

A Comprehensive Investigation of Cobalt Oxide-Modified SiO₂-Al₂O₃ Catalysts: Their Influence on Catalyzing the Conversion of Methyl Oleate into Hydrocarbons

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In continuation of natural clay system unto noble metal palladium for hydrogenation reactions, studies have been conducted to investigate the effect of non-noble metal integration in an synthetic clay SiO₂-Al₂O₃ catalyst for hydrotreatment process. The materials with high oxygen content such as lignin and carbohydrate based substrates are less attractive for generation of fuel from biomass feedstock. However, triglycerides and fatty acid/esters are suitable precursors, and the use of edible/non-edible oils is considered more appropriate. Therefore, several processes such as pyrolysis and transesterification have been developed. However, the presence of oxygen content in these processed products delimits their use in diesel engines due to their different physical and chemical properties. To overcome these limitations, the hydrotreatment process is investigated for converting triglycerides and free fatty acids derived from oils into straight chain diesel-grade hydrocarbons (second generation biodiesel). The use of non-noble metals such as Co is an important feature. Deoxygenation of long chain fatty acids (C12–C22) produces straight chain hydrocarbons with high cetane number, and thus useful for diesel engines.

This work examines the impact of cobalt inclusion into the SiO₂-Al₂O₃ hybrid catalytic system on the conversion, selectivity, and stability of the catalytic conversion of methyl oleate, a model molecule for biofuels. This chapter describes a comprehensive study on the effects of cobalt integration into SiO₂-Al₂O₃ support for its efficiency in catalytic conversion of methyl oleate (MO) to hydrocarbons for diesel fuel production. Employing a facile wet-impregnation method, a series of catalysts with varying cobalt loadings (ranging from 4 to 12 wt. %) on SiO₂-Al₂O₃ were precisely prepared. An extensive characterization analysis was undertaken to gain deeper insights into the modified catalysts, employing various advanced techniques. Remarkably, XRD and TEM analyses unveiled the successful formation of the active catalyst phase Co₃O₄ and its homogeneous dispersion across the SiO₂-Al₂O₃ surface. A range of pivotal parameters, including cobalt loading, reaction time, temperature, and hydrogen gas (H₂) pressure, emerged as crucial factors influencing the conversion of MO and the selectivity of the resultant hydrocarbon products. It was demonstrated that exceptional total ester conversions could be achieved with a selectivity exceeding 50% toward forming n-heptadecane and n-octadecane products. These remarkable results were obtained at relatively mild operating conditions: 280 °C, 10 h at 15 bar H₂ using 6% cobalt loading. It was also observed that increased cobalt loading led to a significant increase in hydrocracking, particularly under similar reaction conditions.

4.1 Experimental section

4.1.1 Preparation of catalyst

An innovative and modified wet-chemical synthesis approach has been adopted to prepare different cobalt-loaded SiO₂-Al₂O₃ (SA) catalysts. It involves three sequential steps: (1) the hydrothermal synthesis of SA, (2) the metal incorporation *via* the wet-impregnation method using dilute nitric acid, and (3) the thermal annealing of the air-dried sample under N₂ atmosphere to obtain the catalyst. A series of cobalt loaded (4, 6, 8, 10, and 12 wt.%) onto SiO₂-Al₂O₃ catalysts were prepared as illustrated in **Figure 4.1**. To synthesize the cobalt oxide/SiO₂-Al₂O₃ supported catalyst, Tetraethylorthosilicate (4 ml), aluminum acetylacetonate (0.4 g), oleyl amine (0.8 ml), and DI water (2 ml) were sonicated for 30 min in a teflon container and was sealed and heated at 160 °C for 16 h. After hydrothermal reaction, the yellow-colored mixture was carefully transferred into a beaker and the cobalt metal was incorporated by wet impregnation

method using cobalt nitrate in a 3N HNO₃ aqueous solution (40 mL). The resulting suspension of cobalt-incorporated silica-alumina was stirred at 80 °C and dried. Powdered materials were calcined at 500 °C for 3 h under a nitrogen atmosphere (flow rate: 2 mL/min) to obtain cobalt oxide/ SiO₂-Al₂O₃ supported catalyst.



Figure 4.1 Schematic illustration of cobalt oxide loaded silica-alumina heterogeneous catalyst synthesis.

4.1.2 Characterization techniques

The synthesized catalyst samples were examined using XRD techniques utilizing a Panalytical-Empyrean X-ray diffractometer (Netherlands). Here, radiation source of Cu K α ($\lambda = 1.54 \text{ \AA}$) was used at 40 mA current and voltage of 45 kV to scan the diffraction angles in a range of 5 to 80° . Phase identification was done using International Centre for Diffraction Data (ICDD) database. HR-TEM analysis was performed on a Tecnai G2 F20 apparatus from FEI, Netherlands, at a voltage of 200 kV. Here, the catalyst samples were first ultrasonically dispersed in water, then drop-cast onto a copper grid and dried overnight. Surface area and porosity measurements were performed on a standard adsorption apparatus, AUTOSORB-1Q-MP-XR from Quantachrome Instruments, USA, using 99.995% pure N₂. Firstly, catalyst samples were activated under vacuum for 3 hours at 150°C before being analysed for nitrogen adsorption-desorption at -196°C . H₂-TPR and NH₃-TPD analysis were carried out using a Chemisorption Analyzer from AMI-300, Altamira Instruments using thermal conductivity detector (TCD). NH₃-TPD was measured in the temperature range of $100\text{--}1000^\circ\text{C}$ at the rate of $10^\circ\text{C min}^{-1}$. For this purpose, pre-treatment was done for 1 hour at 500°C ($10^\circ\text{C min}^{-1}$ in He), and then NH₃ adsorption was monitored at 100°C for 60 minutes. The catalyst sample was subsequently purged with He for 2 hours in order to eliminate the physically adsorbed NH₃.

In the H₂-TPR experiments, the sample was pre-treated with He at 150°C ($10^\circ\text{C min}^{-1}$) for 1 hour before cooling to RT. A mixture of H₂ (5%) and He (95%) gas at a flow rate of 30 mL min^{-1} was used as a reducing agent, and the samples were heated to 900°C at rate of $10^\circ\text{C min}^{-1}$ and maintained for 30 minutes before recording the TPR data. The surface composition and chemical states were examined with monochromatic Al K α radiation using XPS technique from Omicron Nanotechnology (Oxford Instruments). The peak correction was performed using the standard carbon 1s peak measured at 284.1 eV. The catalyst's functional groups were assessed using FTIR on a Jasco FT/IR-4100, at RT between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} , performing 32 scans. ICP-OES measurements were performed on a Teledyne Leeman Labs, Prodigy7 instrument using Co line of 228.615 nm . GC analysis was carried out using PerkinElmer Clarus 580 with a PerkinElmer Elite-5 capillary column of 0.25 mm inner diameter, 30 m length, 0.25 mm inner diameter, 0.10 mm thickness, and a temperature range of -60 to 350°C . NMR measurements of ^{27}Al and ^{29}Si were done using Bruker ASCEND™500WB (11.2 Tesla) spectrometer running at 500 MHz . $10\text{--}15 \text{ mg}$ of the sample catalyst was densely packed in a 20 mm -long 2.5 mm zirconia rotor, and measurements were taken with a Bruker 2.5 mm MAS probe rotating at 10 kHz . The spectra were collected using a single pulse sequence with a 90° pulse duration of $1 \mu\text{s}$ with an inter-scan delay of 1 s . $\text{Al}(\text{NO}_3)_3$ and SiO_2 were utilized to calibrate the NMR shifts of ^{27}Al and ^{29}Si .

4.1.3 Procedure for hydroprocessing of methyl oleate

The catalyst (20 mg to 0.1 g), methyl oleate (100 μL to 1.0 mL), and n-heptane (20 mL) were taken in an air-dried stainless-steel container. A vacuum was created in the container, then hydrogen gas was purged and the required pressure was maintained. The reaction temperature was raised from 25 $^{\circ}\text{C}$ (at 5 $^{\circ}\text{C min}^{-1}$) to attain the desired temperature and maintained for several hours. The reaction mixture was allowed to cool under atmospheric conditions, centrifuged and the resulting liquid fraction was separated off. Afterwards, n-heptane was added to the catalyst twice, stirred well, and centrifuged to extract most of the product. Liquid fractions were collected and used for analysis. Reaction conversion and selectivity were measured using a GC equipped with an FID detector.

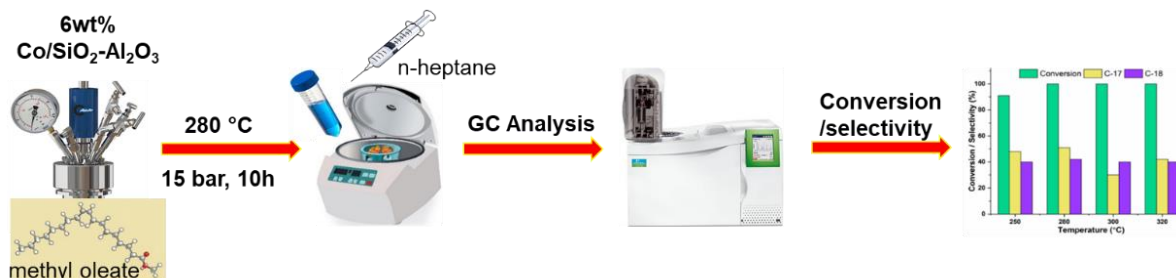


Figure 4.2 Hydroprocessing of methyl oleate.

4.2 Results and discussion

A series of cobalt loaded (4, 6, 8, 10 and 12 wt.%) on to $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts were prepared by a simple wet-impregnation method as described in the procedure above. It is worth noting that during catalyst production, the metal salt is not subsequently reduced to metal nanoparticles, as this can lead to the formation of metal aggregates of different sizes and compositions, which can have a negative impact on the selectivity of the catalysts (Loedolff et al., 2018). Effective inclusion and the amount of cobalt incorporation into the SA were confirmed using ICP-OES analysis and the data obtained are given in **Table 4.1**. The obtained data shows that the amount of cobalt in the catalyst gradually increased upon increase in metal salt loading during the wet-impregnation step. The active catalyst phase in the prepared catalyst samples was identified by performing XRD analysis; the resultant pattern is shown in **Figure 4.3**. The XRD pattern of all the samples revealed the presence of well-defined broad diffraction bands characteristic of the amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed oxide phase centred around $2\theta=23^{\circ}$. The intensity of this peak is decreased gradually as the metal loading increases. The peak obtained at $2\theta = 44^{\circ}$ is attributed to $\gamma\text{-Al}_2\text{O}_3$ phase. Besides the amorphous pattern of SA phase, characteristic peaks of cubic Co_3O_4 were also identified at 18.9° , 31.34° , 36.86° and 65.24° corresponding to (111), (022), (113) and (044) respectively (JCPDS No. 43-1003) (Qu et al., 2017, Natile and Glisenti, 2002). When the Co content in the catalyst is 6 wt.%, the XRD pattern is devoid of any dominant peaks of Co_3O_4 phases. This may be due to the fine dispersion of Co over SA surface at 6 wt.% Co incorporation. While all other samples show evident Co_3O_4 peaks in their spectra. These distinct diffraction peaks suggested that the cobalt precursor has undergone modification into crystalline Co_3O_4 phase. Compared to other samples, 12 wt.% Co loaded catalyst exhibited a dominant $\gamma\text{-Al}_2\text{O}_3$ peak at $2\theta = 44^{\circ}$ and the observed CoO peak was around 51° (Qu et al., 2017). Thus, the formation of cobalt oxide onto SA supported catalyst by wet-impregnation in dilute nitric acid is revealed from XRD.

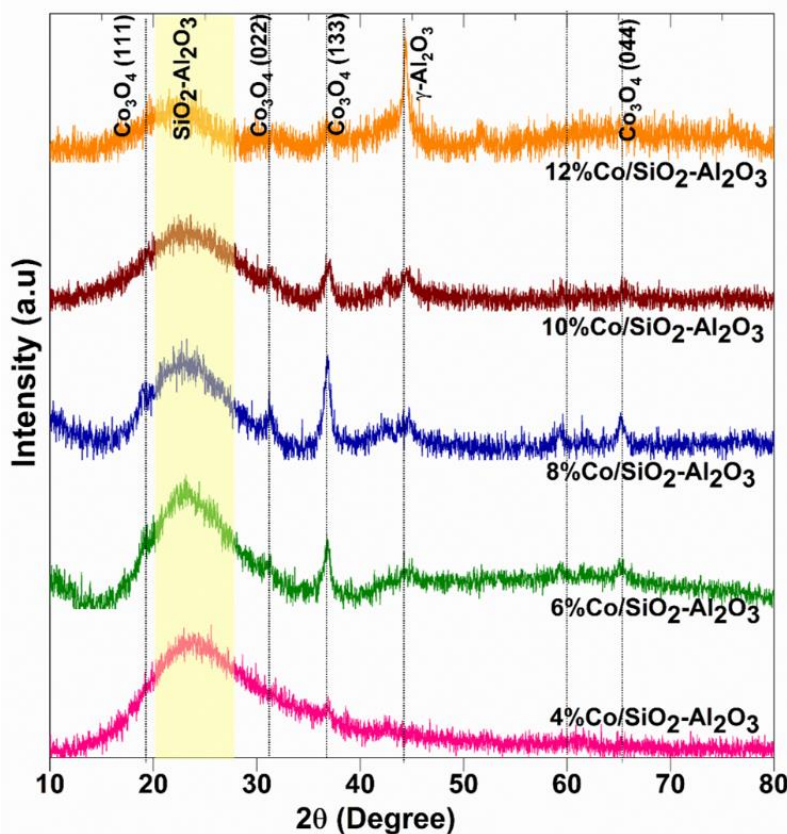


Figure 4.3 XRD patterns of the cobalt oxide/SiO₂-Al₂O₃ catalyst loaded with different wt.% cobalt showing dominant Co₃O₄ cubic crystalline planes.

The surface morphology of the prepared catalyst, the presence of cobalt oxide nanoparticles, and the elemental distributions were determined with TEM-EDS analysis, where the fine dispersion of cobalt oxide nanoparticles over SiO₂-Al₂O₃ was observed in **Figure 4.4 a-o**. The amorphous nature of SA support is evident from the TEM images of all the samples which are in accordance with the corresponding XRD patterns. At lower cobalt concentrations, the TEM images of the catalyst showed a mainly amorphous pattern as the SiO₂-Al₂O₃ is devoid of any crystal fringes. As the metal loading increased up to 8%, well-defined crystal fringes were obtained for spherical cobalt oxide nanoparticles. Upon increasing the cobalt concentration to 10%, the spherical morphology was found to be slightly changed into a hexagonal shape. Finally, the 12%Co/SA sample showed cobalt oxide nanoparticles with well-defined hexagonal crystal structures. The average size of the particle calculated from the TEM images was 10-25 nm and was found to be well-dispersed throughout the SA surface. The d-spacing of 4.7Å and 2.2Å (**Figure 4.3 i and o**) corresponds to the (111) and (113) planes of Co₃O₄ and is corroborated with the XRD results. Similarly, previous literature revealed a 0.467 nm parallel fringe corresponding to the (111) plane of cubic Co₃O₄. (Qu et al., 2017). EDS spectra and the corresponding elemental mapping of the sample confirmed the presence of Si, Al, Co and O species.

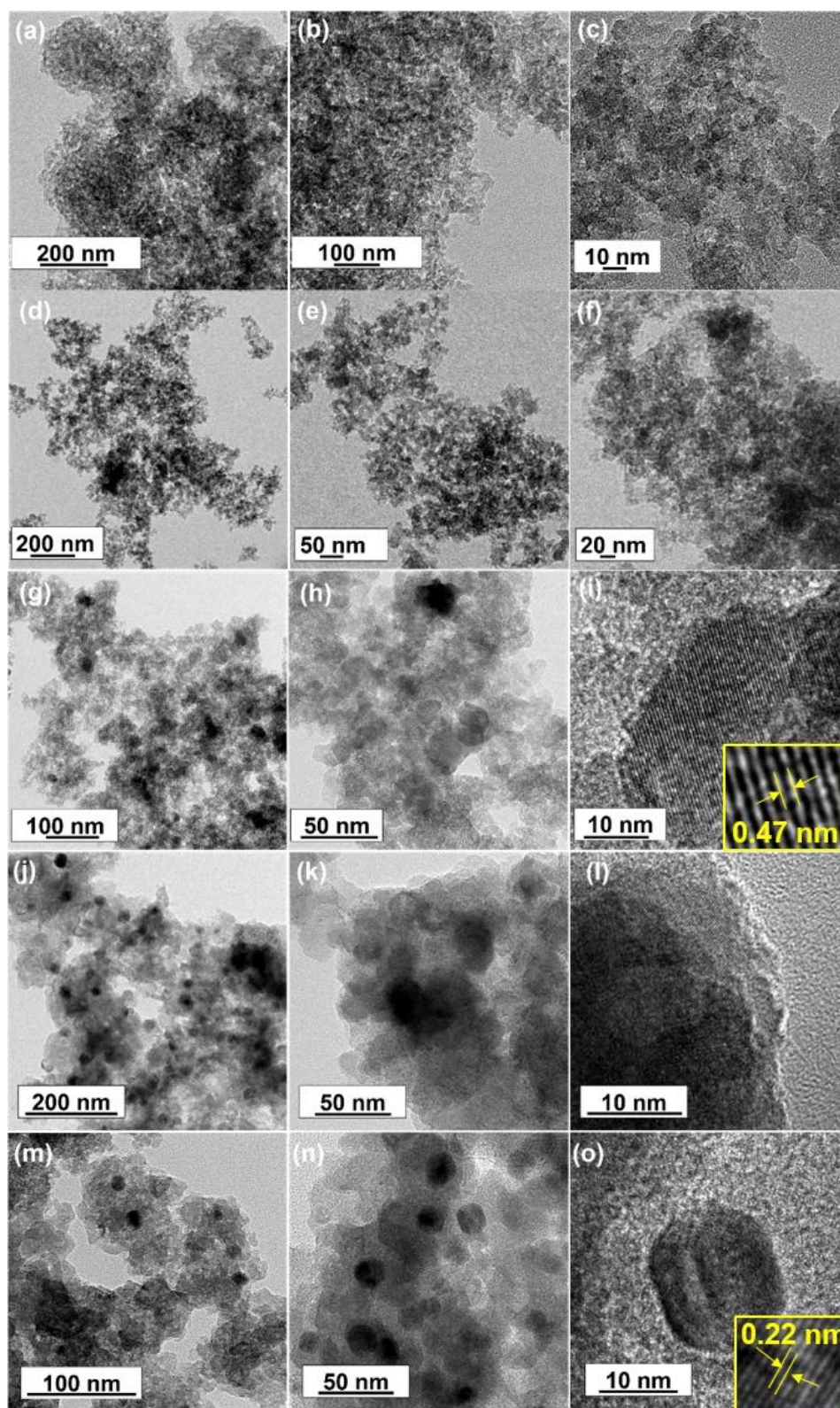


Figure 4.4 TEM images of $\text{SiO}_2\text{-Al}_2\text{O}_3$ loaded with different with (a–c) 4 wt.% Co, (d–f) 6 wt.% Co, (g–i) 8 wt.% Co, (j–l) 10 wt.% Co and (m–o) 12 wt.% Co.

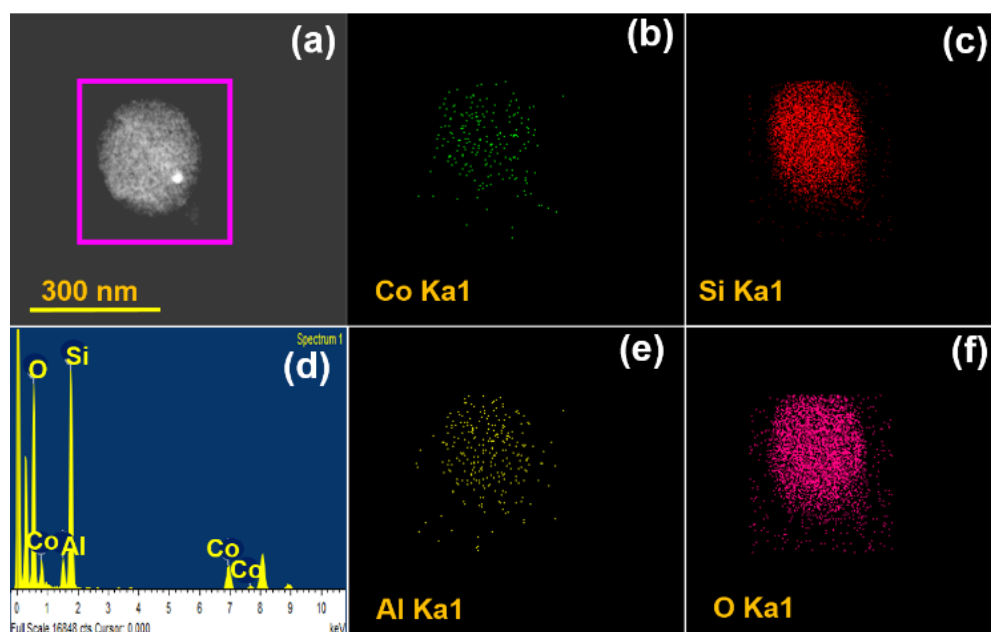


Figure 4.5 Elemental mapping of 4% cobalt oxide/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst showing (b) Co, (c) Si, (e) Al and (f) O and (d) EDS Spectra.

Figure 4.5 shows the EDS spectra of the 4%Co/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ sample. A fine dispersion of cobalt species is evident from the **Figure 4.5 b**. A comparison of the amount of cobalt obtained from ICP-OES and EDS analysis for the prepared catalyst is given in **Table 4.1**. Also, the EDS mapping of the samples doped with 6, 8, 10 and 12% cobalt are given in **Figure 4.6**.

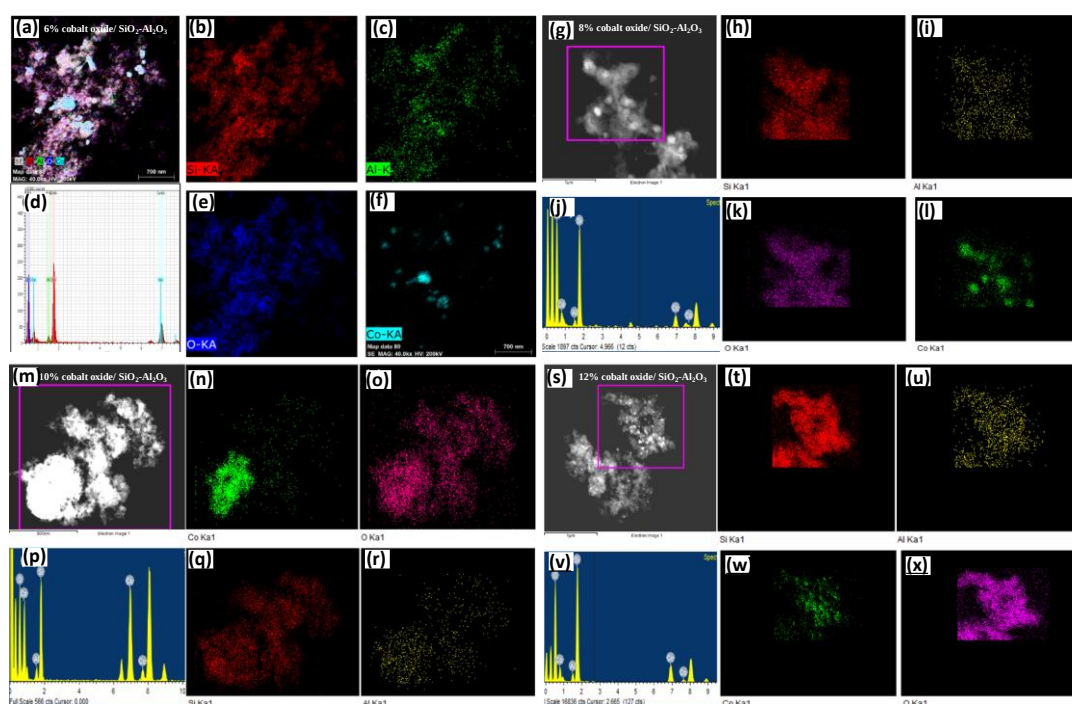


Figure 4.6 EDS mapping of Co, O, Si, Al and EDS spectra of 6, 8, 10 and 12% cobalt oxide/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst.

The surface area of the catalyst plays a crucial role in the catalytic reaction. Thus, in order to find the surface area of all catalysts preloaded with different wt.% of cobalt, N_2 adsorption-desorption isotherm analysis was done, and the values of different parameters such as pore size and pore volume were obtained, which are summarized in **Table 4.1**. All the prepared catalysts showed a large surface area $>250 \text{ m}^2/\text{g}$, and from the obtained data, it is evident that as the metal loading is increased, the surface area of the catalyst is found to be decreased from $567 \text{ m}^2/\text{g}$ to $263 \text{ m}^2/\text{g}$.

The BET surface area plots, N₂ adsorption isotherms, and BJH pore size distribution curves are given in **Figure 4.7 a, b and c** respectively.

Table 4.1. Active metal loading, surface area, pore volume, and the total acid density of all the studied samples.

Catalyst	Metal Loading (Wt.%)		N ₂ Physisorption		NH ₃ Chemisorption
	From TEM-EDS	From ICP-OES	BET Surface area (m ² /g)	Pore volume (cm ³ /g)	Total acid sites (μL)
4%Co/SiO ₂ -Al ₂ O ₃	5.29	4.71	556	5.4	262
6%Co/SiO ₂ -Al ₂ O ₃	7.93	5.69	417	4.08	353
8%Co/SiO ₂ -Al ₂ O ₃	10.63	6.24	457	4.02	235
10%Co/SiO ₂ -Al ₂ O ₃	11.50	9.58	426	3.37	194
12%Co/SiO ₂ -Al ₂ O ₃	12.54	12.11	263	2.08	358

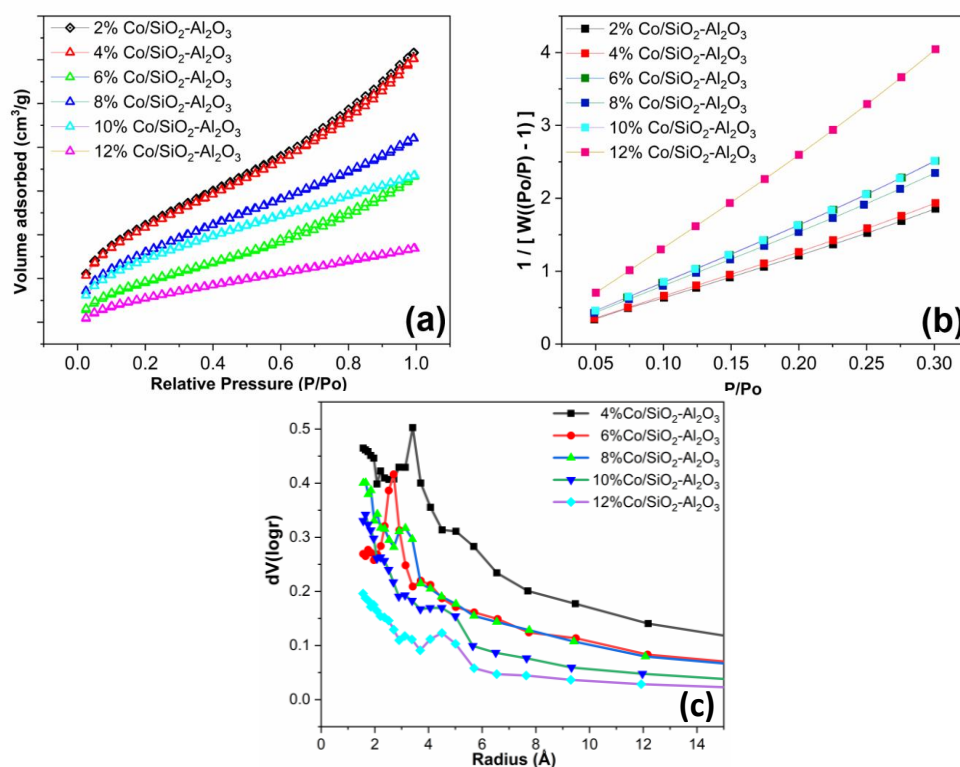


Figure 4.7 (a) N₂ adsorption/desorption isotherms, (b) BET adsorption plot, and (c) Pore size distribution of cobalt oxide/ SiO₂-Al₂O₃ catalyst.

The chemical state and composition of constituent ions in the SiO₂-Al₂O₃ supported cobalt oxide catalysts with different wt.% cobalt was investigated in detail using XPS analysis. **Figure 4.8 (a)-(d)** shows the core level XPS spectra of Al, Si, O and Co elements present in the 6% cobalt oxide supported by the SiO₂-Al₂O₃ sample. The characteristic peaks between 779 and 900 eV signify the presence of Co 2p_{3/2}, Co 2p_{1/2} and Co 2s (**Figure 4.8 d**) (Hao et al., 2011). The Co 2p XPS core spectra indicate multiple peaks in which the binding energy (B.E) around 780.5 eV and 796 eV corresponds to Co 2p_{3/2} and Co 2p_{1/2}, respectively, with spin-energy separation of ~15.9 eV; which is characteristic of a Co₃O₄ phase (Qu et al., 2017, Xiao et al., 2014). While the smaller shake-up satellite peaks around 782.2 and 786.5 eV confirm the existence of Co²⁺ ions in the sample. The peaks around 803 eV is due to Co 2p_{1/2} satellite peaks. These results are well corroborated with high-resolution XPS spectra of the resultant mesoporous Co₃O₄ hierarchical nanobundles, which

displayed that presence of two prominent peaks with binding energies of 780.3 and 795.3 eV, corresponding to the Co 2p_{3/2} and Co 2p_{1/2} peaks, respectively. The gap between these peaks is 15.0 eV, which is typical of the Co₃O₄ phase. Shake-up satellite peaks confirm the presence of Co 2p. The half-width of the shake-up satellite peak is larger, which indicates the stronger interaction between the support and cobalt oxide species. The broadness of Co 2p_{3/2} is greater, which revealed the higher valence state of cobalt ion on the support. The high-resolution O 1s core level spectrum (**Figure 4.7c**) consists of two peaks, and the peak at the lower energy of 532 eV is associated with the lattice oxygen in the spinel Co₃O₄ (Xiong et al., 2012). Previous studies also revealed that the binding energies of O 1s in Co/ SiO₂-Al₂O₃ are lower than SiO₂-Al₂O₃, whilst peak around 532.3 eV is due to O in the Si-O-Si environment. Thus the peak with a slightly different B.E of 532.9 eV is attributed to the Si-O-Si environment. The Al 2p core spectrum shows two deconvoluted peaks at 73.7 and 74.4 eV (**Figure 4.8 a**) which is owing to the Al ions in the aluminosilicate and aluminum oxide environment, respectively. **Figure 4.8 b** shows the high-resolution spectra of Si 2p, which exhibits two peaks. The peak at B.E 103.4 eV is due to the Si ions in SiO₂ environment, whereas the peak at 102.7 eV corresponds to Si in the aluminosilicate environment. Thus, the XPS results further specify that the catalyst contains mixed valence Co₃O₄ (Xiong et al., 2009, Huang et al., 2011).

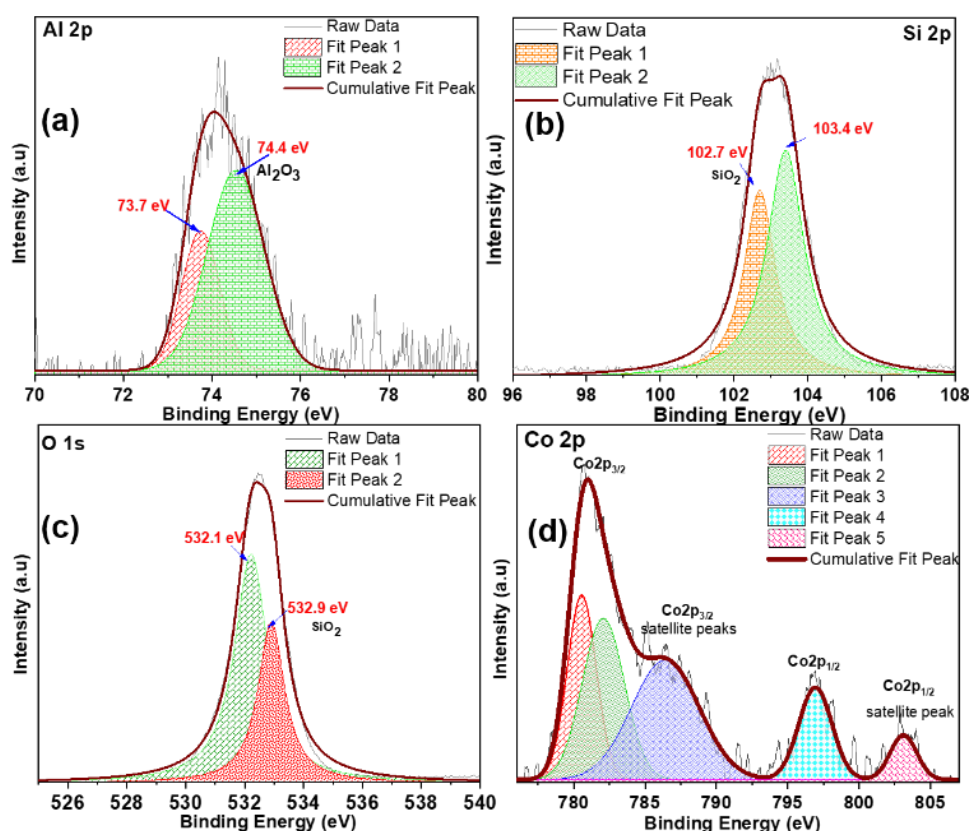


Figure 4.8 XPS core level spectra of the 6% cobalt oxide/ SiO₂-Al₂O₃ catalyst showing (a) Al 2p (b) Si 2p (c) O 1s and (d) Co 2p.

The acidity of the catalyst was determined from the temperature-programmed desorption of ammonia (NH₃-TPD), and the spectra are shown in **Figure 4.9 b**. The number of acid sites that depend upon the ammonia desorbed from the surface of different catalysts is determined by the surface acid density of TPD curve, which is given in **Table 4.1**. The peaks at 420 °C, 540 °C and 712 °C were detected in SA supported cobalt oxide catalysts, which are attributed to the desorption of ammonia from the different Brønsted acid sites. It also confirmed that stronger acid sites appeared as the metal loading was increased. These results are substantiated by the previous report that the Brønsted acid sites are introduced when Al³⁺ is isomorphously replaced by lower valence states of Co²⁺ (Hao et al., 2011). The number of acid sites that depend upon the ammonia

desorbed from the surface of different catalysts is determined by the surface acid density of TPD curve, which is given in **Table 4.1**.

The interactions between Co and the $\text{SiO}_2\text{-Al}_2\text{O}_3$ supports were also studied by H_2 -TPR characterization. The studies carried out for all prepared catalysts in the oxidation state and the corresponding TPR profiles were given in **Figure 4.9 a**. TPR profile of all cobalt incorporated samples showed a broad curve from 200 to 900 °C with three distinct peaks at ~320, ~500, and ~800 °C in which the first peak at 200–400 °C was attributed to the reduction of Co_3O_4 to CoO ($\text{Co}^{3+} \rightarrow \text{Co}^{2+}$) and the second peak at 400–600 °C is ascribed to the successive reduction of CoO species to metallic Co ($\text{Co}^{2+} \rightarrow \text{Co}^0$) (Türk et al., 2023, Srifa et al., 2015, Ochoa-Hernández et al., 2013). The TPR profile of $\text{SiO}_2\text{-Al}_2\text{O}_3$ shows a broad peak around 600–900 °C. Furthermore, the peak at a higher temperature (800 °C) may be assigned as Co species with smaller crystallite sizes and stronger metal-support interactions.

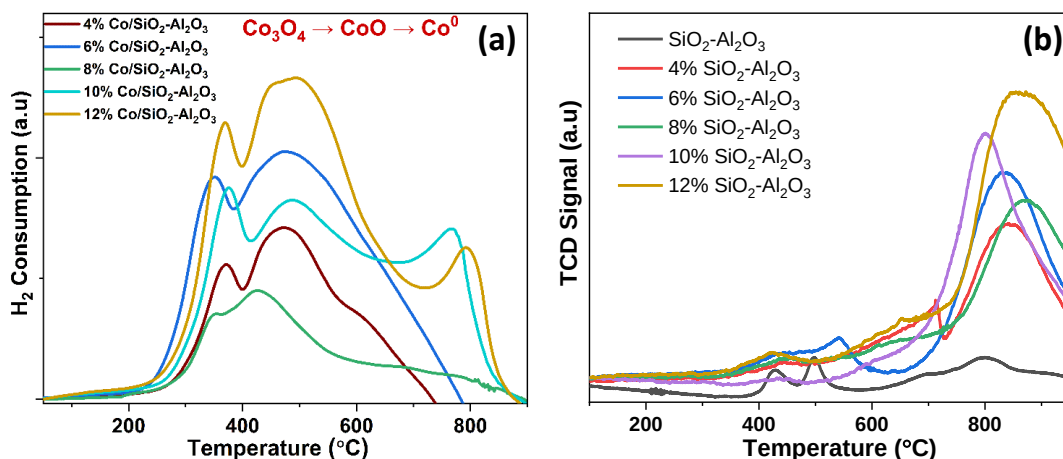


Figure 4.9 (a) H_2 TPR profile and (b) NH_3 -TPD of cobalt oxide/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts.

It is understood from the TPR profile that a high reduction temperature should be avoided for the hydrogenation step owing to the formation of large metal particle size and/or the transformation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ to other phases, thus resulting in low activity and stability.

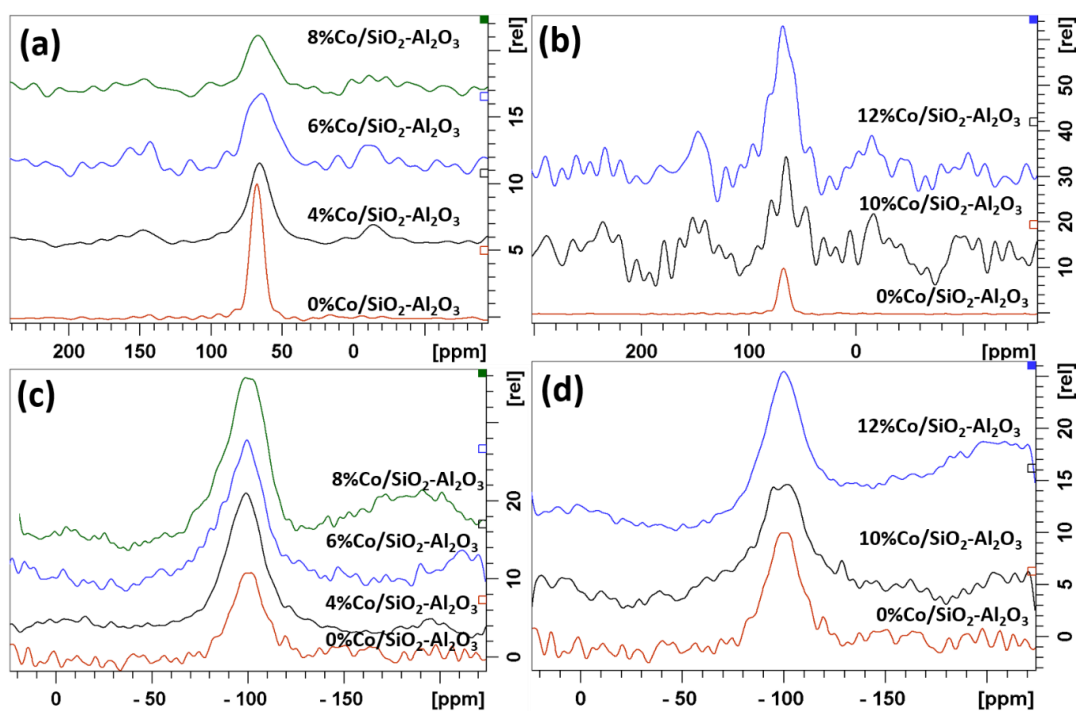


Figure 4.10 Solid-state NMR spectra of cobalt oxide/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst.

Further, coordination properties of Al and Si in the catalyst were confirmed by solid-state NMR spectroscopy. The ^{27}Al NMR spectra of prepared catalysts are shown in **Figure 4.10 (a) and (b)**.

The sharp, intense resonance peak observed around 67 ppm corresponds to aluminum species in tetrahedral coordination (Ren et al., 2014a, Fyfe et al., 2001). This suggests that the aluminium atoms are incorporated into the silica matrix as four-coordinated species. As the concentration of the cobalt was increased, a decrease in the intensity of the peak was observed. Previous studies also demonstrated that the incorporation of cobalt into the $\text{SiO}_2\text{-Al}_2\text{O}_3$ by wet impregnation leads to a slight chemical shift of Al coordination (Wang et al., 2018). **Figure 4.10 (c) and (d)** show the corresponding resonance peak of the ^{29}Si NMR spectra. The dominant peak observed at -100 ppm is assigned to $\text{Si}(\text{Q}^3)$ silicon species ($\text{Si}(\text{OSi})_3\text{OH}$) (Coumans and Hensen, 2017).

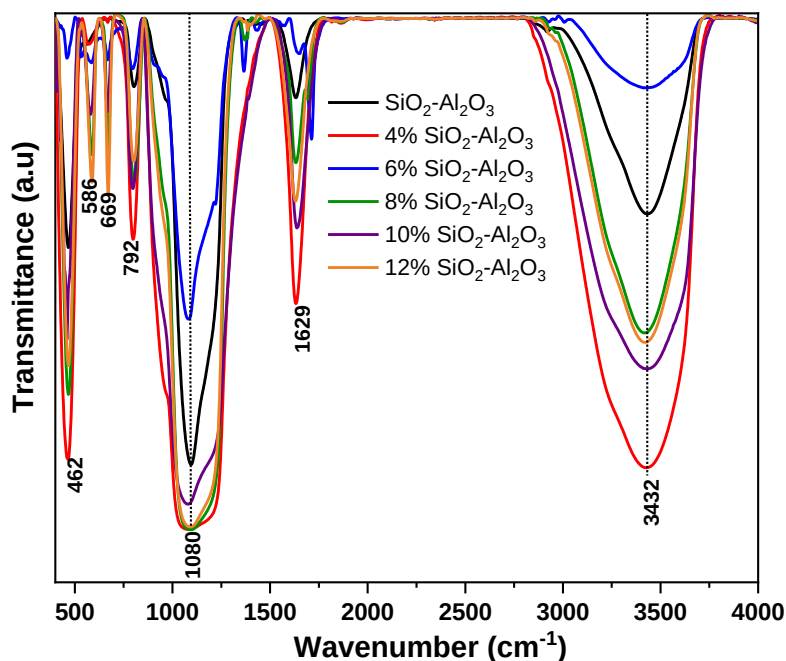


Figure 4.11 FT-IR spectra of cobalt oxide/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst.

Figure 4.11 shows the FTIR spectrum of $\text{Co}_3\text{O}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$. The spectrum exhibited the presence of O-H bonds at 3433 cm^{-1} for the hydroxyl groups in the silica-alumina nanocomposite. A peak at 1629 cm^{-1} was detected and identified as O-H bending. Also, a broad and intense peak was detected at 1099 cm^{-1} for Si-O bonds.

It is well-known from earlier studies that under mild conditions, the double-bond hydrogenation of MO results in the formation of methyl stearate. In contrast, this reaction does not contribute to a decrease in the O/C ratio. Consequently, removing the ester group either by DCO_2 or by HDO to C-17 and C-18 hydrocarbons is preferred in case of the upgradation process of triglyceride (Ochoa-Hernández et al., 2013). Accordingly, the first set of reactions was carried out using the 6% cobalt oxide/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ supported catalysts under different reaction conditions (such as temperature, pressure, and catalyst loading in the presence/absence of n-heptane solvent) to test the catalytic activity. Here, 0.1 g of catalyst with 1 mL of MO was taken. The hydrotreatment reaction was performed at 40 bar H_2 pressure for 8 hr, systematically varying the temperature from 250-320 °C in the presence of n-heptane solvent. When the temperature was 250 °C, total ester conversion was not achieved (**Table 4.2**, exp no 3). Nearly complete conversion of MO to n-alkanes in the C-15 to C-18 range was achieved at temperatures higher than 280 °C.

Table 4.2. Hydrotreatment Experimental Parameters of Methyl Oleate with Prepared Catalyst Under Study.

No	Catalyst	Time (h)	Temperature (°C)	H ₂ Pressure (bar)	Solvent	Conversion	Selectivity (%)	
							n-C-17	n-C-18
1	4%Co/SiO ₂ -Al ₂ O ₃	10	280	10	None	100	41	18
2	4%Co/SiO ₂ -Al ₂ O ₃	10	280	20	None	100	-	-
3	6%Co/SiO ₂ -Al ₂ O ₃	8	250	40	n-heptane	93	52	43
4	6%Co/SiO ₂ -Al ₂ O ₃	8	300	40	n-heptane	100	30	41
5	6%Co/SiO ₂ -Al ₂ O ₃	8	320	40	n-heptane	100	42	40
6	6%Co/SiO ₂ -Al ₂ O ₃	10	280	40	None	100	11	-
7	6%Co/SiO ₂ -Al ₂ O ₃	10	280	10	None	100	51	42
8	6%Co/SiO ₂ -Al ₂ O ₃	10	280	15	None	100	45	47
9	6%Co/SiO ₂ -Al ₂ O ₃	10	280	17	None	100	43	50
10	6%Co/SiO ₂ -Al ₂ O ₃	10	280	20	None	100	45	41
11	6%Co/SiO ₂ -Al ₂ O ₃	10	280	30	None	100	46	42
12	8%Co/SiO ₂ -Al ₂ O ₃	10	280	10	None	100	45	44
13	8%Co/SiO ₂ -Al ₂ O ₃	10	280	15	None	100	43	40
14	8%Co/SiO ₂ -Al ₂ O ₃	10	280	20	None	100	39	35
15	10%Co/SiO ₂ -Al ₂ O ₃	10	280	10	None	100	39	17
16	12%Co/SiO ₂ -Al ₂ O ₃	10	280	10	None	100	30	24
17	SiO ₂ -Al ₂ O ₃	10	280	15	None	43	-	-
18	SiO ₂	10	280	15	None	21	-	-
19	Al ₂ O ₃	10	280	15	None	18	-	-

Other isomerization/cracking products were observed during the GC analysis, most likely due to the relatively low reaction temperature. The lower ester conversion at temperatures below 250 °C may be due to the aggregation of the reaction by-products, which partially blocks the active catalyst sites. Conversely, cracking is observed when the reaction temperature is set as 300 and 320 °C, which leads to alkanes in the C-10 to C-15 range (such as dodecane, tridecane, tetradecane, and pentadecane) (**Table 4.2**, exp no 4 and 5). Since the hydroprocessing reaction under solvent-free conditions could be a reassuring technology for industrial applications, the reaction was performed under the earlier conditions without the solvent. However, the complete conversion was achieved only with the extended reaction time of 10 hours. This may be possible as the solvent plays a substantial role in enhancing the reaction rate (Deng et al., 2018, Dyson and Jessop, 2016). The catalyst yields a rather broad product distribution for the reaction at 280 °C, 40 H₂ pressure within 10 hr constituting n-alkanes in the C-10 to C-17 range (**Table 4.2**, exp no 6 and **Table 4.3**). The active cobalt phases in mesoporous SiO₂-Al₂O₃ support intensified catalytic properties by enhancing the homogenous dispersion and promoting the total number of active sites. In order to achieve the narrow product distribution constituted by the DCO₂ and deoxygenation process, further optimization of reaction parameters was done. Here, 100 µL of methyl oleate was taken, and 20 mg of the catalyst was loaded. The hydrotreatment reaction was performed with 6%Co/SiO₂-Al₂O₃ catalyst at 280 °C for 10 hrs varying H₂ pressure (from 10 – 30 bar) under solvent-free conditions.

Table 4.3. Selectivity of lower hydrocarbons from the hydrotreatment reaction of methyl oleate with prepared SiO₂-Al₂O₃ catalyst.

No	Catalyst	Experiment	Selectivity							
			<C-10	C-10	C-11	C-12	C-13	C-14	C-15	C-16
1	6%Co/SiO ₂ -Al ₂ O ₃	280°C/40 bar/10hrs	-	2	13	16	17	17	14	10
2	6%Co/SiO ₂ -Al ₂ O ₃	280°C/30 bar/10hrs	-	0.5	0.5	2	1	1	2	5
3	6%Co/SiO ₂ -Al ₂ O ₃	280°C/20 bar/10hrs	-	-	-	-	3	1	2	8
4	4%Co/SiO ₂ -Al ₂ O ₃	280°C/20 bar/10hrs	66	31	3	-	-	-	-	-
5	SiO ₂ -Al ₂ O ₃	280°C/15 bar/10hrs	-	-	-	2	12	16	13	-

Interestingly, complete conversion of the reactant with narrow product distribution was observed when H₂ pressure was as low as 10 bar but low HDO selectivity towards n-C18 hydrocarbons (**Table 4.2**, exp no 7). Further increase of H₂ pressure to 15 bar results in the formation of mainly C-17 and C18 with comparable yield (**Table 4.2**, exp no 8). Notably, more selectivity towards C-18 hydrocarbons is beneficial as the by-product (CO) obtained by DCO can consume hydrogen to form CH₄. When we fix the H₂ pressure to 17 bar, the reaction yields mainly C-18 and n-C17 hydrocarbons (**Table 4.2**, exp no 9). If the H₂ pressure is as high as 20 and 30 bar, the resulting products contain hydrocarbons ranging from C-10 to C-18. An additional increase of pressure resulted in the formation of lower hydrocarbons with very low selectivity towards DCO₂ and HDO (**Table 4.2**, exp no 10 and 11). The more selectivity towards the C-18 and n-C17 hydrocarbon formation could be attributed to factors such as fine dispersion of cobalt oxide nanoparticles over the high surface area SiO₂-Al₂O₃ support, availability of active acid sites, which is highly desirable for the HDO process. From the above set of experiments, we can deduce that slight changes in

the reaction temperature H_2 pressure can significantly affect the product distribution and the selectivity towards HDO and DO reaction.

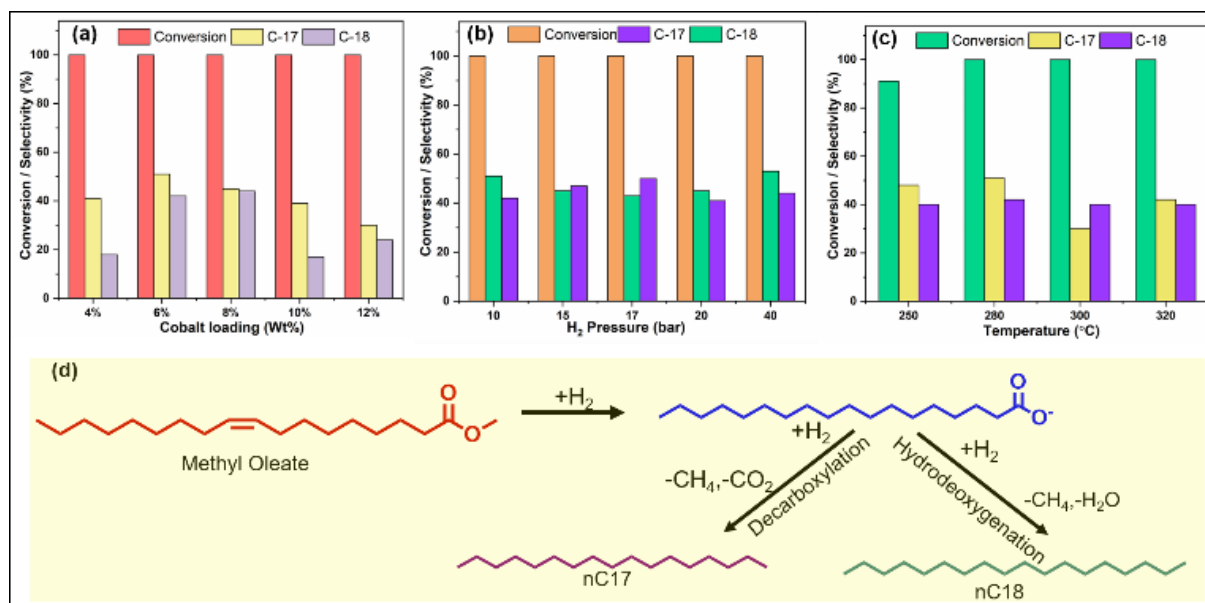


Figure 4.12 Variation of total ester conversion, C-17 and C-18 yield with changes in (a) Cobalt loading, (b) H_2 pressure and (c) reaction temperature. (d) Possible conversion pathways of methyl oleate into nC18 and nC17 hydrocarbons.

In order to understand the impact of cobalt concentration on the catalytic conversion and selectivity, a hydroprocessing reaction was performed with the $SiO_2-Al_2O_3$ catalyst with varied metal loading. Lowering of metal loading (4%Co/ $SiO_2-Al_2O_3$) showed low selectivity towards HDO reaction at $280^{\circ}C$ with 8 bar H_2 pressure (Table 4.2, exp no 1), and when H_2 pressure was increased up to 20 bar; the resulted product contained only lower hydrocarbons (C-10 and C-11, Table 4.3). At 8% Co concentration with low H_2 pressure (10 bar), broad product distribution was obtained and cracking was observed at elevated pressures (Table 4.2, exp no 2). 10% $SiO_2-Al_2O_3$ catalyst showed only lower hydrocarbons devoid of any n-C17 and n-C18 hydrocarbon formation (Table 4.2, exp no 15). Whereas 12% $SiO_2-Al_2O_3$ catalyst demonstrated very low selectivity towards HDO reaction (Table 4.2, exp no 16). Thus the 6% Co metal loading in the $SiO_2-Al_2O_3$ support catalyst is found to be the optimum quantity for adequate n-C17 and n-C18 hydrocarbons yield. Variation of total ester conversion and also the C-17 and C-18 yield in accordance with changes in Cobalt loading, H_2 pressure and reaction temperature is cumulatively given in Figure 4.13 (a), (b) and (c).

This variation of product formation for different metal-loaded catalysts is mainly due to the changes in surface area, reducibility, and the available active acid sites observed from BET, H_2 -TPR, and NH_3 -TPD analysis. An introduction of non-noble metal (cobalt) to amorphous silica-alumina in the acidic medium can significantly alter the acidity and, thus, catalytic efficiency of the catalyst. However, when the metal loading is higher, the active catalyst site may be blocked by the excess cobalt oxide particle present on the $SiO_2-Al_2O_3$ surface, which can adversely affect the acidity and reduction capability based on the above experiments and the obtained results, it can be concluded that the hydroprocessing of methyl oleate takes place following many factors such as the high surface area of the catalyst, uniform dispersion of metal nanoparticles on the solid support etc. Thus, both deoxygenation and DCO₂ occur simultaneously over a Co/ $SiO_2-Al_2O_3$ catalyst. Moreover, the HDO reaction requires contribution from active acid sites, metal surfaces, and the substrate carboxylic group (Lin et al., 2018). Thus, it can be concluded that the reaction proceeds via a fatty acid intermediate due to the slow hydrolysis of the substrate. The formed intermediate is further decarbonylated/decarboxylated to C-17 hydrocarbons through DCO or may get hydrogenated to an alcohol intermediate, which is then hydrodeoxygenated to C18 hydrocarbons by direct HDO route (Coumans and Hensen, 2017). A comparison between the

conversion and HDO selectivity of as-prepared cobalt oxide/SiO₂-Al₂O₃ catalysts and previously reported transition metal-based catalysts is shown in **Table 4.4**.

Table 4.4 Comparison of literature concerning transition metal-based Heterogeneous Catalyst.

Catalyst	Substrate	Solvent	T (°C)	P _{H₂}	Time (h)	Conversion/HDO Selectivity (%)	Reference
Co ₅ /clay	Methyl stearate	n-heptane	300	40	6	100/73	26
Co _{2.5} /clay	Methyl oleate	n-heptane	300	40	6	100/90	26
Co ₅ /clay	Methyl oleate	None	300	40	8	100/75	26
Co _{2.5} /clay	Methyl oleate	None	300	40	8	100/87	26
Ni/HBEA	stearic acid	n-dodecane	260	40	8	100/90	19
NiMoS ₂ /Al ₂ O ₃	Methyl heptanoate	1-heptanol	250	15	4	80/46	12
Ni/Co/Al-SBA-15	Methyl Oleate	n-heptane	340	30	6	100/40	43
Mo ₂ C/CNF	Oleic Acid	n-dodecane	350	50	4	100/86	15
6%Co/SiO ₂ -Al ₂ O ₃	Methyl oleate	None	280	17	10	100/50	This work
6%Co/SiO ₂ -Al ₂ O ₃	Methyl oleate	None	280	15	10	100/47	This work
6%Co/SiO ₂ -Al ₂ O ₃	Methyl oleate	None	280	40	10	100/44	This work

From **Table 4.4**, it is clear that in addition to the cost-effectiveness and facile synthesis method, the proposed catalysts could be favourable in terms of metal-to-substrate ratio and complete ester conversion. These showed similar HDO selectivity as the reported catalysts at very low reaction temperatures and H₂ pressures (Ochoa-Hernández et al., 2013, Şenol et al., 2005). The catalyst activity could be related directly to the specific interactions between acidic centers stimulated by cobalt integration and aluminium sites. Particularly, when the cobalt metal concentration is 6 wt.%, a homogenous dispersion of the metal nanoparticles was observed, resulting in relatively high acid density and, hence more selectivity towards the HDO process.

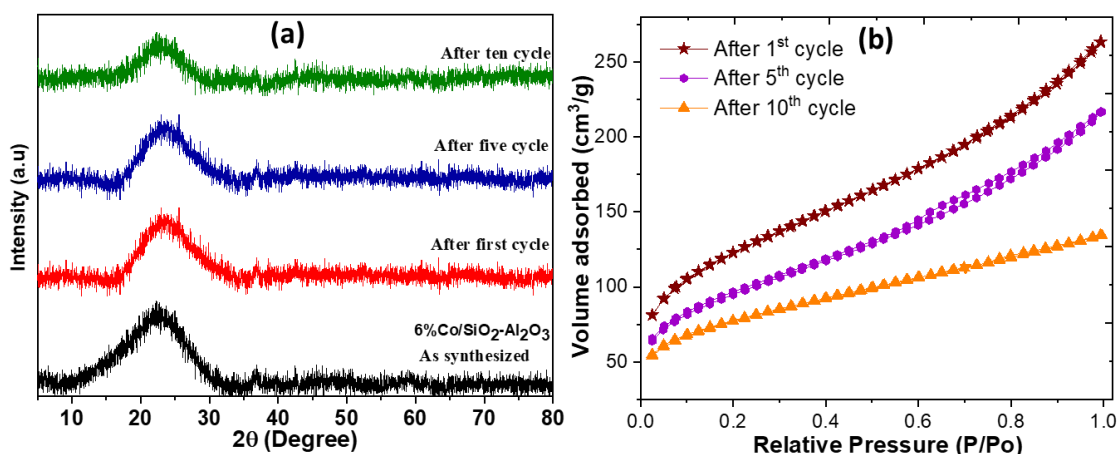


Figure 4.13 (a) XRD Spectra and (b) N₂ adsorption/desorption isotherms of 6% cobalt oxide/ SiO₂-Al₂O₃ spent catalyst for one, five and ten cycles.

The catalyst reusability was tested further to understand the stability of catalysts after the hydrotreatment reaction. A hydrotreatment reaction was performed at 250 °C for 10 hrs and 15 bar H₂ using methyl oleate (First cycle). The spent catalyst was rinsed with n-heptane to extract the reaction products, and the obtained catalyst was heated at 80 °C in N₂ atmosphere for 2 hrs. This catalyst was further used for the hydrogenation reaction up to 10 cycles. **Figure 4.13 a** shows the comparative XRD pattern of as-synthesized 6% cobalt oxide/ SiO₂-Al₂O₃ and spent catalyst

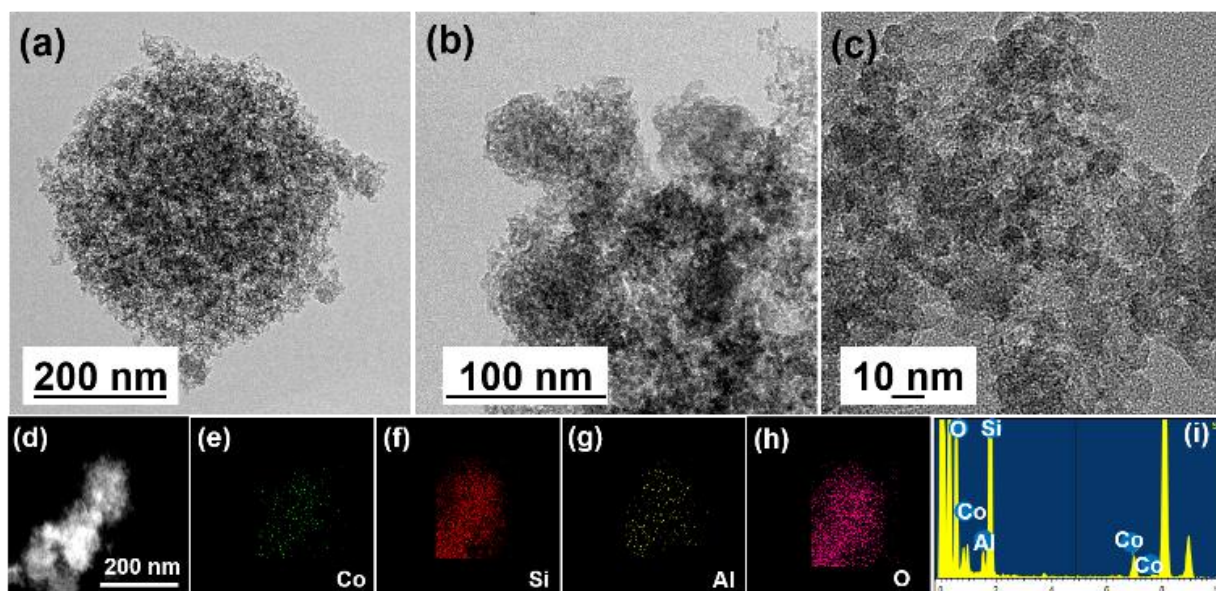


Figure 4.14 (a–c) TEM images of the spent catalyst of 6% cobalt loaded $\text{SiO}_2\text{-Al}_2\text{O}_3$ at different magnifications (d–h) elemental mapping showing the surface distribution of Co, Si, Al and O (i) EDS spectra of the spent catalyst for the selected area.

after one, five, and 10 cycles. The XRD spectra showed decreased intensity after each cycle. The surface area of the catalysts was found to be decreased from $417 \text{ m}^2/\text{g}$ to $402 \text{ m}^2/\text{g}$ after the first cycle and $330.9 \text{ m}^2/\text{g}$ after the 5th cycle (**Figure 4.13 b**). Accordingly, small variations in conversion and selectivity were obtained, given in **Table 4.5**.

Table 4.5: Reusability test results of 6% Co $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst.

S.N o.	Cycles	Conversion	Selectivity	
			n-C17	n-C18
1	1	100	45	47
2	3	99	45	45
3	5	97	43	42
4	10	94	41	40

To check the metal leaching during the hydroprocessing reaction, the ICP-OES analysis was carried out for all samples by collecting the catalyst after the reaction and the metal loss was found to be as low as 1 ppm for all the catalyst. **Figure 4.14** shows the TEM images of the spent catalyst which shows the aggregation of cobalt on the catalyst surface compared to the as-prepared 6% cobalt-loaded catalyst and the EDS spectra clearly shows the presence of Co, Si, Al and O. To further understand the elemental and chemical state information of the spent catalyst, XPS spectra of the catalyst was taken which is shown in **Figure 4.15**. XPS survey spectra confirmed the presence of Si, Al, O, and Co as given in **Figure 4.15 a**.

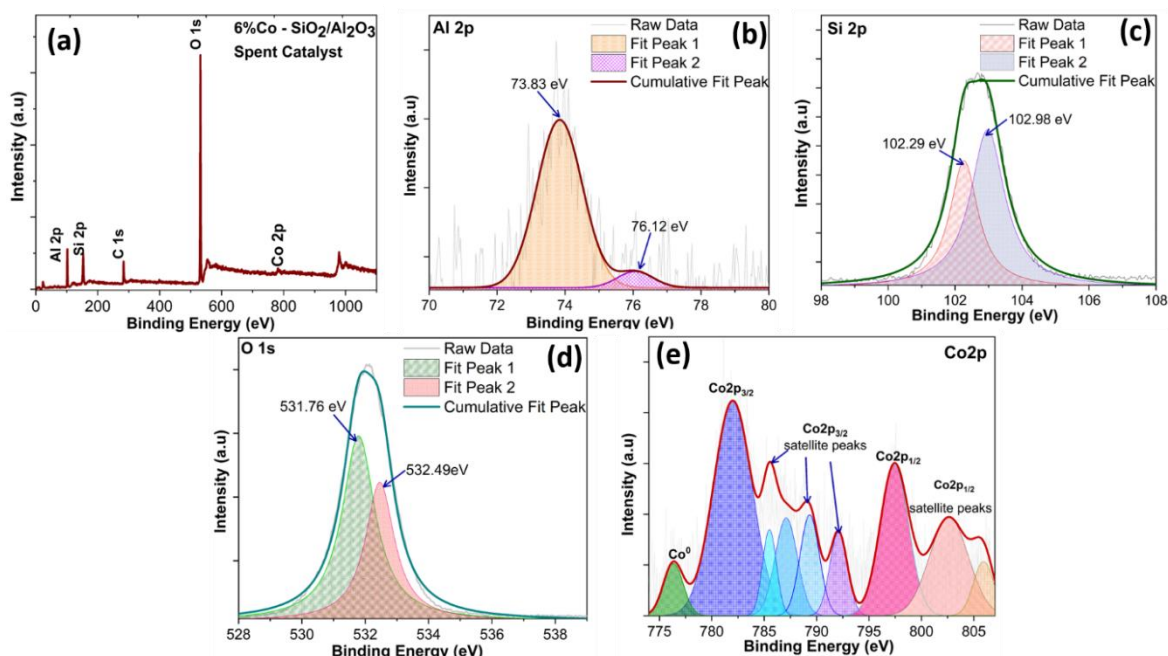


Figure 4.15 The Survey and core XPS spectra of spent catalyst.

The Core spectra for Al and Si in **Figure 4.15 (b)** and **(c)** confirmed the presence of SiO₂ and the Al₂O₃ phase in the spent catalyst. The Co 2p XPS core spectra shown in **Figure 4.15 (e)** with multiple peaks of B.E around 781.9 eV and 797.5 eV correspond to Co 2p_{3/2} and Co 2p_{1/2}. The spin-energy separation of ~15.6 eV between these peaks confirmed the Co₃O₄ active catalyst phase of the spent catalyst. Further, the peak obtained at 776.47 eV is attributed to metallic cobalt. This is due to the reduction of some of the Co₃O₄ species that occurred during the hydrotreatment process. Thus, the catalyst was found to be stable even after the hydrotreatment process, even after several cycles. Our study found that 6% Co/SiO₂-Al₂O₃ catalysts offer the most favorable optimal catalytic conditions. Different hydrotreatment experiments have demonstrated that methyl oleate undergoes hydrogenation of C=C bonds followed by hydrogenolysis of ester bonds during the hydrotreatment process. Here, DCO₂ or successive reduction-DCO results in alkanes with one carbon less (C_{N-1}), such as n-heptadecane. While, in addition, C_N alkanes, i.e. n-octadecane are produced by a reduction-dehydration-hydrogenation (HDO) route. These reactions occur on the plane containing the catalytically active Co₃O₄ (133). In addition, the acidic sites within the support lead to the cracking of alkanes. **Figure 4.16** depicts the plausible reaction pathways during the hydrodeoxygenation of methyl oleate to yield diesel-grade hydrocarbons.

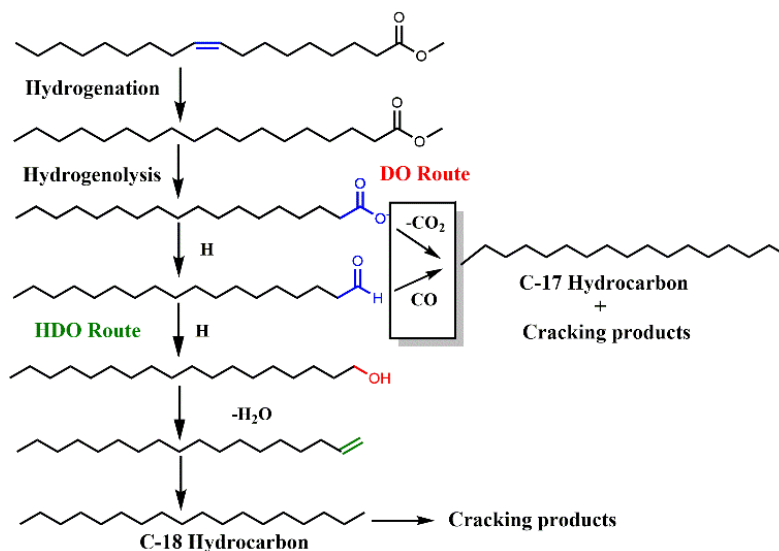


Figure 4.16 Possible Reaction Pathways for HDO/DO reaction.

4.3 Conclusion

A straightforward wet-impregnation technique was used to create a series of cobalt-loaded $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts (4, 6, 8, 10 and 12 wt%). XRD and TEM analysis successively reveal the formation of the active catalyst phase and the homogeneous dispersion of Co_3O_4 over the $\text{SiO}_2\text{-Al}_2\text{O}_3$ surface. The catalyst's reducibility and active acid sites were discovered by the H_2 -TPR and NH_3 -TPD studies. The mixed valence chemical state of the cobalt ions in $\text{Co}_3\text{O}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ supported catalyst was confirmed by XPS studies. In contrast, the coordination properties of Al and Si were revealed from solid-state NMR spectroscopy. Methyl oleate was used as a model compound for the catalytic conversion of triglycerides into green diesel, and a thorough study was done on the effects of the amount of Co incorporated into the $\text{SiO}_2\text{-Al}_2\text{O}_3$ supported catalytic system on conversion, selectivity, and stability. The results also showed that the temperature, reaction time, metal loading, and H_2 pressures strongly influenced the conversion and selectivity. Total ester conversions with more selectivity towards *n*-heptadecane/*n*-octadecane were achieved at temperatures as low as 280 °C and 15 bar H_2 pressure within 10 h reaction time under solvent-free conditions. Owing to the complete ester conversion rates and substantial yields observed under solvent-free conditions, the non-noble metal-based Co_3O_4 -incorporated $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst emerges as a promising and economical green catalyst for the large-scale production of diesel-grade hydrocarbons from both methyl oleate model compounds and vegetable oils. This research marks a significant step toward developing sustainable and economically viable catalysts for producing green diesel.