

Palladium-Incorporated Montmorillonite Clay: A Sustainable Imine Hydrogenation Catalyst

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Imines are synthesized by condensation of ammonia or primary amines with ketones and aldehydes, but this technique is reversible and requires extensive reaction durations and acid catalysts. Recent advances in reducing imines using metal hydrides have shown a more effective strategy for preparing amines, such as LiAlH_4 , which can be used in catalytic imine hydrogenation under mild conditions. However, molecular hydrogen gas is an efficient and environmentally friendly alternative.

Clay-supported metal catalysts offer advantages such as improved catalytic activity, higher conversion rates, better selectivity, compatibility with green chemistry principles, and cost-effectiveness. In the reported industrial methods of catalytic hydrogenation of imines, the purification of the product mixture is necessary as other impurities, such as leached metal species, are incorporated into the mixture. The current innovation uses natural clay as a catalyst, and while the incorporation of relatively expensive Pd metal in the catalytic system is important, the synthesis of amines relies heavily on the catalyst's recyclability and stability. The ease of hydroprocessing and purification of the product makes it profitable. This chapter unveils novel palladium nanoparticles (Pd NPs) intercalated montmorillonite clay catalysts performance for hydrogenation of 3-diphenyl prop-2-en-1-imine under mild reaction conditions. The Pd/Clay catalyst was synthesized using a simple wet-impregnation approach, and its physicochemical properties were comprehensively characterized using a variety of techniques such as N_2 adsorption, XRD, TEM, XPS, and TPR, which indicated the intercalation of active Pd NPs between the clay layers. The characterization results confirmed the successful intercalation of catalytically active Pd NPs between the layers of the clay matrix. The investigation extends to the impact of key reaction parameters such as catalyst loading, temperature, reaction duration, and hydrogen (H_2) pressure, proposing a plausible reaction mechanism. Remarkably, the optimal quantity of 6 wt.% Pd/Clay catalyst exhibited high catalytic activity in yielding 3-phenyl propyl aniline with 100% conversion and selectivity under 5 bar pressure for 3.5 h at 100 °C. Thus, the work showcases the promising potential of Pd/Clay catalysts in sustainable and efficient imine hydrogenation processes under mild conditions.

3.1 Experimental section

3.1.1 Preparation of schiff base

The Schiff base, 3-diphenyl prop-2-en-1-imine, was synthesized by condensation of Equimolar concentrations of Trans Cinnamaldehyde and Aniline (0.01 mol) in ethanol (5ml) and gently stirring the resultant mixture at the ambient temperature. Thin layer chromatography (TLC) was used to monitor the reaction's progress. The resulting mixture was kept undisturbed at room temperature for 30 minutes until little yellowish crystals began to form. The crystallization process was then completed by gently placing it in an ice bath. The cooled solution was then vacuum filtered to separate the pure crystals, which were washed with cold ethanol solvent.

3.1.2 Preparation of catalysts

The clay was sequentially treated for 12 hours at RT with 1N HNO_3 and 1N NH_4OH . The resultant clay was carefully washed with deionized (DI) water and dried overnight in a 120 °C oven for firm support. Wet impregnation was used to include palladium metal. Palladium(II)

nitrate hydrate was impregnated onto clay support (1g) in the required volume of 3N HNO₃ (10 mL), and the mixture was dried at 120 °C with constant stirring until it formed a thick paste. The detailed preparation method of Pd/Clay catalyst is given in **Figure 3.1**.

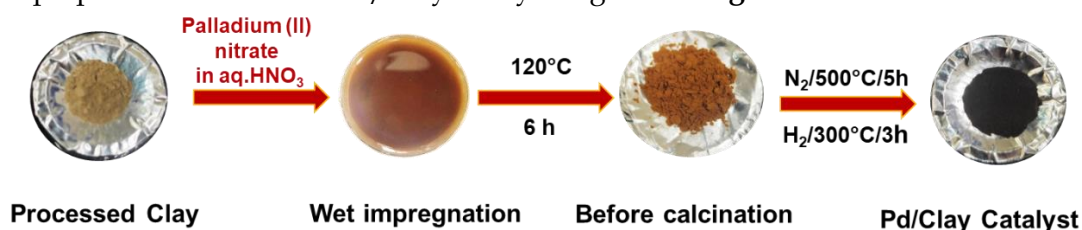


Figure 3.1 Preparation of Pd/Clay catalyst.

3.1.3 Characterization techniques

X-ray diffraction (XRD) measurements were carried out using a D8 Advance diffractometer (Bruker, U.S.A.). Here, Cu K α ($\lambda = 1.54\text{\AA}$) was used as the radiation source at current 40 mA tube and the voltage of 40 kV voltage for scanning diffraction angles between 5 and 90°. For morphological and elemental composition analysis, High-resolution Transmission Electron Microscope (HR-TEM) analysis was done using TALOS F200S G2 apparatus. A thermal conductivity detector (TCD)-equipped chemisorption analyzer, AMI-300, Altamira Instrument was utilised to carry out the hydrogen temperature-programmed reduction (H₂-TPR). Here, the sample is pre-treated at a rate of 10 °C per minute under helium for 1 hour, till it reaches 150 °C and then it is cooled to room temperature (RT). TPR profile was monitored in the range of 30-800 °C, a combination of H₂ (5%) and He (95%) is utilized as a reducing agent, with flow rate of 30 mL/min and heated until it reaches 800 °C at 10 °C/min for 30 minutes. Adsorption-desorption measurements were done using Autosorb-1Q-MP-XR from Quantachrome Instruments, USA for determining the surface area and porosity. The sample was degassed at 180 °C for 3 hours and analysis was done using nitrogen as a carrier gas with a purity of 99.995% at -196 °C. Thermogravimetric (TGA) analysis was performed using Simultaneous Thermal Analyzer (STA) - 6000 (Perkin Elmer) with a heating rate of 10 °C min⁻¹ under nitrogen environment with flow rate of 19.8 mL/min and 3 bar pressure. Fourier transformed infrared spectroscopy (FTIR) spectra was recorded using Bruker (Vertex, 70V+PMA50) in the range of 400 cm⁻¹ to 4000 cm⁻¹ at RT with 32 scan performance. Monochromatic Al K α radiation equipped X-ray photoelectron spectroscope (XPS) from Oxford Instruments (Omicron NanoTechnology GmbH) was used to determine the catalyst's surface composition and elemental states. Charge corrections were done using Conventional carbon 1s peak at 284.1 eV as a reference. Nuclear Magnetic Resonance (NMR) spectra were obtained using an 11.2 Tesla Bruker running at 500 MHz in CDCl₃. Gas chromatography (GC) analysis was done using a PerkinElmer Clarus 580 gas chromatograph equipped with Elite-5 capillary column with 0.10 μm film thickness, 30 m length and 0.25 mm inner diameter.

3.1.4 Hydrogenation of imine

All hydroprocessing was performed in a high-pressure vessel equipped with a steel container with a capacity of 250 mL supplied by Amar Equipments Pvt. Ltd. In the air-dried container, the catalyst (50 mg), as synthesized 3-diphenyl prop-2-en-1-imine (500 mg), and dry methanol (10ml) were mixed. A vacuum was created in the container, and the hydrogen gas was purged. The reaction temperature was increased from 25 °C to the desired temperature (50 - 100 °C) over several hours for time-dependent investigations with varying pressures. After the catalytic test, the reactor was depressurized and allowed to reach RT. The liquid fraction was separated after centrifuging the mixture. Methanol (10 mL*2) was then added to the catalyst, mixed, and centrifuged to extract most of the product. The conversion and selectivity of the reaction were determined using a Gas chromatography (GC) fitted with a Flame ionization detection (FID) detector. The formation of the product was further supported by ¹H NMR, ¹³C NMR. The detailed process of hydrogenation of imine is given in **Figure 3.2**.

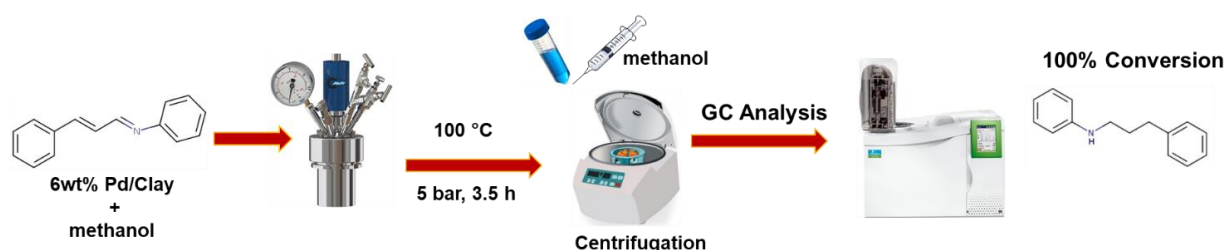


Figure 3.2 Hydrogenation of imine

3.1.5 Catalyst Reusability

To conduct the reusability test, the used catalyst for the hydrogenation process was centrifuged after the reaction. The resulting catalyst was washed three times with methanol to extract all reaction products and any unreacted substrate. The catalyst was dried overnight in a vacuum oven at 60 °C. These were then evaluated for the hydrogenation process, as described above, under optimal reaction conditions for up to 5 cycles.

3.1.6 Leaching Tests

The leaching experiments were carried out in a Berghof HR-1000 high-pressure reactor equipped with a 1000 mL teflon container. Inductively Coupled Plasma Optical Emission (ICP-OES) was used to evaluate the liquid product of a hydrogenation reaction of 5 g of 3-diphenyl prop-2-en-1-imine with 0.5g of 6% Pd/Clay catalyst at 100 °C, 5 bar pressures for 3.5 hours.

3.2 Results and Discussion

3.2.1. Characterization of catalyst

Natural clay is used as a support for palladium NPs and the characterization of Pd intercalated clay catalysts and their application in imine hydrogenation is studied. The general formula of clay employed in this work is $K_3Ca_1Ti_{0.6}Al_{12}Si_{40}Fe_6H_xO_y$, which was determined using collective X-ray fluorescence (XRF) spectrometry and scanning electron microscopy combined with energy dispersive X-ray (SEM/EDX) spectrometry, as described in our earlier paper (Soni et al., 2017). As illustrated in **Figure 3.3**, the natural clay is formed of montmorillonite, which has octahedral AlO_6 sheets sandwiched between two tetrahedral SiO_4 sheets. The interlayer space is occupied by K^+ and Ca^{2+} ions coordinated by the H_2O molecule. A simple wet impregnation method in dilute nitric acid was used to accomplish Pd intercalation in natural clay. In general, clay swelling occurs during intercalation, enhancing cation exchange and effectively incorporating Pd^{2+} ions between the clay interlayers. When Pd^{2+} ions are calcined in a hydrogen environment, they form catalytically active Pd^0 NPs (Zeng et al., 2016). The detailed mechanism of intercalation is depicted in **Figure 3.3**. As a result, natural clay-based catalysts containing 2, 4, 6, and 10% Pd by weight were prepared and labeled as 2% Pd/Clay, 4% Pd/Clay, 6% Pd/Clay, and 10% Pd/Clay, respectively. **Figure 3.4** depicts the X-ray diffraction (XRD) patterns of all produced catalysts as well as the pristine clay to comprehend phase formation.

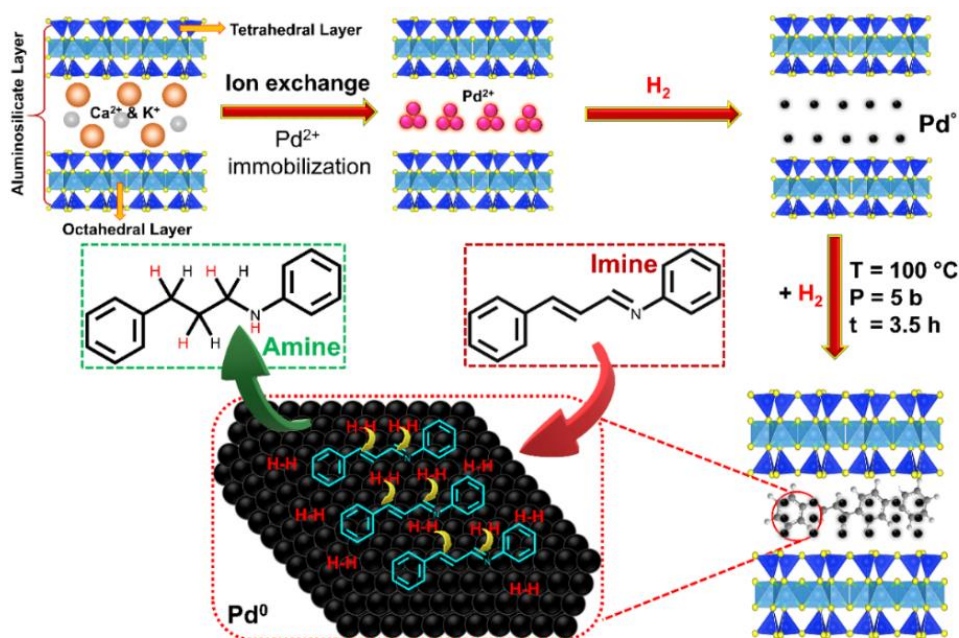


Figure 3.3 Schematic representation of Pd NPs intercalated clay synthesis and proposed working mechanism of the interaction of Pd NPs with adsorbed H_2 and substrate imine.

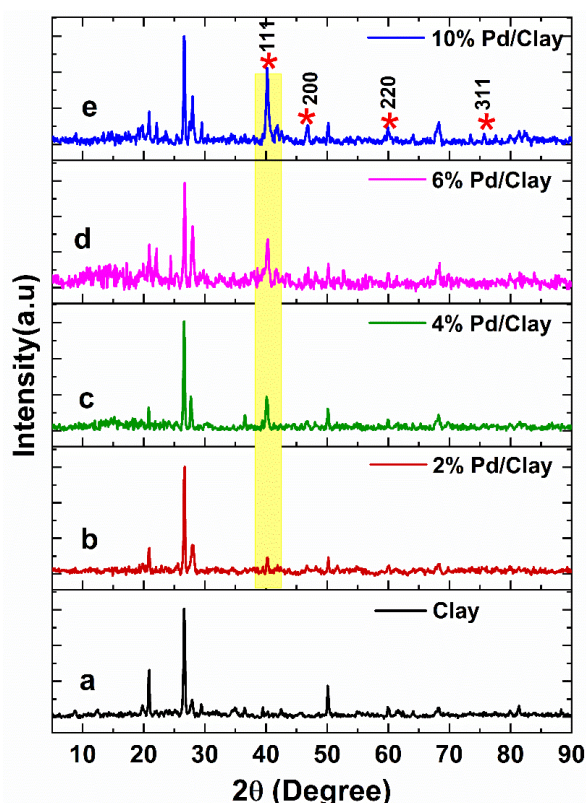


Figure 3.4 XRD patterns of (a) Clay and (b) 2 wt.% Pd/Clay, (c) 4 wt.% Pd/Clay, (d) 6 wt.% Pd/Clay and (e) 10 wt.% Pd/Clay catalysts.

The resulting XRD pattern (**Figure 3.4 a**) confirmed the clay's crystalline nature, with characteristic peaks of montmorillonite and quartz content as shown in (**Figure 3.5**) (Soni et al., 2017). According to Joint Committee on Powder Diffraction Standards (JCPDS) No 05-0681, the wide diffraction peaks centered at 2θ values of 40° , 46.81° , 68° , and 82° correspond to the (111), (200), (220), and (311) crystal planes of the face-centered cubic (fcc) structure of metallic Pd (Varadwaj et al., 2014). The intensity of the (111) plane gradually rises as the Pd loading in clay increases (**Figure 3.4 b, c, d, and e**). This revealed the preferential growth of the (111) plane (Adilina et al., 2021). The XRD pattern given in **Figure 3.4** shows that neither the peak shifting of the d(001) plane of clay nor its disappearance was observed as previously described in

the literature (Adilina et al., 2019) (Varade and Haraguchi, 2013). This might be due to the clay layer's uneven spacing during intercalation. Furthermore, metal intercalation reduces the intensity of the (001), (002), and (003) planes of montmorillonite clay (see **Figure 3.5 b, c, and d**), indicating that efficient metal intercalation occurs during wet impregnation assisted by dilute nitric acid. Previous research on K10 montmorillonite indicated that the (001) peak disappears due to a lack of well-ordered silicate layer structure. It also confirms that the three broad diffraction peaks represent the (111), (200), and (220) crystal planes of metallic Pd's face-centered cubic (fcc) structure.

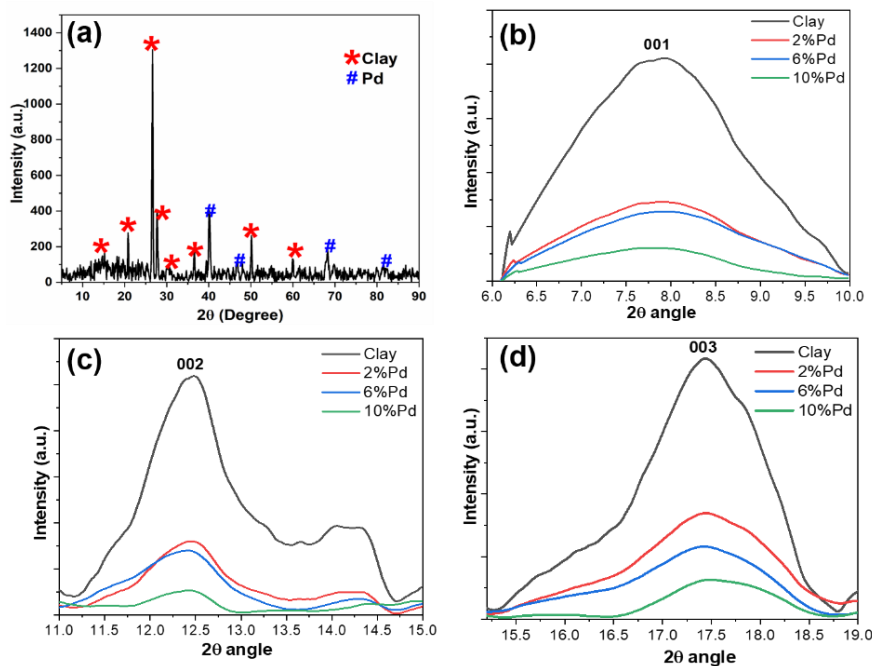


Figure 3.5 (a) XRD spectra of 4 wt.% Pd/Clay showing clay and Pd indexed peak. (b), (c) and (d) Intensity variation of (001), (002) and (003) planes of the montmorillonite clay upon metal intercalation.

Transmission electron microscopy (TEM) was used to confirm Pd's intercalation, surface morphology, and elemental distribution on the clay surface, as shown in **Figure 3.6**. Spherical NPs of Pd with sizes around 2-20 nm were detected in **Figure 3.6 a, b, and c** (for 2%, 6%, and 10% Pd/Clay), and the NPs are well-dispersed on the clay support. The interplanar d-spacing is 2.6 Å and 2.3 Å, respectively, corresponding to the Pd(111) plane for 2% Pd/Clay and 10% Pd/Clay (Wu et al., 2016).

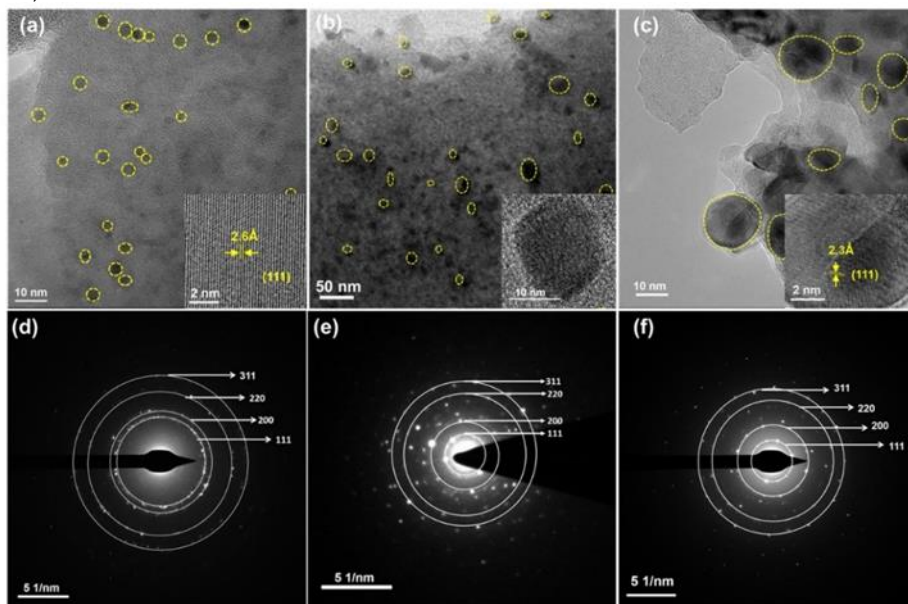


Figure 3.6 TEM images of Pd loaded clay with 2 wt.%, 6 wt.% and 10wt.% (a-c) and their SAED pattern (d-f).

Furthermore, TEM images (**Figure 3.7**) may be used to understand the comprehensive morphological studies and intercalation properties of clay and Pd included clay (for 2%, 6%, 10% Pd/Clay). The layered structure of pristine clay with distinct layers is readily apparent and highlighted in **Figure 3.7 (a)**. Furthermore, **Figure 3.7 (b), (c), (d)** illustrates that Pd intercalation has not significantly altered clay layer structure.

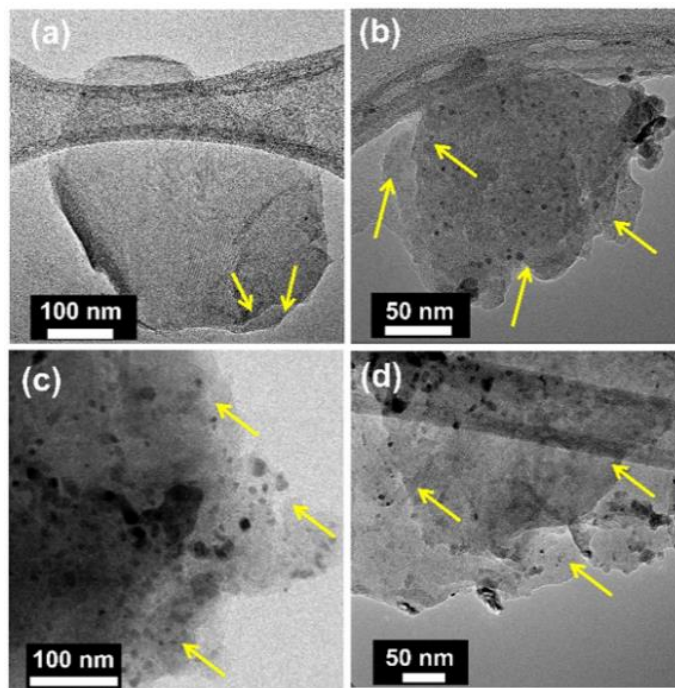


Figure 3.7 TEM images of clay (a) 2 wt.% Pd (b) 6 wt.% Pd (c) 10 wt.% Pd (d) loaded clay.

Figure 3.7 shows a tubular structure that may be caused by traces of halloysite content, which is not apparent from the XRD analysis (Zheng et al., 2020). Furthermore, Pd NPs have been found inside and outside of the clay layers, confirming the effective intercalation of Pd onto the clay (Varade and Haraguchi, 2013). The SAED patterns for the samples (**Figure 3.6 d, e, and f**) displayed bright tiny spots forming rings of Pd (111), Pd (200), and Pd (220) planes, revealing the polycrystalline nature of the catalyst (Xu et al., 2014). The presence of the active metal Pd, as well as other metals from the clay such as Fe, Si, O, Ca, and K, was detected from the catalyst's Energy-dispersive X-ray spectroscopy (EDS) spectra and is shown in **Figure 3.8**.

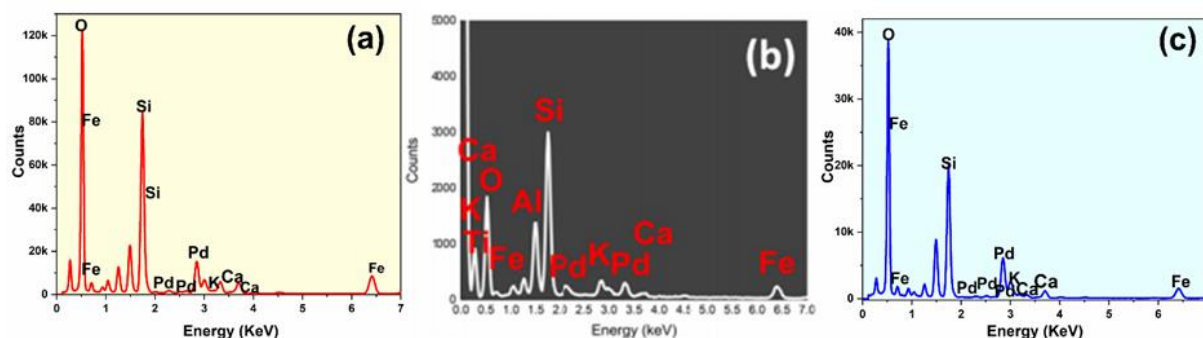


Figure 3.8 EDS spectra of clay loaded with different (a) 2 wt.% Pd (b) 6 wt.% Pd and (c) 10 wt.% Pd.

X-ray photoelectron spectroscopy (XPS) was used to analyze active metals' surface elemental composition and oxidation state in clay catalysts, as shown in **Figure 3.9**. The existence of Pd, Fe, Si, Ca, K, and O species in the catalyst was shown by an XPS survey scan (**Figure 3.9a**), supported by EDS data. For spectral calibration, the C 1s peak at 284.8 eV was employed. In **Figure 3.9c**, the core level spectra of palladium revealed two peaks with binding energies (B.E) of 335.2 and 340.48 eV, which correspond to the 3d_{5/2} and 3d_{3/2} electronic states of Pd(0), respectively, despite having

higher energy than Pd(0) in literature (Duan et al., 2016). The non-coexistence of Pd(0) and Pd(II) suggested the complete reduction of Pd(II) to Pd(0). This could be attributed to the efficient stabilisation of Pd⁰-nanoparticles by alumino-silicate component of the clay matrix.

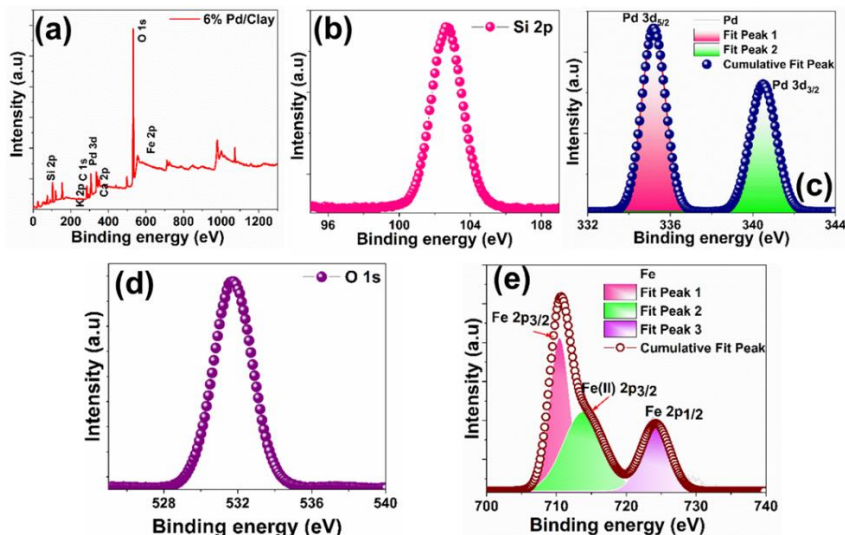


Figure 3.9 (a) XPS Survey scan of 6 wt.% Pd/Clay catalyst, XPS core level spectra of 6 wt.% Pd/Clay catalyst showing (b) Si 2p (c) Pd 3d (d) O 1s (e) Fe 2p.

There were no further Pd²⁺ peaks found in the sample. The core spectra for Fe (Figure 3.9e) revealed two peaks at 710.552 and 723.80 eV, classified as Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Yamashita and Hayes, 2008). At a B.E of 714.05 eV, a satellite peak of Fe(II) 2p_{3/2} is identified. The Si 2p spectra (Figure 3.9 b) show a single band at around 102.6 eV, typical of silicon bound to carbon and/or oxygen (Santana et al., 2016). The O 1s core spectra in Figure 3.9 d showed a single strong peak at 532 eV, corresponding to the silicon oxygen bonding (Si-O-Si) found in silica and fitting well with clay mineral studies (Kloprogge and Wood, 2018).

To understand the reducibility of the synthesized catalyst temperature programmed reduction (H₂-TPR) analysis and the TPR profiles for clay and Pd loaded clay were conducted. Temperature programmed reduction (H₂-TPR) study was performed to understand the reducibility of the synthesized catalyst better, and the TPR profiles for clay and Pd-loaded clay catalyst are presented in Figure 3.10.

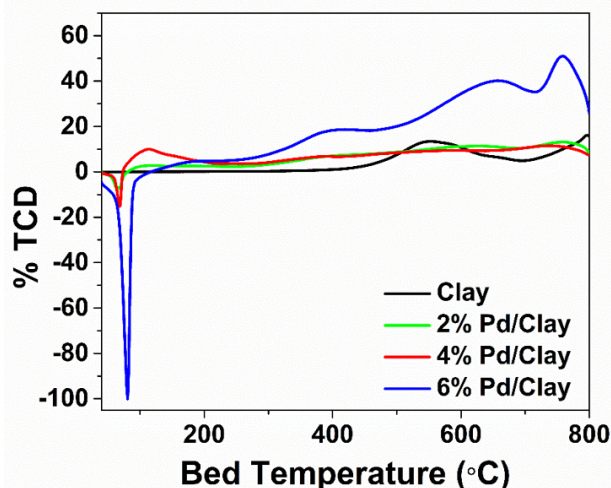


Figure 3.10 H₂ TPR Profile of clay and unhydrogenated Pd/Clay catalysts with different wt.% Pd.

There was no reduction peak identified in a pure Montmorillonite clay sample below 450 °C. However, all of the Pd-loaded clay catalysts showed a pronounced negative peak at 65-72 °C, which is typical of the decomposition of the -PdH phase produced at RT by hydrogen adsorption on the Pd-based catalyst, as shown by the equation (Aznárez et al., 2015):



The size of the supported Pd metal particles influences the intensity and position of this negative peak. The TPR profile shows that as the palladium loading rises, it leads to a more prominent negative peak. H₂ consumption is clearly detected between 100 and 200 °C for Pd 2% and Pd 4%, resulting from the decrease of small nano-sized PdO species, and can be confirmed by TEM analysis (Oh et al., 2019). The reduction process in the high-temperature range of 250-550 °C is caused by PdO particles interacting intensively with the surface of the support.

Figure 3.11 presents BET (Brauner Emmett Teller) adsorption-desorption isotherms, adsorption plots, and BJH (Barrett Joyner Halenda) pore distribution curves at 77 K for montmorillonite and metal intercalated clays. According to the Brunauer-Deming-Deming-Teller (BDDT) classification, the clay exhibits typical type IV N₂ isotherms with an H3 type hysteresis loop, indicating that it is mesoporous layered in nature (Thommes et al., 2015). Palladium-loaded clay has a lower N₂ adsorption capacity than pristine clay, and its associated surface area has decreased from 44.547 m²/g to 16.519 m²/g in 6 wt.% Pd/Clay. This might be attributed to the metallic Pd occupying space on the clay surface.

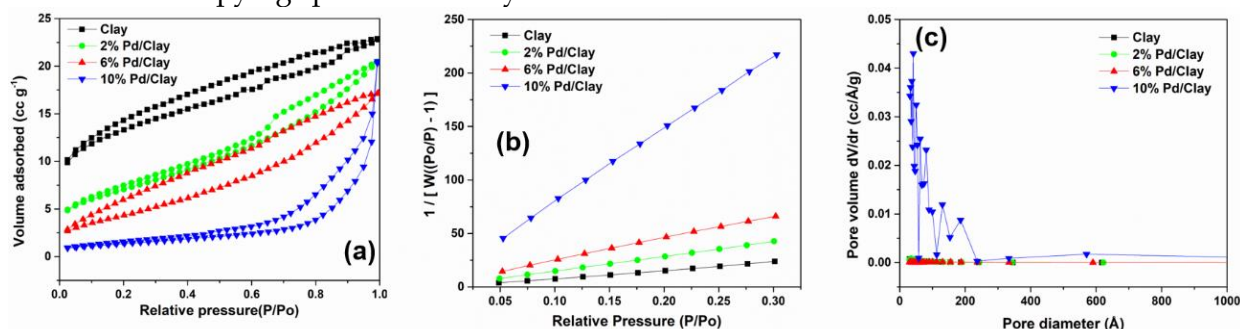


Figure 3.11 (a) N₂ adsorption/desorption isotherms (b) BET adsorption plot and (c) BJH Pore distribution curve of Pd/Clay catalyst.

Furthermore, as shown in **Table 3.2**, the significant increase in the average pore size of the Pd integrated clay from 25.25 (2 wt.% Pd/Clay) to 165.7 (10 wt.% Pd/Clay) as compared to pristine clay (15.83) suggests the presence of Pd NPs in interlayered clay. This is evident from the previous literature that due to the presence of nanocrystals in the clay interlayers, the average pore size and volume of the composite material are slightly larger than that of clay. (Varade and Haraguchi, 2013). For 10% Pd/Clay, the average pore size increases dramatically. When metal loading increases, smaller pores are closed, while larger pores are only available for physisorption.

Thermogravimetric analysis (TGA) revealed the prepared catalyst's thermal stability, as shown in **Figure 3.12 a**. The TGA profile of processed clay shows that weight TGA indicates the thermal stability of the produced catalyst. TGA profiles of processed clay demonstrate weight loss owing to the removal of physisorbed water (below 100 °C), loss of firmly bound water molecules present in the first coordination sphere of the interlayer ions (100-500 °C), and loss of structural hydroxyl groups (500-900 °C) (Motokura et al., 2012). TGA examination of palladium intercalated catalysts demonstrated that higher metal loadings (Pd 6 wt.% and Pd 10 wt.%) were stable up to 900 °C with slight initial weight loss, which may be attributed to water molecule loss (Aldhayan and Aouissi, 2017). However, considerable weight loss was seen with lower metal loadings, especially Pd 2 wt.% and Pd 4 wt.%, indicating that catalysts with more significant metal loadings are more thermally stable. The most significant weight loss (%) was found in 4 wt.% Pd/Clay, most likely due to the weakening of clay bonds in this case.

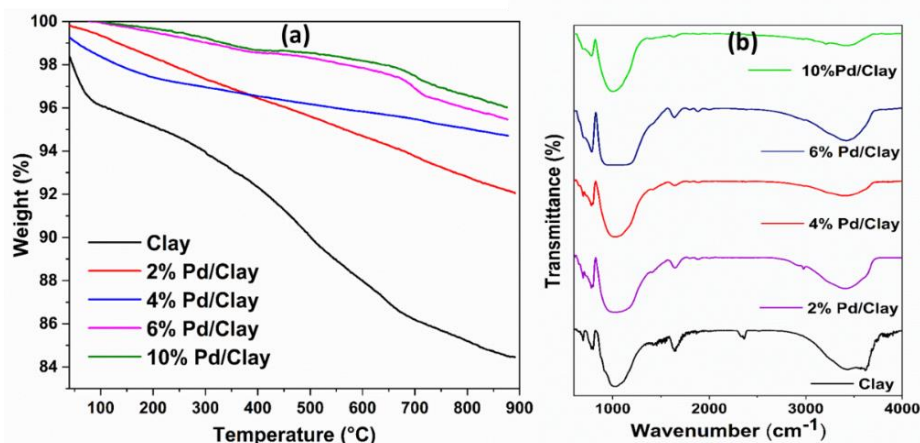


Figure 3.12: (a) TGA curves and (b) IR spectra of Pd intercalated clay of different Pd loading.

The Fourier-transform infrared (FTIR) spectra of clay and palladium intercalated clay was recorded and shown in **Figure 3.12 b**, and it revealed the existence of OH bonds at 3627 cm⁻¹ (OH stretching) and 3408 cm⁻¹ (H-O-H stretching), which correspond to the hydroxy groups of clay and interlayer water molecules, respectively. For OH bending, a peak at 1629 cm⁻¹ was found. broad and intense peak at 1018 cm⁻¹ (Si-O-Si stretching) indicates the presence of silica (Bentahar et al., 2019). Quartz presence is generally detected in the wavenumber range of 1200 - 500 cm⁻¹. The peak intensities related to O-H bonds were lowered after wet impregnation due to nitric acid dihydroxylation.

Table 3.1: Catalytic hydrogenation of 3-diphenyl prop-2-en-1-imine with prepared catalyst

Catalyst	Reaction time [h]	Temperature [°C]	Pressure [bar]	Conversion [%]	Selectivity ^[b] A%	Selectivity ^[c] B%	Substrate to Metal ratio	TOF [h ⁻¹]
2% Pd/clay	5	100	15	84 ± 0.9	84 ± 0.9	-	1: 4 × 10 ⁻³	39.23
2% Pd/clay	8	100	15	97 ± 0.8	97 ± 0.8	-	1: 4 × 10 ⁻³	28.26
2% Pd/clay	12	100	15	100	100	-	1: 4 × 10 ⁻³	19.25
2% Pd/clay	12	70	15	98 ± 0.6	98 ± 0.6	-	1: 4 × 10 ⁻³	18.98
2% Pd/clay	12	50	15	87 ± 0.5	85 ± 0.2	2 ± 0.3	1: 4 × 10 ⁻³	16.49
4% Pd/clay	3	100	15	84 ± 1	84 ± 1	-	1: 9 × 10 ⁻³	29.61
4% Pd/clay	5	100	15	100	100	-	1: 9 × 10 ⁻³	20.91
4% Pd/clay	8	100	15	100	100	-	1: 9 × 10 ⁻³	13.07
4% Pd/clay	10	100	15	100	100	-	1: 9 × 10 ⁻³	10.45

6% Pd/clay	5	100	15	100	100	-	1: 11 x 10 ⁻³	17.62
6% Pd/clay	5	100	12	100	100	-	1: 11 x 10 ⁻³	17.62
6% Pd/clay	5	100	10	100	100	-	1: 11 x 10 ⁻³	17.62
6% Pd/clay	3	100	12	100	100	-	1: 11 x 10 ⁻³	29.38
6% Pd/clay	3	100	7	100	100	-	1: 11 x 10 ⁻³	29.38
6% Pd/clay	3.5	100	5	100	100	-	1: 11 x 10 ⁻³	25.18
6% Pd/clay	3	100	5	96 ± 0.5	92 ± 0.7	3 ± 0.5	1: 11 x 10 ⁻³	27.24
6% Pd/clay	3	50	5	96 ± 0.4	90 ± 0.1	6 ± 0.2	1: 11 x 10 ⁻³	26.46
10% Pd/clay	5	100	15	100	100	-	1: 18 x 10 ⁻³	10.60
6% Pd/SiO ₂	5	100	5	88 ± 0.5	80 ± 0.5	7 ± 0.6	1: 1 x 10 ⁻³	14.19
6% Pd/Al ₂ O ₃	5	100	5	89 ± 0.6	86 ± 0.5	3 ± 0.4	1: 12 x 10 ⁻³	15.20

3.2.2. Optimization of reaction parameters

Table 3.1 depicts the effects of reaction parameters (catalyst loading, temperature, reaction duration, and H₂ pressure) on the hydrogenation of 3-diphenyl prop-2-en-1-imine to 3-phenylpropylaniline. The influence of varying Pd catalytic loadings (2, 4, 6, and 10 wt.%) was explored to determine the optimal quantity of palladium. Increasing the metal loading improves conversion efficiency. As shown in **Table 1**, complete conversion was only obtained after a 12 h prolonged reaction with a lower metal loading of 2 wt.% Pd/Clay (**Table 3.1**, exp no. 3). In comparison, it occurs in a shorter reaction period of 5 h at higher metal loading (4 wt.% Pd/Clay) (**Table 3.1**, exp no. 7). This is due to an increase in the number of active sites in conjunction with an increase in palladium concentration (Gawade et al., 2016). The effect of change in reaction time on 3-diphenyl prop-2-en-1-imine conversion was also investigated. At 100 °C and 15 bar pressure, the conversion of 3-diphenyl prop-2-en-1-imine rose from 84.66% to 97.84% when the reaction time was increased from 5 h to 8 h (**Table 3.1**, exp no 1, 2). Interestingly, increasing the reaction time to 12 h leads to total conversion (**Table 3.1**, exp no. 3). The temperature was changed in the range of 50-100 °C to understand the effect of temperature on conversion and selectivity of the reaction. Temperature changes affected both conversion and selectivity. Complete conversion was observed at 100 °C with a reaction time of 12 h for 2 wt.% Pd/Clay.

However, once the temperature is reduced to 70 °C, the conversion rate drops to 98.60% (**Table 3.1**, exp no. 4). When the temperature is reduced further to 50 °C, the conversion value decreases to 87.94%, with a decrease in selectivity towards 3-phenylpropylaniline expressed as selectivity A% (**Table 3.1**, experiment 5). H₂ pressure is another significant variable influencing catalytic activity in liquid-phase hydrogenation reactions. As the H₂ pressure rises, the dissolved H₂

content in the reaction mixture increases, resulting in high conversion values (Gong et al., 2017). Thus, maintaining optimum pressure is key to obtaining a high-yield product. For 6 wt.% Pd/Clay catalyst, complete conversion is achieved despite the pressure being decreased from 15 bar to 10 bar (**Table 3.1**, exp no. 10-12). To further investigate the optimized reaction conditions, H₂ pressure and reaction time were decreased simultaneously, and their effect on the conversion

Thus, maintaining optimum pressure is critical for obtaining a high-yield product. Despite reducing the pressure from 15 bar to 10 bar for the 6 wt.% Pd/Clay catalyst, full conversion is obtained (**Table 3.1**, exp no.s. 10-12). To further test the optimal reaction conditions, H₂ pressure and reaction time were lowered simultaneously, and their influence on conversion was investigated at 100 °C. To our delight, when the H₂ pressure is as low as 5 bar, and the reaction duration is 3.5 hours, full hydrogenation of 3-diphenyl prop-2-en-1-imine occurs with 3-phenylpropylaniline as the only result (**Table 3.1**, exp no. 15). When the time was lowered to 3 hours, nearly complete conversion was attained. However, the presence of side product was expressed by Selectivity B% (Table 3.1, exp no. 16). Furthermore, the control experiment for SiO₂ and Al₂O₃ loaded with 6% Pd/Clay was carried out. As indicated in Table 3.1, entries 19 and 20, full conversion was not attained. This clearly demonstrates the superiority of clay as a support over SiO₂ and Al₂O₃. The proposed catalyst is cost-effective and has remarkable reactivity towards imine hydrogenation, as shown in **Table 3.1**. The inherent properties of the clay support played a significant influence in increasing catalytic efficacy. This is in accordance with hydrogenation studies based on the Horiuti-Polanyi mechanism (Mattson et al., 2013), which suggest adsorption of the C=C bond on the catalyst forms two M-C chemical bonds, resulting in a classical three-centered transition state (C, M, H). By comparing GC chromatograms and NMR data of imines and products (**Figure 3.13, 3.14**), we were able to identify the reaction products and calculate conversion and selectivity.

Table 3.2 Average pore size value of clay and Pd intercalated clay.

S.no.	Catalyst	Average pore size
1	Clay	15.83Å
2	2 wt.% Pd/Clay	25.25Å
3	6 wt.% Pd/Clay	32.06Å
4	10 wt.% Pd/Clay	165.7Å

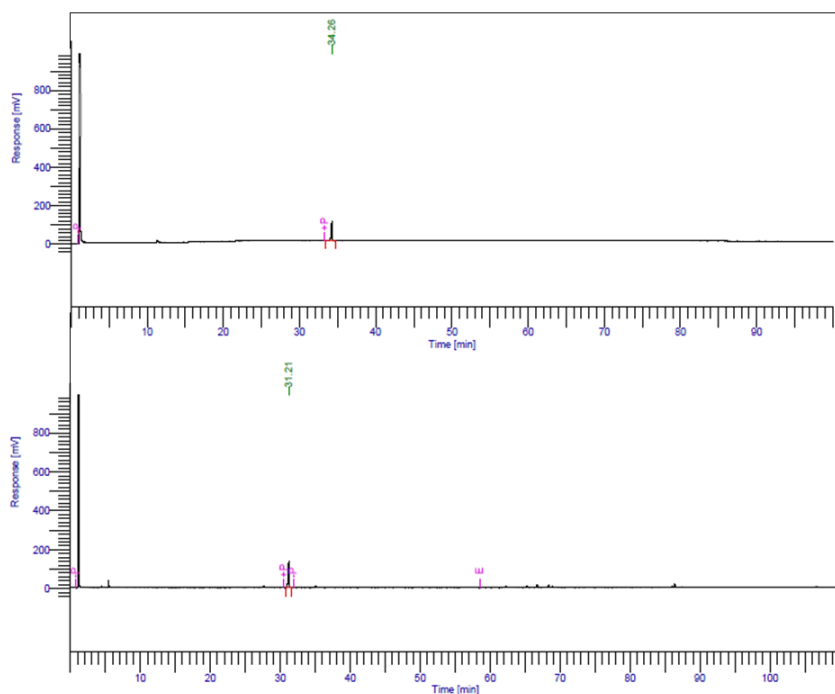


Figure 3.13 GC analysis of starting material 3-diphenyl prop-2-en-1-imine and product 3-phenyl propylaniline.

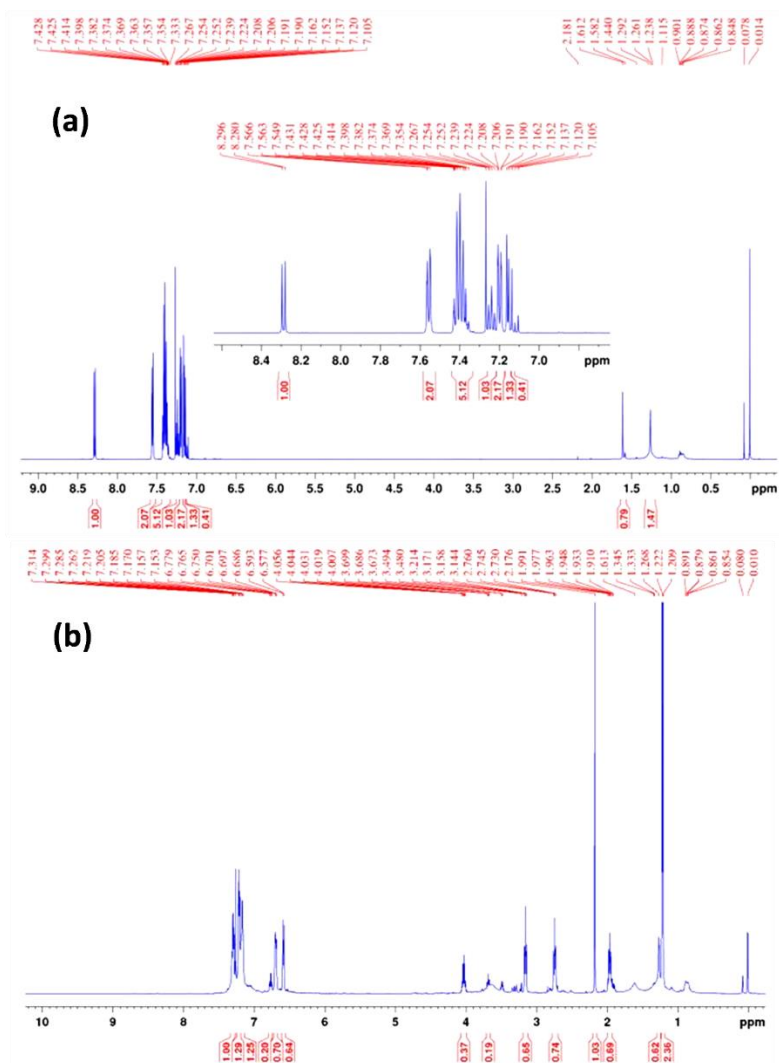


Figure 3.14 (a) ¹H NMR spectra of starting material 3-diphenyl prop-2-en-1-imine (b) product 3-phenyl propylaniline.

According to **Figure 3.3**, it can be seen that the increase of interlayer spacing in clay enables the creation of Pd NPs with highly faceted Pd (111) planes, which is corroborated by XRD investigation (**Figure 3.4**). Zheng and associates confirm the resulting result (Zhao et al., 2015). According to their report, the hydrogenation process catalyzed by Pd nanocrystals is a facet-dependent catalysis reaction. A study of imine-mixed catalyst was carried out to indicate the catalyst's reactivity further. In this respect, an equal quantity of 2-diphenyl prop-2-en-1-imine and a highly reactive 6 wt.% Pd/Clay catalyst were mixed together in methanol at 10 bar H₂ pressure for 2 hours at RT, and then the methanol was air-dried overnight at 80 °C. The XRD patterns of imine-mixed clay catalyst (**Figure 3.15 a**) exhibit a slightly pronounced distinctive Pd (111) peak compared to the pristine catalyst, suggesting significant imine adsorption on the Pd surface at RT. This illustrates the importance of the Pd (111) plane in influencing catalytic activity (Kumar et al., 2010). This strong metal-substrate interaction enables C=N and C=C bonds to be activated for efficient hydrogenation. The IR spectra of imine-mixed 6 wt.% Pd/Clay (**Figure 3.15 b**) show a narrowing of IR bands with sharper peaks, confirming the significant adsorption of imines on the Pd surface.

Table 3.3 Metal loadings in catalysts (wt.%) and catalyst after hydrogenation reactions.

Before Hydrogenation Reaction					
Sample	Initial concentration	Final Dilution	Conc. From ICP	Result ppm for 1000 mL	% composition
4% Pd	10	50	9.4275	0.481554	4.81554
6% Pd	10	50	11.3917	0.571375	5.71375
10% Pd	10	50	19.1608	0.94973	9.4973
After Hydrogenation Reaction					
Sample	Initial concentration	Final Dilution	Conc. From ICP	Result ppm for 1000 mL	% composition
4% Pd	10	50	8.5021	0.425105	4.25105
6% Pd	10	50	11.1398	0.55699	5.5699
10% Pd	10	50	18.6365	0.931825	9.31825

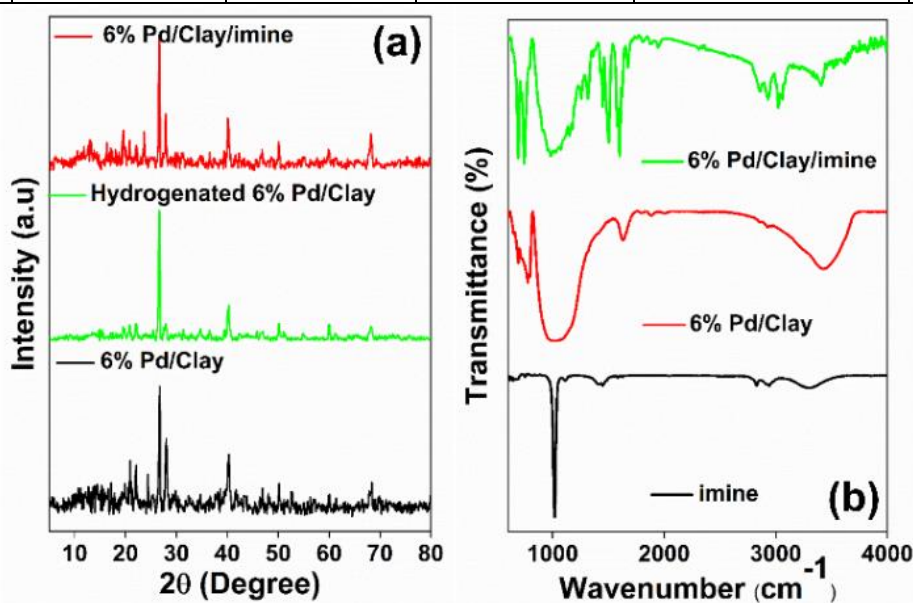


Figure 3.15 (a) XRD spectra of 6 wt.% Pd/Clay, imine-mixed 6 wt.% Pd/Clay and its hydrogenated product and (b) FTIR spectra of prepared imine, 6 wt.% Pd/Clay and 6 wt.% Pd/Clay/imine.

3.2.3. Reusability and metal leaching studies

After establishing the reactivity of the catalyst, reusability was determined to assess the catalyst's stability (Jeganathan et al., 2014). The catalyst was retrieved after the hydrogenation reaction to conduct the reusability test. The obtained catalyst was washed three times with methanol to extract the whole reaction product. The remaining catalyst was dried at 60 °C and evaluated for further hydrogenation reactions up to 5 cycles under optimum conditions. The comparative XRD patterns of a 6 wt.% Pd/Clay catalyst after 3 and 5 cycles are presented in (Figure 3.16) for fresh and reused catalyst which shows no significant difference.

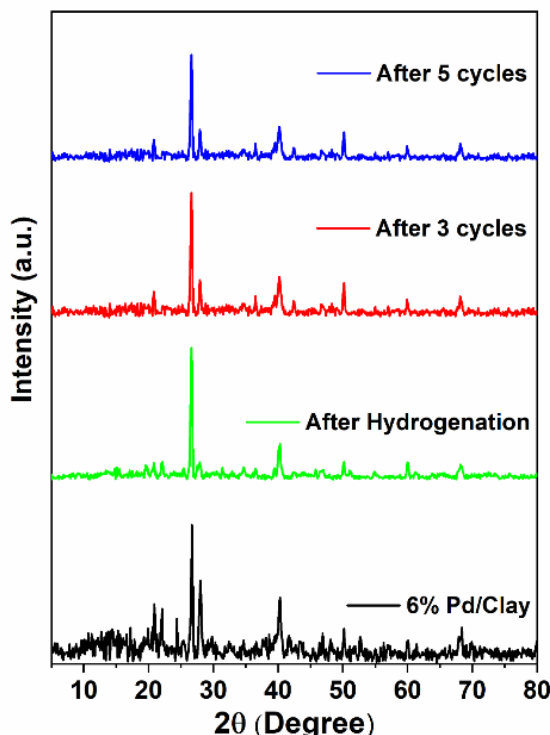


Figure 3.16 XRD patterns of the 6 wt.% Pd/Clay catalyst: (a) before reaction (b) after hydrogenation (c) after three and (d) after five reaction cycles.

Metal leaching tests using a 6%Pd/Clay catalyst were also carried out. The hydrotreatment process was performed using 5g substrate and 500 mg catalyst in 100 mL of methanol (at 100 °C, 5 bar H₂ pressure for 3.5 hours). After the reaction was completed, the liquid product was separated from the catalyst using centrifugation. The palladium leaching content is determined using ICP-OES measurements. The remaining catalyst was rinsed with methanol and dried before and reused in the next five cycles. During each cycle, the quantities of catalyst and palladium in the product were determined, as shown in **Table 3.3**.

After each cycle, the quantity of Pd leaching in the separated product was less than 0.5 ppm. The conversion value is reduced to 94% after the third cycle as shown in **Table 3.4**. This is most likely due to the loss of the catalyst during the centrifugation process and metal leaching. These results show that the Pd/Clay catalysts have outstanding stability and efficiency for imine hydrogenation under mild reaction conditions.

Table 3.4: Recyclability of the Pd/Clay catalyst in the hydrogenation of 3-diphenyl prop-2-en-1-imine.

S.no.	Cycles	Conversion
1	0	100
2	1	100
3	2	99
4	3	97
5	4	94

3.3. Conclusion

In conclusion, an environmentally friendly and affordable natural clay-based catalytic system is developed using a simple one-step wet impregnation method and utilized for imine hydrogenation. Clay plays a vital role in supporting the immobilization of Pd NPs owing to its inherent properties. Various characterization methods such as XRD, TEM, and BET analysis validated the clay's interlayered structure and efficient intercalation. Among the various Pd-loaded clay catalysts, 6 wt.% Pd loading displayed exceptional stability and excellent high catalytic performance for imine hydrogenation. This is due to the interlayered clay structure's dominant highly faceted Pd (111) plane. Hydrotreatment experiments demonstrated that reaction parameters significantly impact activity and selectivity. The GC results showed that under optimum 5 bar H₂ pressure conditions for 3.5 hours, 6 wt.% Pd/Clay showed 100% imine conversion and 100% selectivity of 3-phenylpropylaniline. The catalyst is robust and can be utilized over five cycles. This work would aid in investigating alternative hydrogenation processes by bridging the two fields of metal NPs and clay systems owing to its low cost, simple synthesis procedure, and outstanding catalytic activity.

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