

$\text{Fe}_x\text{Ni}_y/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyzed hydrodeoxygenation of bio renewable platform molecules

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A series of $\text{Fe}_x\text{Ni}_y/\text{SA}$ ($\text{SA} = \text{SiO}_2\text{-Al}_2\text{O}_3$) catalysts were synthesized via solvothermal assisted deposition precipitation synthesis method and explored for low-temperature HDO reaction of methyl oleate into n-alkanes and vegetable oils. A comprehensive study on the effects of increasing iron oxide loading in catalyst samples, i.e., $\text{Fe}_1\text{Ni}_1/\text{SA}$, $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$ and $\text{Fe}_7\text{Ni}_1/\text{SA}$, on the crystallographic, morphological, textual and surface chemical behavior were investigated thoroughly using various spectroscopic techniques. The study disclosed excellent surface area, high acidic strength and reducibility of $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst due to the lowest Fe^{2+} or FeO species. In contrast, higher iron oxide loading leads to the accumulation of Fe^{2+} ions on the surface with reduced metal acid centers and diminished surface area. The catalytic conversion as well as C17-C18 selectivity in catalytic HDO was also scrutinized with particular reference to $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion ratio. The obtained superior catalytic activity and C18 selectivity of $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst are due to the lowest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion ratio. However, the iron oxide loading increased the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion ratio, which ultimately decreased the catalytic activity. Thus, the role of Fe^{2+} species in the deactivation of the catalyst was discussed in detail to establish conversion and selectivity control in the catalytic HDO pathway.

5.1 Experimental section

5.1.1 Catalyst Preparation

The $\text{SiO}_2\text{-Al}_2\text{O}_3$ support was synthesized using a method previously described by R Krishnapriya et al. (Krishnapriya et al., 2020). To prepare, $\text{SiO}_2\text{-Al}_2\text{O}_3$ (SA) support Tetraethylorthosilicate (4 ml), Oleyl amine (0.8 ml), Aluminium acetylacetonate (0.4 g), and DI water (2 ml) were ultra-sonicated for 30 minutes in a Teflon seal (100 ml) and hydrothermally treated at 160 °C for 16 hours. The yellow-colored mixture was dried in an oven at 110 °C for 6 hours. Following that, $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalysts were prepared by chemical deposition precipitation employing liq. NH_3 as a pH regulator and iron and nickel nitrate precursors. To maintain the theoretical weight% of $\text{Fe}/\text{Ni} = 1:1$, a fixed amount of nickel nitrate (0.10 gm) and iron nitrate (0.15 gm) was added to 20 ml of DI water containing 2 gm of the aforementioned synthesized support. The pH of the stated above solution was then maintained at 10-11 by adding liq. ammonia to produce a dark brown precipitate. The precipitate was then filtered, washed until pH 7 was reached, and dried overnight in a vacuum oven at 80 °C. After that, the sample was calcined in a N_2 environment for 3 hours at 700 °C. The remaining catalysts, $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$, and $\text{Fe}_7\text{Ni}_1/\text{SA}$, were made using the same process and were labeled with different Fe/Ni loadings of 3:1, 5:1, and 7:1, respectively.

5.1.2 Characterization techniques

XRD patterns were recorded on an X-ray diffractometer (Ultima IV, Rigaku) using $\text{Cu K}\alpha$ radiation spanning the range $5^\circ < 2\theta < 80^\circ$, operating at 60 kV and 60 mA. TGA was conducted on Rigaku TG-8120 using nitrogen flow (10 ml min^{-1}). The heating rate was maintained at $10^\circ \text{C min}^{-1}$ until the temperature reached 800 °C. Scanning electron microscopy (SEM) EVO 18 microscope is used to evaluate the surface morphology of the synthesized catalyst at 200 kV accelerated voltage. The elemental composition was detected by EDS-51-ADDD-0048 detector, where powdered catalysts were adhered on the double-sided carbon tape as a thin layer. The morphology and elemental composition were investigated using an FEI Tecnai-G2 T20 TEM. BET surface area and pore volume of the sample catalysts were determined using ASAP 2010, Micromeritics and nitrogen adsorption-desorption isotherms measured at -196 °C. Samples were

degassed using helium gas at 150 °C over 3 hours prior analysis. XPS studies equipped with monochromatic Al K α radiation were performed using K-alpha, Thermo Scientific Inc. The pressure in analytical chamber was kept at 4.8×10^{-9} mbar. Detector was set to constant energy mode, using 50 eV for detailed scanning and pass energy of 100 eV for the survey spectrum. During XPS analysis, peak correction was performed by calibrating binding energies of C 1 s transitions at 284.6 eV. The active concentration of iron species was validated using an electron paramagnetic resonance (EPR) spectrometer, the JEOL JES-FA200.

H₂-TPR, NH₃-TPD and CO₂-TPD were conducted on a chemisorption analyzer from AMI-300, Altamira Instruments equipped with a TCD. In H₂-TPR, samples were heated at 150 °C for 1 h in a helium environment, cooled at RT, then heated to 750 °C at 10 °C min⁻¹ in a 5% H₂ flow (30 ml/litre). Prior to NH₃-TPD experiment, catalysts were heated under helium flow up to 300 °C for 30 min and then cooled to RT. NH₃ was then adsorbed on the catalysts at 100 °C for 30 min and treated catalysts were then heated from 100 °C to 900 °C under a flow of He at a rate of 10 °C min⁻¹. The CO₂-TPD measurement was accompanied by a 1 h prior treatment using He at 500 °C, then followed by a 2 h purging with He ensuring the elimination of any potentially adsorbed species. The CO₂-TPD was evaluated at temperatures ranging from 50 to 700 °C, with a heating rate of 10 °C min⁻¹.

5.1.3 Catalytic Activity Test

For the catalyst test, 100 μ L of methyl oleate and 10 mg of synthesized catalysts were put in a stainless steel autoclave with a capacity of 25 ml. All hydro-treatment processes were carried out in a solvent-free environment. In the sealed reactor, a hydrogen atmosphere was achieved by purging pure hydrogen gas three times to eliminate air residue, and the initial pressure was kept at 10 bar throughout every experiment. The temperature of the reactor was then gradually raised (5 °C min⁻¹) to 250 °C and kept for the desired reaction period. After the reaction, the reactor was cooled, and the products were extracted using n-heptane (5 ml), followed by centrifugation to separate the solid catalyst. The liquid fraction was then qualitatively assessed by Gas Chromatography (GC) using a FID detector (Phimsen et al., 2017). The product hydrocarbon distribution was evaluated in terms of conversion and selectivity, as previously reported (Krishnapriya et al., 2020).

5.2 Results and Discussion

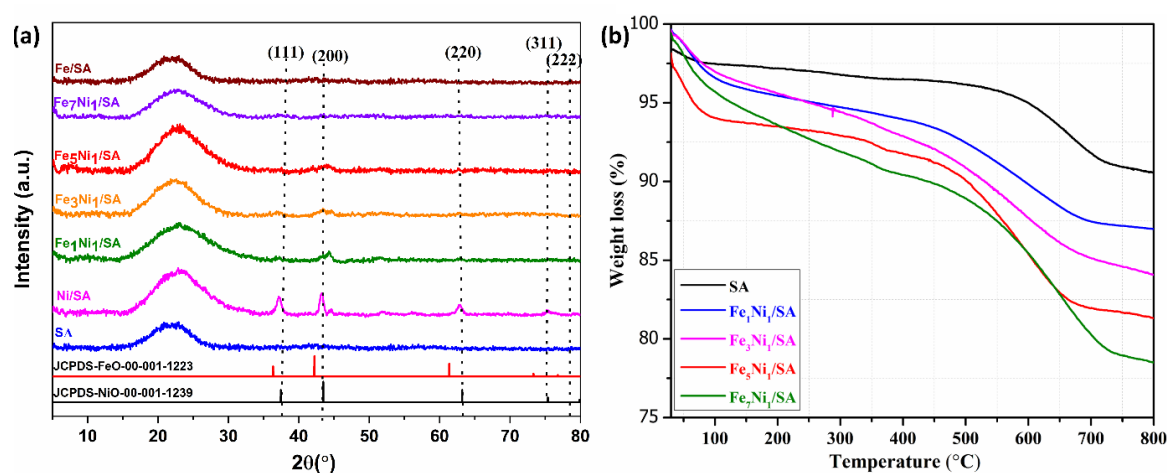


Figure 5.1 (a) Diffraction pattern (b) thermogram of Fe_xNi_y/SA catalysts with various iron oxide and nickel oxide loadings and support SA.

Figure 5.1 (a) illustrates the diffraction pattern of the synthesized catalyst (Fe_xNi_y/SA) with different amounts of iron oxide-nickel oxide and support (SA). As observed in **Figure 5.1 (a)**, the SA support showed a prominent diffraction peak at 20~22° corresponding to amorphous SiO₂, present in excess molar ratio, i.e., SiO₂/Al₂O₃ = 15 (Cheng et al., 2017).

To understand the incorporation of nickel oxide and iron oxide particles supported over support SA, pristine Ni/SA and Fe/SA, were synthesized and examined by XRD as depicted in **Figure 5.1 (a)**. The Ni/SA samples revealed NiO (JCPDS 00-001-1239) diffraction peaks at $2\theta = 37.14^\circ$ (111), 43.2° (200), 62.8° (220), 75.2° (311) and 79.3° (222), in addition to a wide peak at $2\theta \sim 22^\circ$ corresponding to amorphous SA support. However, the XRD pattern of the Fe/SA pattern indicated no significant peak of the iron oxide crystalline phase, which might be due to the presence of extensively dispersed or amorphous particles, as previously reported by Hu et al (Hu et al., 2020).

In the diffractogram of $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst, the additional characteristic diffraction peaks of NiO at 44.01° were observed (JCPDS 00-001-1239). However, these peaks are deflected at (200) plane due to lattice strain originated by the incorporation of iron oxide particles into nickel oxide crystal lattice. The intensity of peaks decreased when iron oxide loading increased from $\text{Fe}_1\text{Ni}_1/\text{SA}$ to $\text{Fe}_7\text{Ni}_1/\text{SA}$. The $\text{Fe}_7\text{Ni}_1/\text{SA}$ shows diffractogram patterns similar to support [16]. The characteristic diffraction peaks of SA support remain unchanged with iron oxide-nickel oxide loading. Notably, the iron oxide characteristics peaks were not found in any of the $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalyst samples (Hu et al., 2020). The XRD pattern of the entire bimetallic catalyst lacks sharp diffraction peaks for Fe-Ni alloy formation, suggesting that the Ni^{2+} is not reduced to Ni and there is no presence of metallic iron, confirming the absence of FeNi_3 phase. After the reductive reaction environment, partial Fe^{n+} ions are not reduced and do not interact with surface Ni, hence no Fe-Ni alloy formation (Theofanidis et al., 2015).

Figure 5.1 (b) reports the representative thermogram for the uncalcined $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalyst and SA support. All of the catalyst samples, as well as the support, exhibit a mass loss in two stages. In the first stage, mass loss in the temperature range of $30\text{--}200^\circ\text{C}$ can be related to surface adsorbed and/or crystalline water removal from the catalyst and support, respectively. While in the second stage, slow mass removal was observed in the temperature range of $400\text{--}800^\circ\text{C}$, which can be assigned to the decomposition of inorganic moieties such as nitrates and ammonia that are chemisorbed on the surface of catalyst particles. The decomposition of inorganic moieties can be further identified using basic thermodynamics, which shows the ammonia decomposition process is endothermic ($2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}); H^\circ = 92 \text{ kJ mol}^{-1}$) and achieves 99.99 % ammonia conversion at 400°C . This confirms that a high working temperature is required to carry out the ammonia decomposition (Lucentini et al., 2021). Furthermore, the slow change in the mass loss likely originates from the decomposition of the nitrate anion at higher temperatures (Breternitz et al., 2018). In addition, Ashok and co-authors supported our result of the decomposition of nitrates (Ashok et al., 2015). A total weight loss of 8.63 %, 13.31 %, 17.45 %, 19.1 % and 23.07 % were observed for SA, $\text{Fe}_1\text{Ni}_1/\text{SA}$, $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$ and $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalyst samples, respectively (Sancheti et al., 2020). A very high weight loss for $\text{Fe}_7\text{Ni}_1/\text{SA}$ samples might be attributed to the highest iron loading amount.

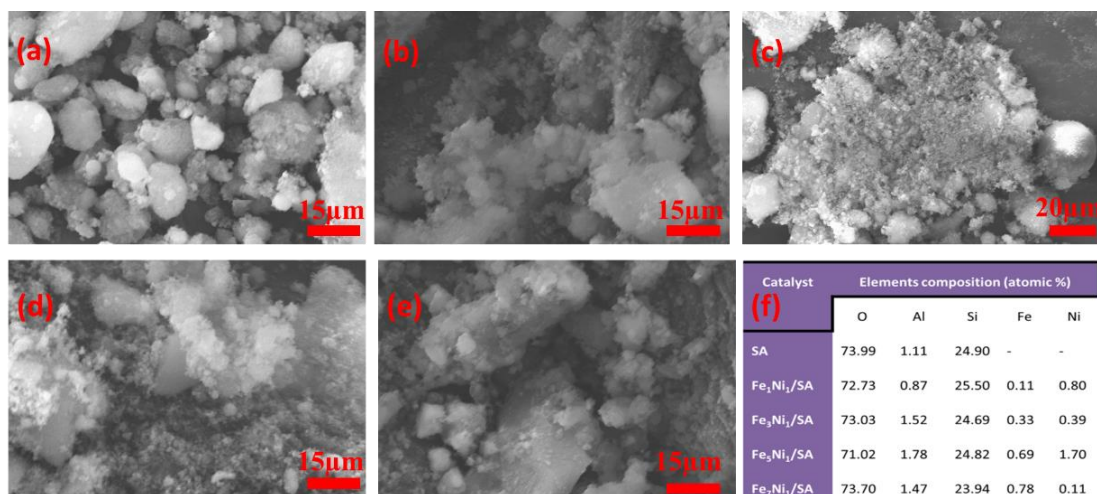


Figure 5.2 SEM micrographs (a) SA (b) $\text{Fe}_1\text{Ni}_1/\text{SA}$ (c) $\text{Fe}_3\text{Ni}_1/\text{SA}$ (d) $\text{Fe}_5\text{Ni}_1/\text{SA}$ (e) $\text{Fe}_7\text{Ni}_1/\text{SA}$ with (f) elemental composition detected by EDX.

The SEM micrographs revealed the irregular particle morphology of synthesized SA support and iron oxide-nickel oxide modified catalyst ($\text{Fe}_x\text{Ni}_y/\text{SA}$) samples. As shown in **Figure 5.2 a**, SA support shows irregular round-shaped agglomerations of loose glazed nano-particles. During deposition precipitation synthesis, the dispersion of iron oxide and nickel oxide in various weight ratios, the surface of these particles becomes burrlike (**Figure 5.2 b–e**) (Adnan et al., 2017). Furthermore, we have performed the TEM analysis of SA loaded with different Fe/Ni ratios in **Figure 5.3**. EDX spectra provided the semi-quantitative analysis of surface elements. For all the catalyst samples, Si, Al, and O are the constituents of the support structure ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 15:1$ M ratio). After loading with the various amounts of iron oxide and nickel oxide, EDX mapping confirms the presence of iron and nickel elements (**Figure 5.4**). EDX elemental mapping validated the elemental composition and distribution of the elements Si, Al, Ni, Fe and O have been established by EDS spectra.

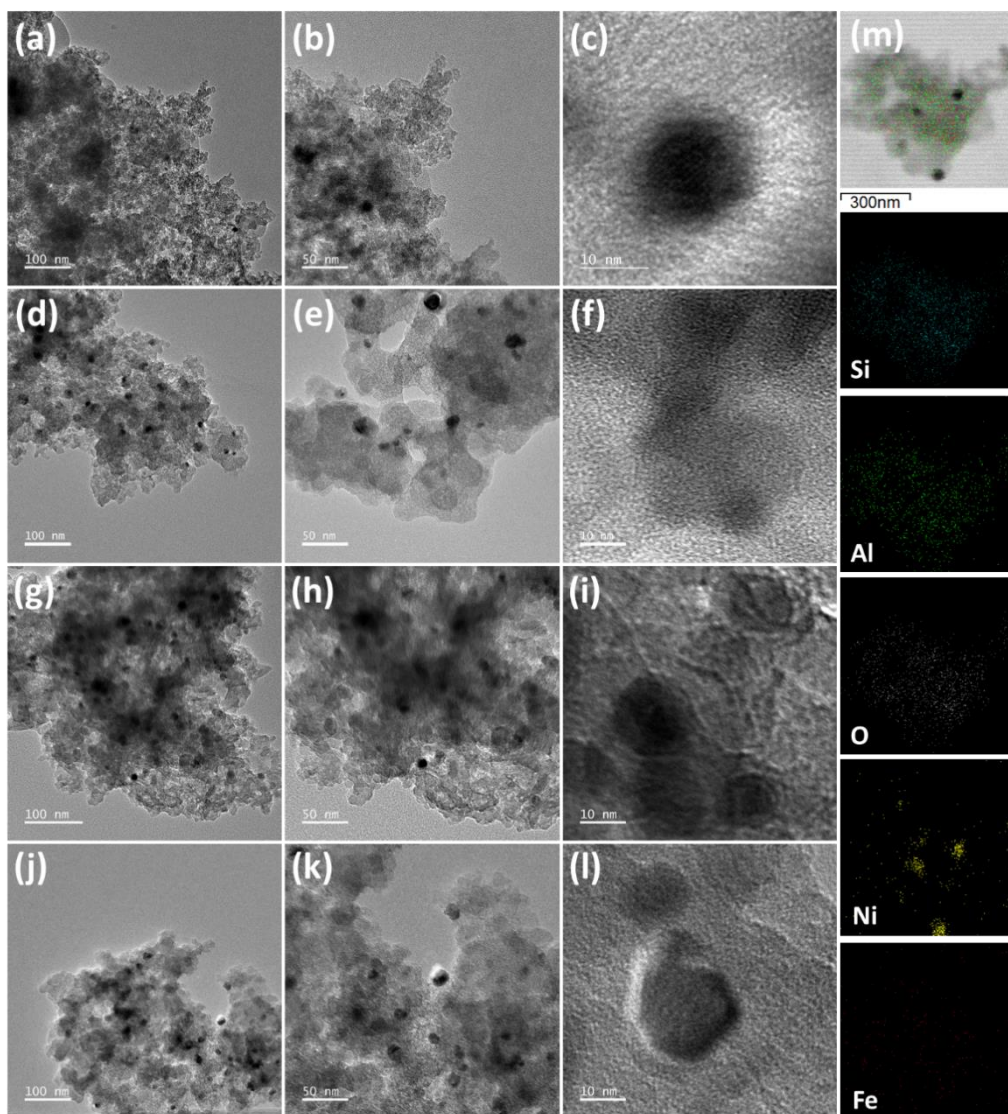


Figure 5.3 TEM images of $\text{SiO}_2\text{-Al}_2\text{O}_3$ loaded with different Fe/Ni ratio (a-c) Fe_1Ni_1 , (d-f) Fe_3Ni_1 , (g-i) Fe_5Ni_1 , (j-l) Fe_7Ni_1 , and (m) elemental mapping of Fe_1Ni_1 , showing Si, Al, O, Ni and Fe distribution.

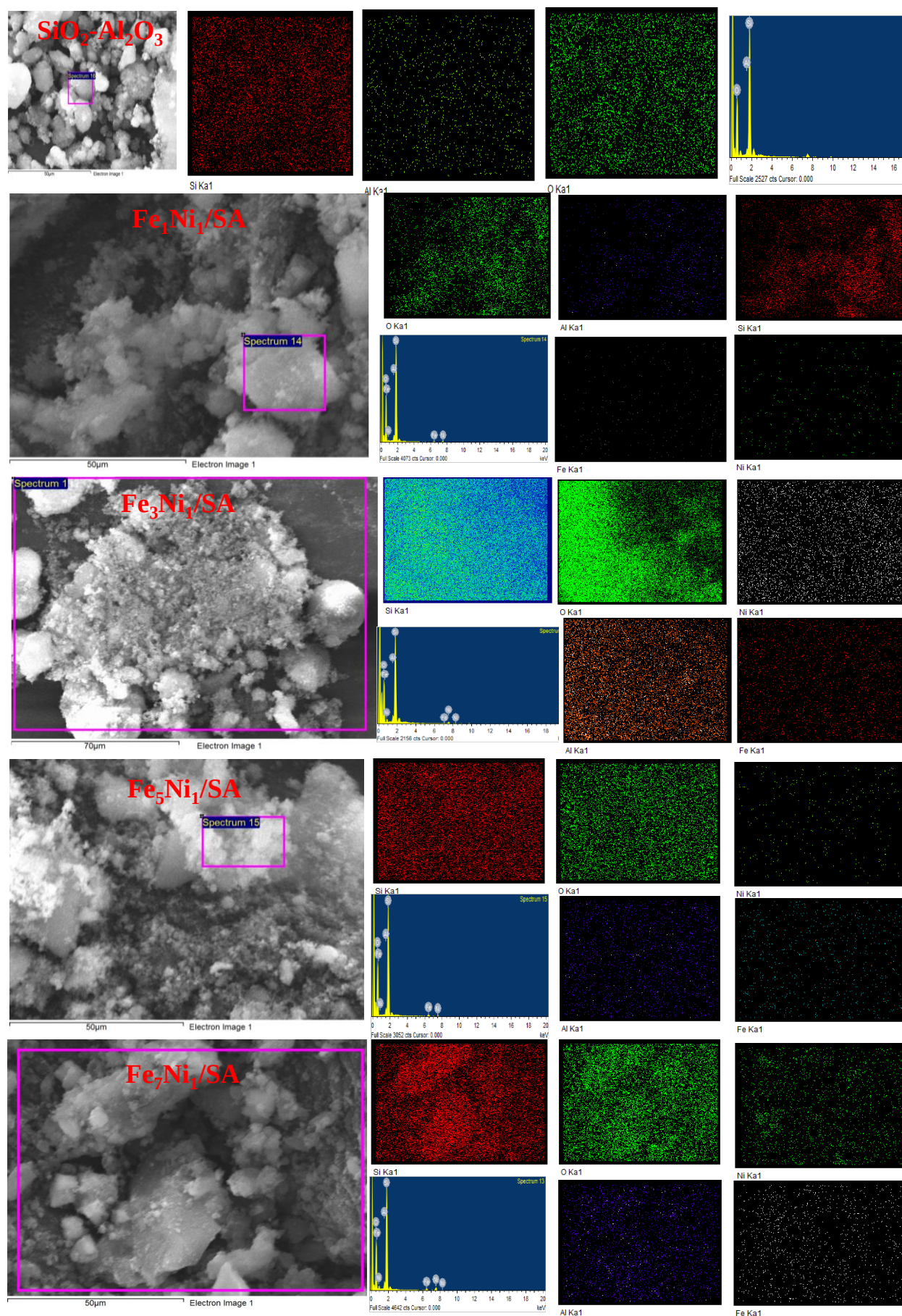
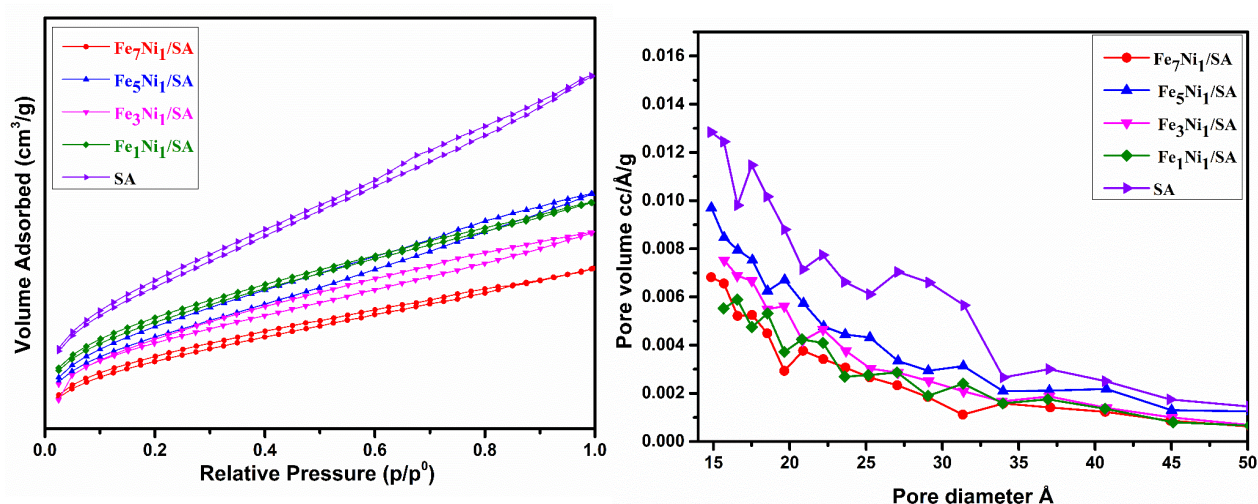


Figure 5.4. Elemental mapping of as-synthesized $\text{SiO}_2\text{-Al}_2\text{O}_3$ support, $\text{Fe}_1\text{Ni}_1/\text{SA}$, $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$ and $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalysts.

Table 5.1 Textural properties and total Acidity of various catalysts $\text{Fe}_x\text{Ni}_y/\text{SA}$ and support SA.

Samples	BET-BJH analysis			Total Acidity (mmol g^{-1})
	Surface Area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	
SA	430.5	0.40	3.75	0.20
$\text{Fe}_7\text{Ni}_1/\text{SA}$	337.9	0.28	3.69	0.85
$\text{Fe}_3\text{Ni}_1/\text{SA}$	305.4	0.27	3.45	0.69
$\text{Fe}_5\text{Ni}_1/\text{SA}$	287.1	0.24	3.36	0.35
$\text{Fe}_7\text{Ni}_1/\text{SA}$	265.5	0.22	3.23	0.24

**Figure 5.5.** BET-BJH analysis of as-synthesized $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalyst.

The N_2 adsorption-desorption analysis was performed to obtain the BET surface area. The surface area is positively related to the exposure of the active centres for reactions (Liu et al., 2022). The surface area and textural properties, such as pore diameter and pore volume of synthesized support SA and catalyst samples $\text{Fe}_x\text{Ni}_y/\text{SA}$, are summarised in **Table 5.1**. As shown in **Figure 5.5 a**, the support and all catalyst samples exhibited type IV adsorption-desorption isotherms and H1 hysteric loop which signifies the multilayer adsorption on the porous adsorbent. The capillary condensation in mesopores of adsorbent was responsible for H1 hysteric loop in N_2 adsorption-desorption isotherms. The support SA demonstrated the highest surface area of $430.49 \text{ m}^2\text{g}^{-1}$. After impregnation with iron oxide and nickel oxide in an equal weight ratio, i.e., $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst sample, the surface area is reduced to $337.92 \text{ m}^2\text{g}^{-1}$. Further, increment of iron oxide in the catalyst resulted in the reduction in the surface area to 29.06 %, 33.30 %, and 38.30 % for $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$, and $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalysts, respectively.

All the catalyst samples were mesoporous ($2 < \text{pore size} < 50 \text{ nm}$) as per IUPAC nomenclature. A similar trend of decreasing pore volume and pore diameter was observed in **Figure 5.5 b**, which may be attributed to the partial coverage of available pores of parent SA support after impregnation with metal oxides (Xue et al., 2018).

Table 5.2. XPS peaks of iron and nickel in Fe_xNi_y/SA catalyst.

Elements	Electronic state	Photoemission peaks (eV)			
		Samples			
		Fe ₁ Ni ₁ /SA	Fe ₃ Ni ₁ /SA	Fe ₅ Ni ₁ /SA	Fe ₇ Ni ₁ /SA
Fe	2P _{3/2}	711.09	711.06	711.01	711.04
		714.45	714.56	714.37	714.47
	2p _{1/2}	724.34	724.46	724.54	724.17
	Sat.	729.23	729.48	729.13	729.22
	Fe ²⁺ /Fe ³⁺	0.29:1	0.42:1	0.75:1	0.81:1
	Atomic %	0.23	0.21	0.31	0.44
Ni	2P _{3/2}	855.80	855.43	855.35	855.60
	2p _{1/2}	873.76	873.93	872.90	873.82
	Sat.	861.92	861.05	861.14	861.41
		880.66	880.16	878.74	880.54
	Atomic %	0.25	0.18	0.25	0.21

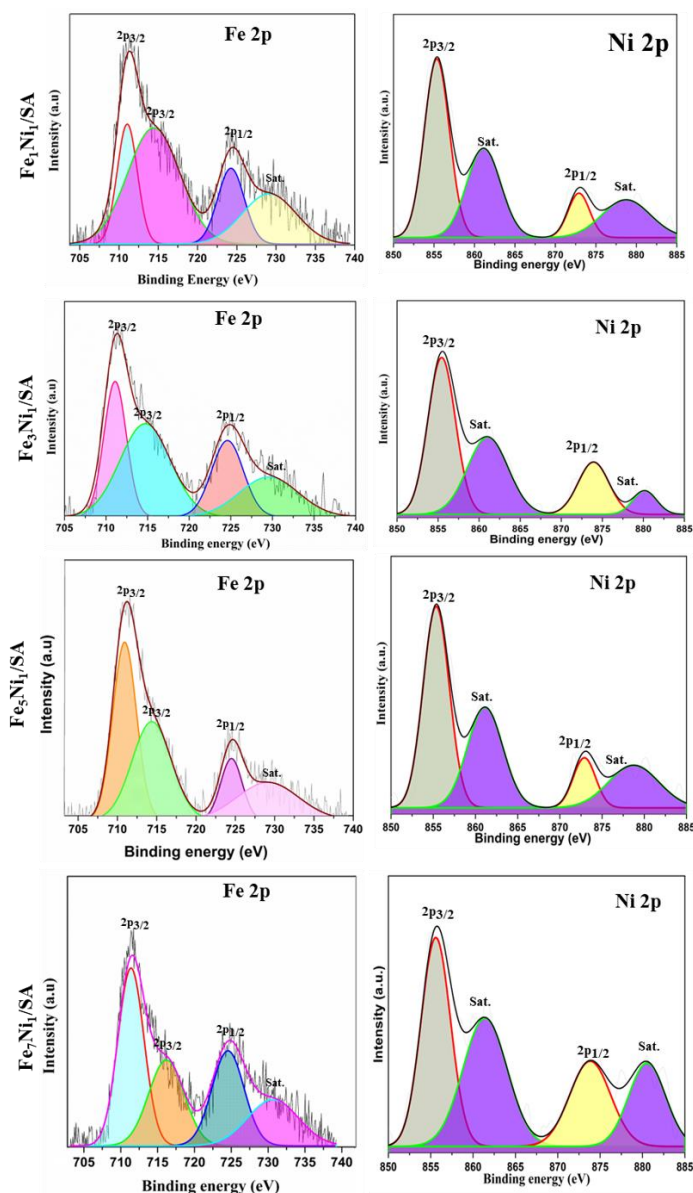


Figure 5.6 XPS spectra of Fe_xNi_y/SA catalyst in the Fe 2p region and Ni 2p.

To investigate the chemical and electronic states of surface elements such as Fe, Ni, Si, Al, and O, XPS analysis of $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalyst samples was carried out, and the data obtained was deconvoluted using Gaussian fitting. **Figure 5.6** shows the XPS spectra of Ni and Fe components, while **Table 5.2** summarizes the photoemission peaks. As shown in **Figure 5.6**, two strong photoemission peaks at 855.16 ± 0.8 eV and 872.81 ± 0.3 eV were observed in all catalyst samples, confirming the Ni $2p_{1/2}$ and Ni $2p_{3/2}$ spin-orbit splitting of NiO and Ni(OH)₂ species, respectively (Mitchell et al., 2021). The two satellite peaks are also detected at 862-864 eV and 879-880 eV (Huang et al., 2017). Furthermore, the iron XPS spectra in all catalyst samples showed a binding energy (B.E) peak in the of 710-730 eV region. The two XPS peaks at 714.45 ± 0.15 eV and 724.37 ± 0.25 eV in the spectral range were ascribed to spin-orbit split of Fe $2P_{3/2}$ and Fe $2P_{1/2}$ resembling Fe^{3+} species (Sarkar et al., 2020). The precise positions of the satellite peaks for the Fe 2p peaks are extremely sensitive to oxidation states, and these peak locations have been employed to identify the ionic states of iron qualitatively. The satellite peak due to Fe $2P_{1/2}$ at 729.3 ± 0.2 eV confirms the $\gamma\text{-Fe}_2\text{O}_3$ phase in the synthesized catalysts. It should be noted that the peak at 711.04 ± 0.05 eV is the characteristic of Fe^{2+} species in $2p_{3/2}$ spin state and is continuously intensified with the increase of iron loading (Sarkar et al., 2020).

The chemical state of the iron on the surface of a catalyst may be expressed as Fe_aO_b (where a and b represent the stoichiometric ratio of Fe and O, respectively) to be 2^+ or 3^+ and 2^- . For catalysts $\text{Fe}_1\text{Ni}_1/\text{SA}$, $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$, and $\text{Fe}_7\text{Ni}_1/\text{SA}$, the Fe^{2+} and Fe^{3+} ion ratios are 0.29:1, 0.42:1, 0.75:1, and 0.81:1, respectively (Graat and Somers, 1996). According to a previous report, Fe^{3+} ions existing inside the multilayer structure were rapidly reduced to Fe^{2+} in the temperature range of 300–400 °C (Shi et al., 2019). The most noticeable consequence is a shift in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, i.e., a substantial increase in structural Fe^{2+} and a concurrent drop in structural Fe^{3+} . The reduction of structural Fe^{3+} to Fe^{2+} is associated with a rise in layer charge and consequently leads to a change in cation exchange capacity, which might be explained by structural iron leaving the octahedral sheet (Lerf et al., 2010). A slight shift in the photoemission peaks of nickel in a lower B.E and iron with a higher B.E. This means that there has been long-range electronic interaction via partial charge transfer between nickel and iron atomic orbitals ($\text{Fe}^{3+} \rightarrow \text{Ni}^{2+}$). In bimetallic catalysts, this bimetallic interaction between neighboring Fe and Ni atoms could act as the intrinsic driving force for the formation of Fe-Ni pairs (Al-Gaashani et al., 2013, Wang et al., 2022).

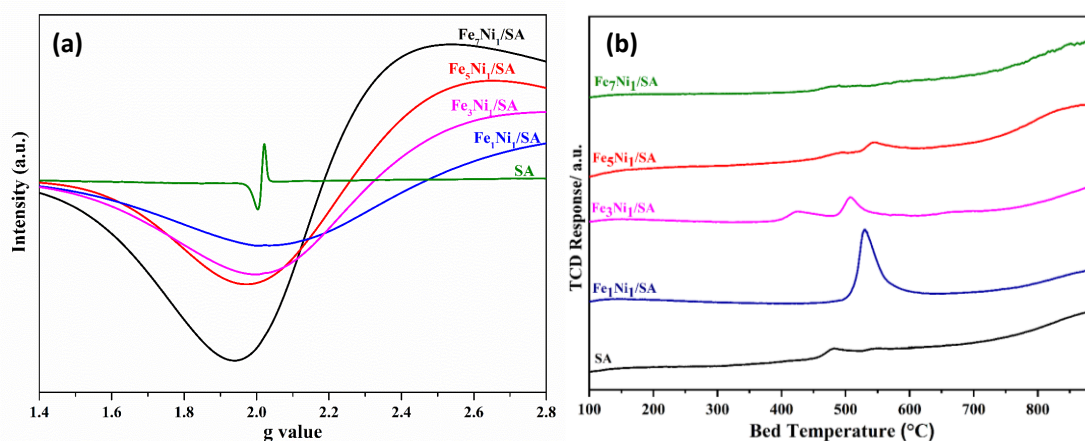


Figure 5.7 (a) EPR spectra and (b) NH_3 -TPD curves of $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalysts.

Electron Paramagnetic Resonance (EPR) experiments are used to study the oxidation state and site occupancy of transition metal ions in minerals, as well as local site symmetry and unpaired spins of different paramagnetic ions. Fe^{3+} and Fe^{2+} can be easily differentiated by EPR spectra due to their different numbers of unpaired electrons in their outer-most orbitals and significant differences in spin-lattice relaxation times (Huang et al., 2017). It was reported that EPR intensity increases at higher Fe loading owing to the clustering of Fe ions, leading to concentration quenching (Borse et al., 1999). In another study, EPR spectroscopy was employed to investigate Fe^{3+} . It was found that when the Fe^{3+} concentration decreases, the spin exchange interaction

between two neighboring Fe^{3+} sites reduces, resulting in gradual increase in EPR signal intensity (Sambasivam et al., 2009). Furthermore, EPR spectroscopy validated the existence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions. The Fe^{2+} species is EPR silent and non-Kramer's, while the Fe^{3+} species is EPR active and provides a well-defined symmetrical one-line peak centered at $g \sim 2$. The $\text{Fe}_7\text{Ni}_1/\text{SA}$ sample had an intense absorption peak due to the maximum quantity of iron loading in the sample, whereas the $\text{Fe}_1\text{Ni}_1/\text{SA}$ sample showed the lowest intensity peak (Sambasivam et al., 2009). Spectral signal position (value of g) is a characteristic associated with molecule interactions such as ligands, solvent medium, and molecule environment. The g value of the sample $\text{Fe}_1\text{Ni}_1/\text{SA}$ was 2.47, but the subsequent increase in Fe loading, i.e., $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$, and $\text{Fe}_7\text{Ni}_1/\text{SA}$, followed a decreasing trend of g values of 2.32, 2.25, and 2.18, respectively. This might be due to the unavailability of Fe^{3+} species due to cluster formation with nanoparticles of SA support or dominant Fe^{2+} ions, as validated by XPS analysis (Liu et al., 2021).

NH_3 -TPD was used to examine the surface acidity of the synthesized catalysts ($\text{Fe}_x\text{Ni}_y/\text{SA}$), and support (Figure 5.7 b), and the total acidity results are presented in Table 5.1. The acidic sites on the catalyst sample significantly impact the conversion pathways of lipids into biofuels and the product selectivity. As shown in Table 5.1, the acidity of catalyst materials with varied iron oxide content and support follows decreasing patterns: $\text{Fe}_1\text{Ni}_1/\text{SA} > \text{Fe}_3\text{Ni}_1/\text{SA} > \text{Fe}_5\text{Ni}_1/\text{SA} > \text{Fe}_7\text{Ni}_1/\text{SA}$ (Saini et al., 2022). All samples showed two types of surface acidity: the small peak at 100-200 °C was due to mild ammonia adsorption, i.e., a weak acidic site, while the peaks between 400-800 °C were related to medium to strong acidic sites. The literature shows Lewis acid sites comprise medium to high acid sites, whereas Bronsted acid sites are low acid sites (Li et al., 2014a). The acidity of the SA support was 0.20 mmol/g of ammonia desorbed, but when nickel oxide and iron oxide were incorporated in a 1:1 weight ratio, the acidity increased to 0.85 mmol/g. Remarkably, increasing the iron oxide content of the catalyst reduced the total acidity substantially. A lowered iron oxide loading in the catalyst, for instance, $\text{Fe}_1\text{Ni}_1/\text{SA}$ or $\text{Fe}_3\text{Ni}_1/\text{SA}$, suggests that nickel oxide and/or iron oxide are well dispersed or exposed on a high surface area support. These produce high-acid sites and metal centers (Ni^{+2} or Fe^{3+}) responsible for surface acidity. In the case of high iron oxide loading using $\text{Fe}_5\text{Ni}_1/\text{SA}$ and $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalysts, Fe^{2+} species predominate, further nullifying the acidic sites caused by basicity center generation (Golubeva et al., 2020).

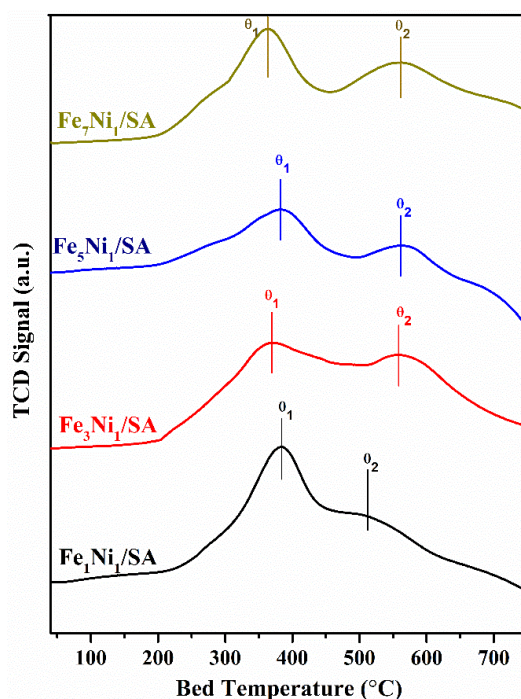
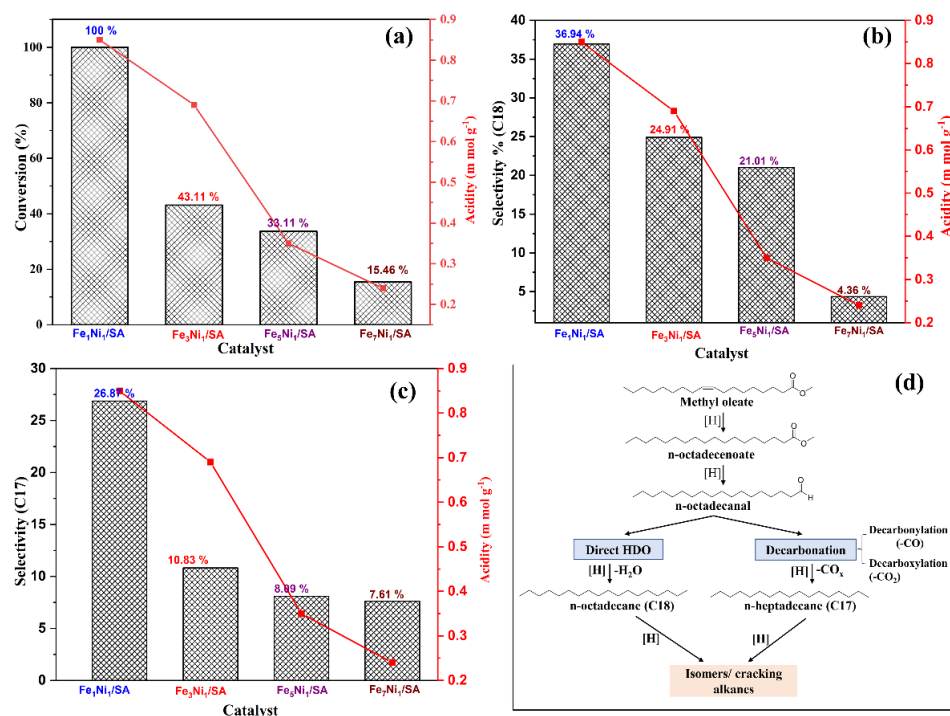


Figure 5.8 H_2 -TPR curves of various catalysts $\text{Fe}_x\text{Ni}_y/\text{SA}$.

Table 5.3. Results of H₂TPR for Fe_xNi_y/SA catalyst samples.

Samples	Peak position (°C)		H ₂ consumption (mmol g ⁻¹)	Degree of reduction (%)
	θ ₁	θ ₂		
Fe ₁ Ni ₁ /SA	384.4	509.8	4.18	351.78
Fe ₃ Ni ₁ /SA	369.5	557.3	4.59	482.33
Fe ₅ Ni ₁ /SA	380	559.6	4.29	360.91
Fe ₇ Ni ₁ /SA	365.1	561.2	5.37	527.29

The H₂-TPR curve and total hydrogen consumption for Fe_xNi_y/SA catalysts with varied iron oxide and nickel oxide loading are depicted in **Figure 5.8** and **Table 5.3**. TPR spectra for all catalyst samples showed two distinct stages of reduction behaviour: θ₁ (weak interaction, at approximately 365-385 °C) and θ₂ (moderate interaction, around 500-560 °C). (Chen et al., 2018, Li et al., 2014b, Wang and Xie, 2001) The Fe₁Ni₁/SA sample displayed an intense reduction peak at 384.4 °C with small shoulder peaks over the temperature that ranged from 500-550 °C, with a degree of reduction of 351.78%. The other catalyst samples showed two strong reduction peaks, θ₁, and θ₂, implying weak to medium metal support interaction (Yang et al., 2013). As seen in **Figure 5.6**, increasing iron loading amplifies the second peak (500-700 °C). According to the available literature, the low-temperature peak might be due to the reduction of loaded M^{2+/3+} species to M⁺ species which interact weakly with the support. Furthermore, emergence of the second peak might be attributed to the reduction of M⁺ into M⁰. The sharpness of the second peak increases gradually with iron loading from Fe₁Ni₁/SA to Fe₇Ni₁/SA, indicating the intensified metal-support interaction, which may lead to difficulty in reduction (Ye et al., 2019). H₂-TPR is used to evaluate the bimetallic interaction between Ni and Fe and the reducibility of catalysts supported on silica-alumina support. The H₂-TPR profiles of bimetallic catalysts in Fe₁Ni₁/SA, Fe₃Ni₁/SA, Fe₅Ni₁/SA, and Fe₇Ni₁/SA catalysts show desorption peaks at varying temperatures than monometallic Ni and Fe catalysts, indicating the bimetallic interactions between Fe and Ni (Arora et al., 2018).

**Figure 5.9** Catalytic performance of Fe_xNi_y/SA over methyl oleate in HDO; (a) Conversion, (b) C18 selectivity, (c) C17 selectivity, and (d) Possible reaction scheme for hydrodeoxygenation of methyl oleate.

The textural properties, surface acidity and basicity contribute to the high deoxygenation performances of the synthesized catalysts. Due to the high acidity of the surface of the

synthesized catalyst, the textural properties and surface acidity facilitate high deoxygenation performances, resulting in promoted cracking. The effect of iron oxide concentration on the catalytic efficacy of $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalysts was investigated for HDO of methyl oleate. All the experiments were performed at 250 °C temperature and 10 bar H_2 pressures for 6 h. The obtained results of conversion into diesel-grade alkanes, C17 and C18 selectivity are demonstrated in **Figure 5.9**. As seen in **Figure 5.9 (a)**, the $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst showed 100% methyl oleate (MO) conversion into hydrocarbons. The exceptionally high catalytic activity of $\text{Fe}_1\text{Ni}_1/\text{SA}$ in the HDO reaction is attributed to the highest surface area along with excellent surface acidity (Soni et al., 2017). Furthermore, the C18 and C17 selectivity were also evaluated and presented in **Figure 5.9 (b) and (c)**, respectively. Notably, selectivity towards C17 and C18 n-alkane is a function of acidic sites on the catalyst surface (Ding et al., 2022). The HDO process requires a metallic hydrogenation site and support that adsorbs the oxy molecule, it occurs on the metal-support interface (Teles et al., 2020). The cracking reaction of the C-C bond and C-O bond, illustrated in **Figure 5.9 (d)**, involves the decarbonization ($-\text{CO}_x$) and deoxygenation ($-\text{H}_2\text{O}$) pathways, respectively. The weak acidic sites allow the adsorption of the oxygen-containing functional group due to their enhanced electrophilicity, resulting in C-C bond activation adjacent to the C-O bond (Yang et al., 2013). The DCO and DCO_2 reactions then cleave the C-C bond, resulting in C-17 products. Meanwhile, increased acidity synergistically triggers the dissociation of hydrogen gas into hydrogen atoms and the activation of the C-O bond. It leads to removal of water molecules via the HDO pathway, resulting in the synthesis of additional C18. Strong acidity centers predominate over weak or Bronsted acidic centers in all synthesized catalyst samples (Jeon et al., 2020). As shown in **Figure 5.9 (b & c)**, the proportion of C18 n-alkanes is more predominant, i.e., 36.94%, 24.91%, and 21.01%, compared to the C17 fractions of 26.87%, 10.83%, and 8.09% employing $\text{Fe}_1\text{Ni}_1/\text{SA}$, $\text{Fe}_3\text{Ni}_1/\text{SA}$, and $\text{Fe}_5\text{Ni}_1/\text{SA}$ catalysts, respectively. However, because of its weak acidity, the $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalyst created more C17 (7.61%) than C18 (4.36%).

The inclusion of a second metal has a significant influence on HDO's activities and product distribution. The surface area and pore volume of the $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalyst decreased as a result of Fe poisoning during the HDO experiment. Metal sintering and Lewis acid site blockage both contribute to the catalyst's deactivation (Forzatti and Lietti, 1999). Persistent pore blockage accelerated deactivation over time, due to increased Fe loading and the formation of the less active FeNi phase. This results in a drop in overall activity and a slight rise in DCO_2 product (C17) formation (Liao et al., 2021). In addition, literature studies showed that HDO of phenol over the bimetallic catalyst, PdSn/ZrO_2 catalyst displayed considerably slower reaction rates as compared to monometallic catalysts (Resende et al., 2018). The reduction in activity was caused by the segregation of the second metal on the surface. The Pd dispersion reduced significantly during the reaction, which suggests that the sintering of Pd particles contributes to the catalyst's deactivation. Additionally, studies demonstrated that the introduction of iron into a monometallic nickel catalyst renders it resistant to ring hydrogenation (Kiméné et al., 2019). The authors proposed that the Ni-Fe surface is poorly ordered, with Fe atoms present in significant excess in the first atomic layers, causing maximum repulsion between aromatic rings and the metal, explaining its poor hydrogenation activity. On the other hand, the addition of a second metal in the catalyst may alter the structure and morphology of the catalyst which might result in a change in activity (Jiao et al., 2021).

The present study demonstrates that increasing iron oxide content in a catalyst leads to a significant reduction in surface area and pore volume. This is attributed to the partial coverage of available pores of the parent support ($\text{SiO}_2\text{-Al}_2\text{O}_3$) after impregnation with metal oxides. Increasing the iron oxide loading from 3:1 ($\text{Fe}_3\text{Ni}_1/\text{SA}$) to 7:1 ($\text{Fe}_7\text{Ni}_1/\text{SA}$) reduces surface acidity due to an increase in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion ratio as well as smaller pore size, diminishing the conversion value from 43.11% to 15.46%. As can be seen, the order of the catalytic activity was observed as $\text{Fe}_1\text{Ni}_1/\text{SA} > \text{Fe}_3\text{Ni}_1/\text{SA} > \text{Fe}_5\text{Ni}_1/\text{SA} > \text{Fe}_7\text{Ni}_1/\text{SA}$. The acidic characteristics of the catalyst surface are influenced by the dispersity and reducibility of active metal centers on the support. The textural properties and surface acidity simultaneously facilitate high deoxygenation performances of the synthesized catalysts, as high acidity is the center of oxygen removal, resulting in promoted cracking products. In the current study, we added Fe^{3+} precursor into the

catalyst but the presence of intimate and stronger Ni-Fe interactions results in increased Fe^{2+} species as revealed by the XPS technique. The bimetallic interactions are also substantiated using TPR results. Increasing Fe loading doesn't affect general TPR shape, but shifts the reduction peaks to higher temperatures. This indicates difficulties in the reduction of the bimetallic catalyst, contributing to the poisoning of the catalysts (Ratkovic et al., 2011) (Xue et al., 2017). The monometallic Fe catalyst is the least active with a final conversion of 59 %. With final conversions of 15.46 %, the activity of $\text{Fe}_7\text{Ni}_1/\text{SA}$ bimetallic catalysts diminishes as Fe increases in concentration. As a result, Fe exerts a poisoning/dampening effect on Ni activity. A more comprehensive investigation of the interactions between Ni and Fe oxides, metallic Ni, metallic Fe, and the reducible metal oxide supports is necessary to comprehend the observed variations in activity and selectivity.

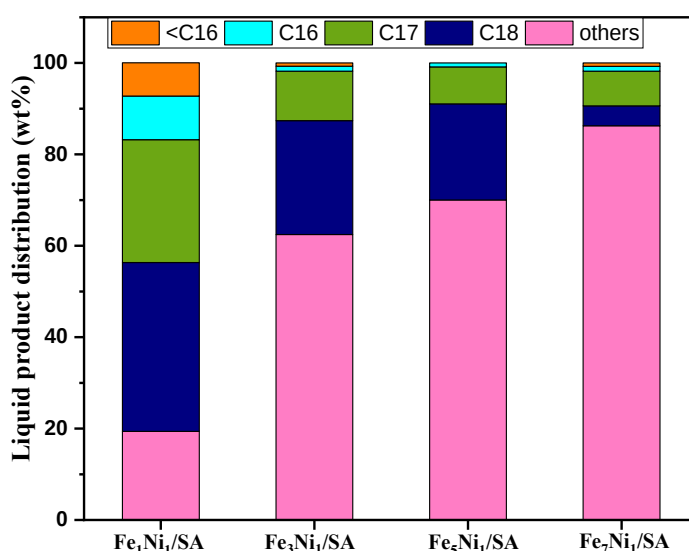


Figure 5.10 Liquid product distribution during hydro-processing reactions of methyl oleate.

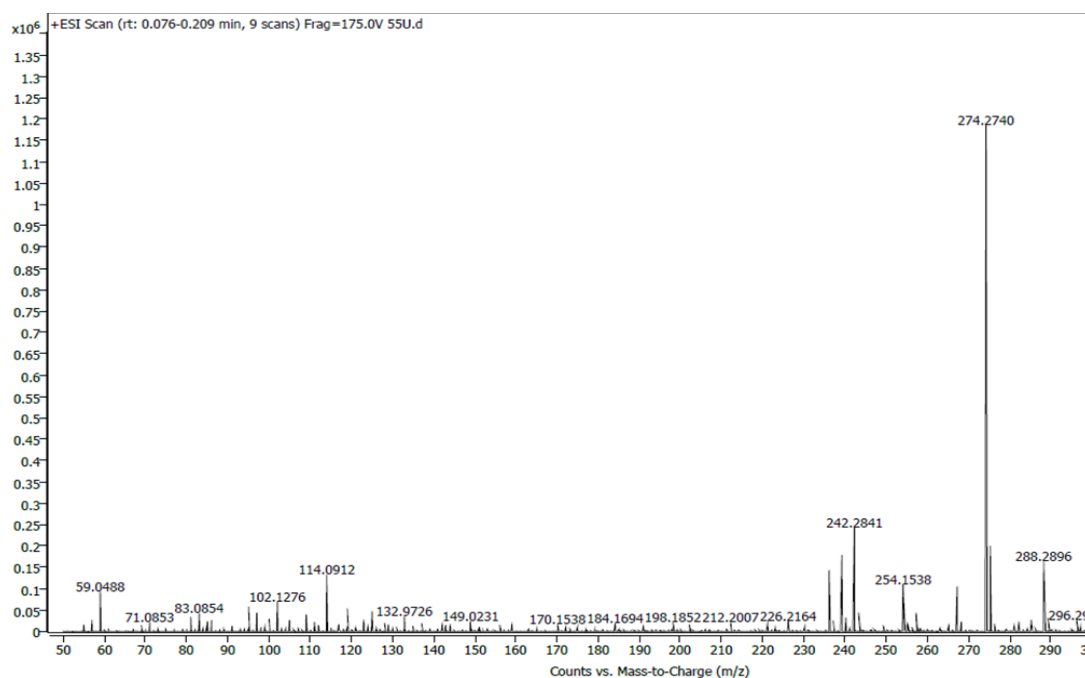


Figure 5.11. HR-MS spectra of products after hydrotreatment of methyl oleate using $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalysts.

Additionally, in order to justify the mass balance, the fractions of liquid products obtained during hydro-processing reactions were also reported here as indicated in **Figure 5.10**. The lower alkane of C16 and <C16 were also formed as a result of further cracking of the above synthesized C17 and C18 hydrocarbons while >C18 was due to unreacted methyl oleate and other polymerised

moieties. The HR-MS spectra of products after hydrotreatment of methyl oleate using $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalysts and a total mass fraction (including liquid and gas fraction) are depicted in **Figure 5.11** and **Figure 5.12**, respectively.

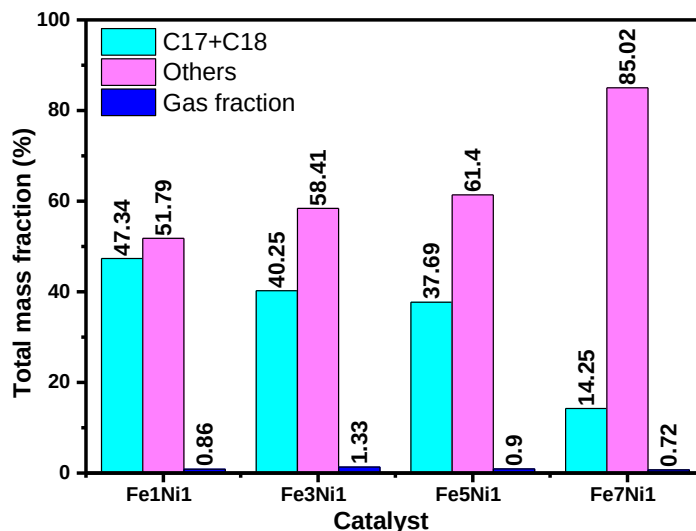


Figure 5.12 The total mass fraction (%) of the $\text{Fe}_1\text{Ni}_1/\text{SA}$, $\text{Fe}_3\text{Ni}_1/\text{SA}$, $\text{Fe}_5\text{Ni}_1/\text{SA}$ and $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalyst.

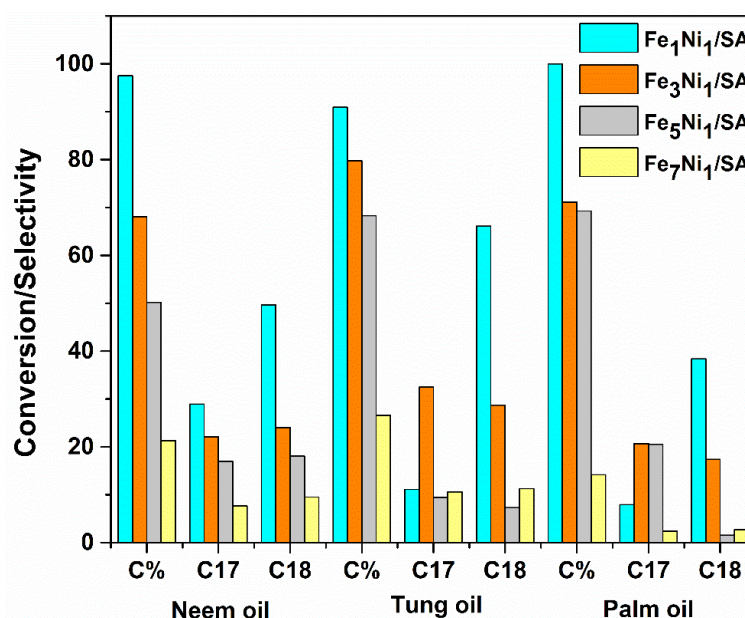


Figure 5.13 Catalytic performance of $\text{Fe}_x\text{Ni}_y/\text{SA}$ in HDO using neem, tung, and palm oil.

* C % = Conversion %

** C17= Selectivity towards C17 n-olefins

*** C18 = Selectivity towards C18 n-olefins

Furthermore, the catalytic activity for $\text{Fe}_x\text{Ni}_y/\text{SA}$ catalysts was confirmed in HDO reactions using palm, neem, and tung oil samples under optimised reaction conditions, i.e., 250 °C temperature and 10 bars of H_2 pressures over 6 hours. As shown in **Figure 5.13**, palm, neem, and tung oil had their highest conversion values, i.e., 100%, 97.52%, and 90.94%, respectively, when using $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst. However, as the iron oxide loading in the catalyst was raised, the conversion value decreased substantially. Due to the reduced acidic sites and surface area, the $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalyst yields the lowest conversion, 14.18%, 21.31%, and 26.6% using palm, neem, and tung oils, respectively. Similarly, the $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst preferred C18 n-alkanes over C17 n-alkanes as the primary product. Due to weak acidic sites, the $\text{Fe}_7\text{Ni}_1/\text{SA}$ catalyst also demonstrated comparable selectivity towards C17 and C18 n-olefins.

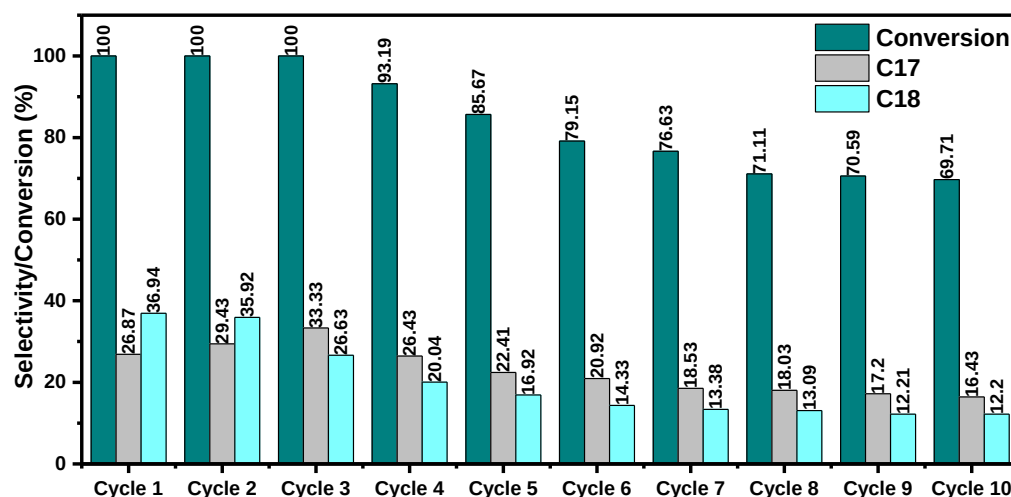


Figure 5.14 Recyclability of the $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst at reaction conditions: methyl oleate (1 mL), catalyst (100 mg), temperature (250 °C) H_2 pressure (10 bar) and reaction time (6 h).

Apart from strong catalytic activity, $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst displayed high stability under operating conditions, which is a crucial attribute for practical applications. A set of experiments was carried out to examine the stability of the $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst implementing the hydro-treatment method at 250 °C temperature and 10 bar of H_2 pressures over 6 hours. After every run, the catalyst was separated utilizing a centrifuge, rinsed with n-heptane, dried at 80 °C for 6 hours, and used directly for the next run. In the conversion of methyl oleate to hydrocarbons, the $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst maintained its catalytic activity for three cycles without loss (**Figure 5.14**) (Cao et al., 2022). During the third cycle, however, there was a slight decline in C18 selectivity. During the fourth and fifth rounds of recycling, conversion reduced from 100% to 93.19% and 85.67%, respectively. After the fifth run, the C17 and C18 selectivity maintained 22.41% and 16.92%, respectively. When the stability test was extended to 10 cycles, it was found that there is a modest decrease in conversion to 69.71 % and C17 and C18 selectivity to 16.43 % and 12.2%, respectively.

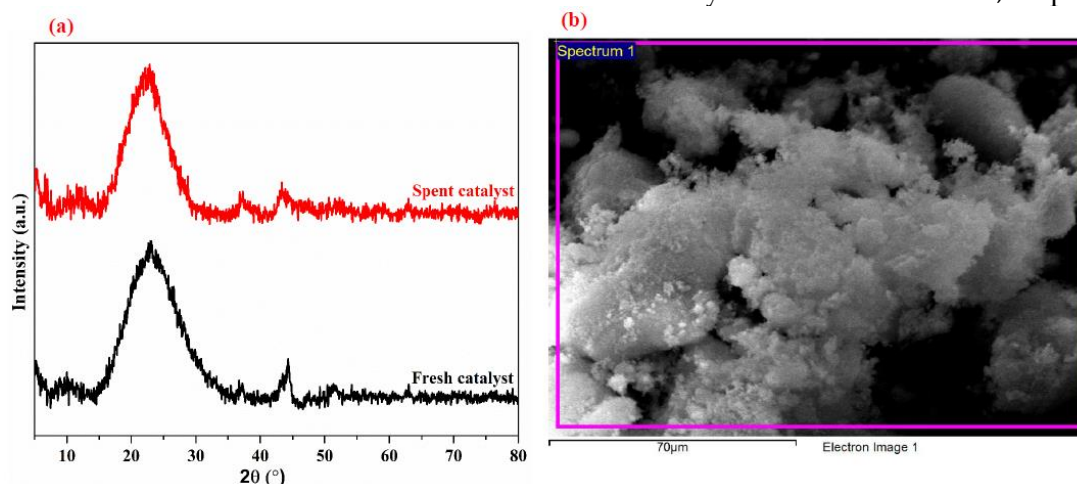


Figure 5.15 (a) XRD analysis of fresh and spent $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst (b) SEM analysis of spent $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst.

The XRD and SEM characterization of the spent catalyst (after 5th cycle) were conducted to measure the structural changes. **Figure 5.15 (a)** represents the XRD analysis of fresh and spent $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst, XRD pattern of spent catalyst revealed the no-obvious changes in the diffraction pattern compared to the fresh catalyst eliminating the formation of Fe-Ni alloy. **Figure 5.15 b** depicts the SEM of spent $\text{Fe}_1\text{Ni}_1/\text{SA}$ catalyst, respectively. It showed the agglomeration of catalyst particles which might be responsible for the catalytic activity loss during 4th and 5th cycles. Furthermore, comparative TEM analysis of fresh and spent catalyst are shown in **Figure 5.16**.

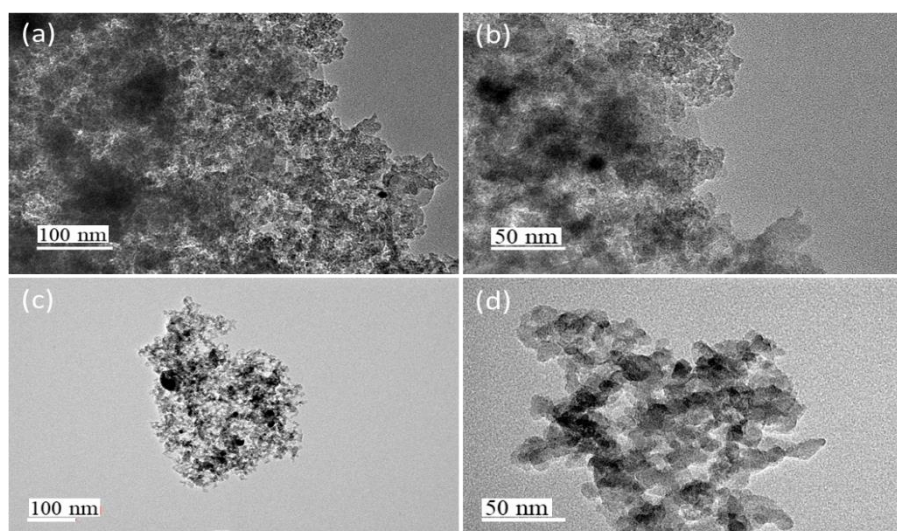


Figure 5.16 TEM images of fresh (a and b) and spent (c and d) Fe_xNi_y/SA catalyst.

5.3 Conclusion

In summary, we demonstrated the synthesis of Fe_xNi_y/SA catalysts with varying iron oxide and nickel oxide loading ranging from 1:1 to 7:1, respectively via hydrothermal followed by chemical deposition route and evaluated them in the hydrotreatment of methyl oleate. The presence of varied amounts of Fe²⁺/Fe³⁺ ions in Fe_aO_b on the silica-alumina support containing NiO species has been studied using structural characterization results. On increasing the iron loading in the catalyst from Fe₁Ni₁/SA to Fe₇Ni₁/SA, the Fe²⁺/Fe³⁺ ratio increases, which leads to a drop in specific surface area, pore volume, and acidity, thereby ultimately influencing the conversion and carbon distribution of alkanes in hydrotreatment product. The Fe₁Ni₁/SA catalyst demonstrated an outstanding HDO efficiency as well as conversion (100 %) and hydrocarbon selectivity (C17=26.87 % & C18=36.94 %) at the 250 °C temperature and 10 bar of H₂ pressures, whereas Fe₇Ni₁/SA exhibited 15.46 % conversion and poor hydrocarbon selectivity (C17 = 7.61 % & C18 = 4.36 %) respectively. The maximum conversion values of 100%, 97.52%, and 90.94% are achieved with Tung, Palm, and Neem oils, respectively in the case of Fe₁Ni₁/SA catalyst. The present study provides a promising strategy for designing an efficient HDO catalyst as the carbon number distribution of produced hydrocarbons is controlled by the Fe²⁺/Fe³⁺ ratio in Fe_aO_b species on the Fe_xNi_y/SA catalyst.

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