble metal (Shi et al., 2016, Yan et al., 2017, Kiméné et al., 2019) based catalytic systems have shown remarkable deoxygenation reactivity and selectivity. Non-noble metal-based deoxygenation is often carried out at a higher temperature (above 280 °C) and H<sub>2</sub> pressure (40-80 bar). Though the use of expensive noble metal-based catalysts reduces the temperature (200-260 °C) and H<sub>2</sub> pressure (5-20 bar), the development of cost-effective, high-efficiency catalysts is extremely sought for industrial applications. The utilization of precious metals Pd > Pt > Rh > Ru (catalytic activity order) and HDS catalysts (sulfided NiMo, NiW, and CoMo) for HDO reactions of vegetable oils and model compounds, with high conversion rates into diesel-grade alkanes, has been extensively described in the literature (Fan et al., 2022). However, the high cost and scarcity of these noble metals-based catalysts, as well as harsh synthesis conditions and product sulfur contamination, encouraged the scientific community to seek competent, cost-effective, and sulfur-free catalysts for future applications (Lee et al., 2016).

The inclusion of non-noble metals such as Ni, Co, and Mo in these catalysts is critical for industrial applications; nevertheless, the expense of solid support is also vital. Transition metal catalysts based on W, Mo, Fe, Cu, Ni, and Co are very suited to large-scale processing of biomass feedstocks due to their cost effectiveness and abundance (Liang et al., 2019). However, only a few investigations on triglyceride deoxygenation have been reported. The cost-effectiveness of other transition metal-based catalysts like NiMo/Al<sub>2</sub>O<sub>3</sub>, (Hočevár et al., 2019) Ni-WO<sub>x</sub>, (Dhillon and Vasudevan, 2021), Ni/Co-natural clay (Soni et al., 2017), Co-ZrO<sub>2</sub> (Zhou et al., 2021) (Al-Dalama and Stanislaus, 2006) and Mo, W, and Ta modified supported catalyst (Raikwar et al., 2019) have caused considerable interest in large-scale hydroprocessing of biomass feedstocks. This porous structure, adjustable acidity, and high catalytic performance of these transition metal oxides make them highly suitable as promoters for many support materials, such as alumina, natural clay, zirconia, activated carbon, and zeolites. To date, only a few articles have been published on catalyst deactivation studies on HDO reactions of renewable oils (de Souza et al., 2017). Interestingly, Cordero-Lanzac et al. proposed a Pd-Pt/C catalyst for HDO of raw bio-oil and reported that coke production owing to thermal lignin and aromatics are the main reasons for catalyst deactivation (Cordero-Lanzac et al., 2018).

Kadarwati et al. also examined coke production during the hydrotreatment of bio-oil using pre-sulphided NiMo and CoMo catalysts at low temperatures (150-300 °C) (Kadarwati et al., 2017). Similarly, Li et al. (Li et al., 2017) and Foo et al. (Foo et al., 2016) the formation and deposition of graphitic coke on the surface of Ni-Cu/HZSM-5 and Pt/HBEA catalyst during bio-oil HDO. Wang et al. (Wang et al., 2017) explored the mechanistic aspects of CoMoS catalyst deactivation during waste cooking oil hydrotreatment. Kiatkittipong et al. (Kiatkittipong et al., 2013) and Plaola et al. (Plaola et al., 2022) observed that impurities in feedstock substances, such as gums, deactivate the catalyst by adhering to or producing coke at active sites. Furthermore, Arora et al. investigated the catalyst deactivation caused by the incorporation of metal and nonmetals (Fe, K, P, and Na) in the HDO of bio-oil. Furthermore, the study discovered that surface Fe deposition shuts off Ni's promoting impact in a NiMoS/Al<sub>2</sub>O<sub>3</sub> catalyst for HDO of diverse renewable feedstock. In this work, the effect of different iron oxide loadings on the structural and surface chemical characteristics of synthesized catalysts Fe<sub>x</sub>Ni<sub>y</sub>/SA has been investigated using various characterization approaches to elucidate the structure-activity link. HDO of methyl oleate was used to investigate the effect of iron oxide loading on the catalytic activity of several Fe<sub>x</sub>Ni<sub>y</sub>/SA catalysts. Furthermore, conversion and C17-C18 selectivity were discussed, with an emphasis on the Fe<sup>2+</sup>/Fe<sup>3+</sup> ion ratio. This study will provide new insights into the rational selection of active metal components with the best acidity and textural features for green diesel production.

**Table 2.2** Literature survey of Hydrotreatment of Model compounds and vegetable oils with Metal(s) based heterogeneous Catalysts.

| Catalyst                                                 | Metal (wt.%)                | Substrate     | Time (h) | Temperature (°C) | H <sub>2</sub> Pressure | Solvent     | Conversion/Selectivity       | References                 |
|----------------------------------------------------------|-----------------------------|---------------|----------|------------------|-------------------------|-------------|------------------------------|----------------------------|
| Co <sub>2.5</sub> /clay                                  | 1                           | Methyl oleate | 6 h      | 300 °C           | 40 bar                  | n-heptane   | 100%/90% C18                 | (Soni et al., 2017)        |
| Ni/Hbeta                                                 | 2                           | Stearic acid  | 8 h      | 260 °C           | 40 bar                  | n-dodecane  | 100%/90% C18                 | (Peng et al., 2012a)       |
| W/CNF                                                    | 1.87                        | Stearic acid  | 5 h      | 350 °C           | 50 bar                  | n-dodecane  | 100%/85% C18                 | (Gosselin et al., 2013a)   |
| Mo <sub>2</sub> C/AC                                     | 2.9                         | Stearic acid  | 4 h      | 280 °C           | 15 bar                  | hexane      | 100%/86% C18                 | (Han et al., 2011)         |
| Co/H-ZSM-5-GR                                            | 0.76                        | Stearic acid  | 4 h      | 260 °C           | 30 bar                  | n-heptane   | 100%/81% C18                 | (Wu et al., 2018)          |
| Fe-N-C@Al <sub>2</sub> O <sub>3</sub>                    | 13.6                        | Stearic acid  | 8 h      | 320 °C           | 40 bar                  | n-dodecane  | 100%/92% C18                 | (Li et al., 2019)          |
| 4%Pd/10%Nb <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> | -                           | Tristearin    | 24h      | 170 °C           | 2.5 MPa                 | n-dodecane  | 100%/94.2% C18               | (Hollak et al., 2014)      |
| Ir-ReO <sub>x</sub> /SiO <sub>2</sub>                    | Re/Ir=3                     | Stearic acid  | 1 h      | 180 °C           | 2 MPa                   | Cyclohexane | 100%/94% C18                 | (Liu et al., 2018)         |
| Pt/beta (20%)-Al <sub>2</sub> O <sub>3</sub>             | 0.7 wt.%                    | FAME          | -        | 350 °C           | 2 MPa                   | -           | 99.5%/84.7% C15-C18          | (Ouyang et al., 2019)      |
| 0.3 NiMo/Al <sub>2</sub> O <sub>3</sub>                  | 4.63 Ni<br>20.84 Mo<br>wt.% | Rapeseed oil  | 6 h      | 260–280 °C       | 3.5 MPa                 | -           | 50–70% C18                   | (Kubička and Kaluža, 2010) |
| Mo <sub>2</sub> C/CNF                                    | 0.25 g                      | Oleic Acid    | 5 h      | 350 °C           | 50 bar                  | dodecane    | Hydrocarbon yield (90 mol %) | (Hollak et al., 2013)      |
| Mo <sub>2</sub> C/Graphene                               | -                           | Oleic acid    | 1h       | 350 °C           | 5.0 MPa                 | -           | ≥85% yield<br>≥90% C18       | (Kim et al., 2015)         |
| CuCo-R catalyst                                          | -                           | Stearic acid  | 4 h      | 260 °C           | 3 MPa                   | decane      | 100%<br>/94.82% C18          | (Liang et al., 2019)       |

|                                                    |             |                          |                                |        |          |                |                                 |                                           |
|----------------------------------------------------|-------------|--------------------------|--------------------------------|--------|----------|----------------|---------------------------------|-------------------------------------------|
| Ru(1%)-Sn(2%)-B/<br>Al <sub>2</sub> O <sub>3</sub> | 1 g         | Methyl<br>Oleate         | 2h                             | 290 °C | 50 atm   | n-<br>dodecane | 100%<br>conversion              | (Sánchez<br>et al.,<br>2015)              |
| Pt/Al <sub>2</sub> O <sub>3</sub>                  | 1 wt.%      | Microalg<br>ae           | 1.5 s<br>resid<br>ence<br>time | 310 °C | 500 psig | n-<br>dodecane | 76.5% Yield                     | (Sánchez<br>et al.,<br>2015)              |
| Pd/C                                               | 1 g         | Stearic<br>Acid          | 6 h                            | 300 °C | 6 Bar    | n-<br>dodecane | 100%/98%<br>C17                 | (Snåre et<br>al., 2006)                   |
| Pd/C                                               | 1 g         | Methyl<br>oleate         | 6 h                            | 300 °C | 15 bar   | -              | 100% /71%<br>methyl<br>stearate | (Snåre et<br>al., 2008)                   |
| Pd/C<br>catalyst                                   | 5 wt.%      | Stearic<br>acid          | 5 h                            | 300 °C | 15 bar   | dodecane       | 100% / 98%<br>C17               | (Immer<br>et al.,<br>2010)                |
| Rh/ZrO <sub>2</sub>                                | 0.3 g       | Methyl<br>heptanoa<br>te | 24 h                           | 300 °C | 8 MPa    | -              | 78%/81.8%<br>hexane             | (Bie et<br>al., 2013)                     |
| Ni/SiO <sub>2</sub>                                | 0.25g       | Stearic<br>acid          | 6 h                            | 300 °C | 30 bar   | dodecane       | 100%/96.3%<br>C17               | (Hachemi<br>et al.,<br>2016)              |
| Pt-Re/H-<br>ZSM-5                                  | 1 g         | Jatropha<br>Oils         | 12 h                           | 543 K  | 6.5 MPa  | -              | 100%/ 47.6%<br>C18              | (Murata<br>et al.,<br>2010)               |
| Ni/HBEA                                            | 15<br>wt.%  | Microalg<br>ae oil       | 2 h                            | 260 °C | 40 bar   | -              | 79%/43%<br>C18                  | (Song et<br>al., 2013)                    |
| Ni/ZrO <sub>2</sub>                                | 0.5 g       | Palmitic<br>acid         | 6 h                            | 260 °C | 12 bar   | dodecane       | 100%/ 90%<br>pentadeca<br>ne    | (Peng et<br>al., 2013)                    |
| Ni <sub>2</sub> P/SBA-<br>15                       | 20 wt.<br>% | Methyl<br>Oleate         | 6 h                            | 290 °C | 30 bar   | -              | 100%/ 25%<br>C18                | (Yang et<br>al., 2012)                    |
| 20% Ni/P-<br>2/SBA-15                              | 20<br>wt.%  | Methyl<br>oleate         | 6 h                            | 290 °C | 30 bar   | -              | 80%/40%<br>C18                  | (Yang et<br>al., 2012)                    |
| Co/Al-<br>SBA-15                                   | 5 wt.%      | Methyl<br>oleate         | 6 h                            | 340 °C | 30 bar   | n-<br>heptane  | >70%<br>Conversion              | (Ochoa-<br>Hernánd<br>ez et al.,<br>2013) |

|                                     |          |              |     |        |         |   |                         |                        |
|-------------------------------------|----------|--------------|-----|--------|---------|---|-------------------------|------------------------|
| AlSi <sub>40</sub> Ni <sub>15</sub> | 15 wt.%  | Guaiacol     | 1 h | 300 °C | 50 bar  | - | 87% conversion /72% C18 | (Broglia et al., 2019) |
| MoN <sub>x</sub>                    | 1.5 wt.% | Rapeseed oil | 4 h | 350 °C | 5.5 MPa | - | 90 wt.% yield           | (Horáček et al., 2020) |
| CoMo catalyst                       | 0.6875 g | Oleic acid   | 3 h | 300 °C | 20 bar  | - | 88.9% /48.1% C9–C17     | (Shim et al., 2018)    |

## 2.6 Summary

Clay-supported metal catalysts offer advantages such as improved catalytic activity, higher conversion rates, better selectivity, compatibility with green chemistry principles, and cost-effectiveness. Palladium-based catalysts supported on clay have been investigated for various reactions, including the conversion of Hydroxymethylfurfural to 2,5-dimethylfuran (2,5-DMF), regioselective arylation of 3,4-ethylenedioxythiophene, furfural hydrogenation to 1,2-pentanediol, and oxidation of methane. Pd nanoparticles and Ni/Co intercalated montmorillonite clay have shown efficacy as green catalysts for hydrogenation reactions, including chemo-selective hydrogenation of squalene and the conversion of microalgae oil to diesel-grade hydrocarbons. A Pd/Clay catalytic system utilising molecular H<sub>2</sub> is proposed for hydrogenation of imines under mild reaction conditions.

Deoxygenation and hydrodeoxygenation procedures in vegetable oil are a feasible solution for engine instability and compatibility issues. Various catalysts, including noble metals and hydrodesulphurization (HDS) catalysts, have been investigated for DO reactions. However, these catalysts typically exhibit low to moderate selectivity for HDO over DCO<sub>2</sub>/DCO. Recent research shows good to high selectivity toward CN alkanes in the transformation of microalgae and vegetable oil into hydrocarbons. Transition metal carbides supported by various carbon structures have been reported as promising materials for DO of vegetable oils. The development of cost-effective, high-efficiency catalysts is highly sought for industrial applications. Transition metal catalysts like W, Mo, Fe, Cu, Ni, and Co are suitable for large-scale biomass feedstock processing. However, few studies have been conducted on catalyst deactivation studies on HDO reactions of renewable oils. Numerous significant research gaps exist in the field of heterogeneous solid acid catalysts-based catalytic biofuel generation. The structure-activity relationship, metal dispersion on support materials, role of different oxidation states, which are essential for excellent conversion and selectivity of the biomass feedstock, is not well understood. Additionally, hydrogenation reactions were performed using noble metals like Pd Pt and Rh due to their high activity. Furthermore, there is a lack of research on the catalytic effectiveness of many abundant and inexpensive biomass feedstock's (mainly non-edible oils), with difficulties resulting from feedstock unpredictability and contaminants. There are many obstacles in the way of scaling up these catalytic processes from laboratory to industrial levels and integrating them into the current biofuel production systems.

This research gap has been filled by optimization of different reaction parameters like time, temperature, H<sub>2</sub> pressure, and catalyst loading using novel solid acid catalysts. Also, recyclability and mechanistic route were analyzed. Our lab has been working on biomass feedstock (mainly non-edible oils) to biodiesel, bio jet fuel and bio-CNG production using sustainable clay and Silica-alumina-based catalysts for the last 10 years. The scale-up parameters have already been established to the Technology Readiness Level (TRL) Scale-5 with the startup company Technip Energies and TATA Chemicals by developing highly active, stable, and robust solid acid catalysts for a variety of biomass feedstock's as well as for different bio-oils (linseed, rapeseed, neem, and tung oils). A comprehensive investigation is done to study the Co incorporated into the SiO<sub>2</sub>-

Al<sub>2</sub>O<sub>3</sub> supported catalytic system on the selectivity, stability, and conversion of methyl oleate, a model compound. Further, this study examines the impact of iron oxide loadings on the structural and surface properties of Fe<sub>x</sub>Ni<sub>y</sub>/SA catalysts, using HDO of methyl oleate. It also explores the conversion and C17-C18 selectivity, focusing on the Fe<sup>2+</sup>/Fe<sup>3+</sup> ion ratio. The findings offer new insights into selecting active metal components for green diesel production.

The principal objective of my PhD research is to design and characterize new heterogeneous solid acid catalysts for organic transformation and biofuel generation. Natural and synthetic clay catalyst system have gained attention as catalysts in synthetic organic chemistry due to their ability to catalyse various organic reactions. These inexpensive and environmentally friendly materials can be easily modified with metal cations or organic compounds, enhancing selectivity in product structure and yield. Firstly, we choose the metal incorporated clay as a support for the hydrogenation of imine. The use of clay as a cost-effective, environmentally benign, and abundant support is an ideal choice. Clay-supported metal catalysts are compatible with green chemistry principles, leading to increased productivity and a reduced need for potentially hazardous solvents with increased activity, stability, and selectivity. The detailed analysis was done to analyse the physio-chemical properties of the metal incorporated clay catalysts. Secondly, highly dispersed non-noble metal-based (Co and Fe-Ni doped SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) heterogeneous catalytic systems are developed that displayed excellent conversion and selectivity to convert standard model biomass feedstock (Methyl Oleate) and non-edible oil into diesel grade hydrocarbons. Emphasis was put on comprehending the effect of feedstock variability and contaminants on the catalyst durability and activity. Third, for better understanding of the mechanistic route and improving operational circumstances, HR-MS, NMR and GC techniques were used. Fourth, aside from the high catalytic activity, stability under operating conditions is an essential parameter for practical applications and was addressed to ensure for the industrial application. The stability of the catalyst was analyzed with characterization techniques such as SEM, TEM, TGA, XRD and XPS. Lastly, we focused on increasing the efficiency and scalability of catalytic biofuel generation from the industrial point of view. One of the most important goal is to keep the catalyst's performance intact as we scale up from the lab to the pilot and industrial stages. Considering the catalyst's high surface area, excellent acidic sites, and unique textural properties under relatively mild conditions, the results are promising.