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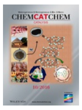

Palladium-Nanoparticles-Intercalated Montmorillonite Clay: A Green Catalyst for the Solvent-Free Chemoselective Hydrogenation of Squalene

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Squalane is an important ingredient in the cosmetic, nutraceutical, and pharmaceutical industries. It has also been used as a model compound for the hydrocracking of crude and microalgae oil. Thus, a series of green heterogeneous metal catalysts were prepared to achieve complete hydrogenation of highly unsaturated squalene into squalane. Surface modification of the clay and metal intercalation simultaneously occurred during wet impregnation. The Pd-nanoparticles-intercalated clay with a dominating Pd(111) facet showed the highest reactivity and selectivity. The catalyst was stable with very low Pd leaching (≈0.03 ppm) and was recyclable without losing any significant catalytic activity.

The cost effectiveness and easy availability of clays and clay-based materials make them good choices as catalysts for the development of green methods for various chemical transformations.[1] Clay-based metal catalysts are preferred over metal catalysts owing to the advantages associated with the clays.[1b] Easy replacement of the interlamellar cations in clays provides further possibilities to incorporate other cations or small molecules. Thus, several properties such as acidity, pore size, and surface area can be modified to influence catalytic performance. Naturally occurring clays can be modified either by physical or chemical modification.[2] The treatment of natural montmorillonite clay with mineral acid is important for its improved adsorption and catalytic properties.[3]

The hydrogenation of unsaturated C=C bonds by using heterogeneous catalysts[4] is an important industrial process.[5] Among these processes, the chemoselective hydrogenation of highly unsaturated all-*trans* linear squalene into squalane is highly desirable.[6] Squalane is an exceptional emollient with the distinct ability to penetrate human skin without feeling greasy and without harmful effects.[7] It is widely used in the cosmetic, nutraceutical, and pharmaceutical industries.[8] Recently, squalane has drawn significant attention as a hydrocracking model for crude and microalgae oil.[9]

The hydrogenation of squalene was reported by Tsujimoto[10] in 1916 by using a large amount of a platinum catalyst in diethyl ether under H_2 pressure and was later reported by Chapman[11] in 1917 without any solvent at 190 °C and under atmospheric H_2 pressure. An unsupported Raney-nickel catalyst was also used.[12] The industrial method for the hydrogenation of squalene into squalane involves a nickel-Kieselguhr catalyst under 4 bar (1 bar = 0.1 MPa) of H_2 pressure at 200 °C.[13] However, extensive purification is required to remove most of the nickel that leaches into the squalane product to meet the maximum acceptable levels of toxic nickel compounds. In one report, the reaction over Ni-based platinum catalysts resulted in extensive bond migration and dehydrogenation of squalene.[14] Phytosqualane was obtained[15] from *trans*-β-farnesene.[16] Recently, an impressive advancement was made by Pagliaro and co-workers,[17] who used SiliaCatPd^0, an organosilica catalyst.[18] The reaction proceeded at ambient temperature under atmospheric pressure in ethanol with a Pd loading of 0.2 mmol per gram of squalene. The hydrogenation was performed under milder conditions and required low H_2 pressure and temperature. However, the reaction was nonselective in the absence of a solvent and the catalyst was not prepared in a cost-effective manner.

With the view to develop a natural-clay-based catalytic system, herein, we report the chemoselective hydrogenation of squalene into squalane catalyzed by a Pd-nanoparticles-intercalated clay. Hydrotreatment of squalene was performed with different catalysts under hydrogen pressure without any solvent.

The cations in the interlaminar space of clays are susceptible to ion exchange to give a metal-intercalated system, and the meatal can be reduced to catalytically active zero-valent metal nanoparticles.[19] Barbaro and co-workers[20] reported the preparation of Pd nanoparticles immobilized on solid supports under mild conditions for hydrogenation reactions. A general formula of clay was calculated by collective X-ray fluorescence (XRF) spectrometry and scanning electron microscopy coupled with energy-dispersive X-ray (SEM/EDX) spectroscopy, that is, $K_3Ca_1Ti_{0.6}Al_{12}Si_{40}Fe_6H_xO_y$. The SEM images were recorded at 2 μm magnification, at which a change in the morphology of the clay was observed after metal incorporation (Figure 1 a–d). The amount of metal in the catalyst was determined by inductively coupled plasma coupled with mass spectrometry (ICP-MS). The elemental distributions in the clay and the metal-intercalated clay catalysts were ascertained by EDX spectroscopy (Figure 1, see also the Supporting Information).

The presence of metal nanoparticles in all three catalysts was observed during transmission electron microscopy (TEM) analysis. The majority of the Pd particles were 5–15 nm in size and were highly dispersed in the clay/Pd catalyst with an inter-

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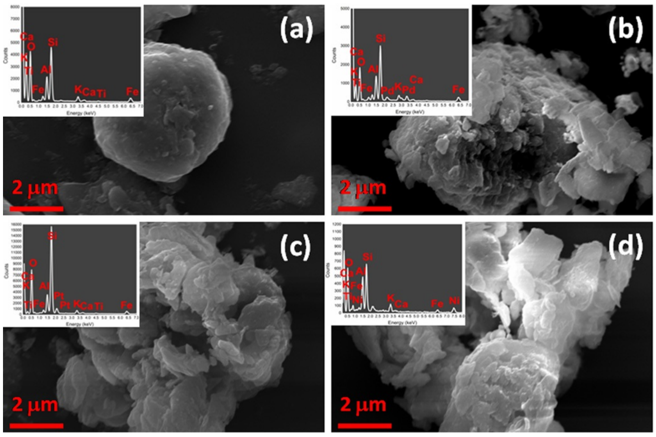

Figure 1. SEM images of a) clay, b) clay/Pd, c) clay/Pt, and d) clay/Ni at 2 µm magnification.

planar distance of 2.13 Å for the Pd(111) facet (Figure 2).[21] The high-resolution (HR) TEM data was used to obtain fast Fourier transform (FFT) patterns of the Pd nanoparticles, and these patterns confirmed the presence of the (111) plane. However, moderate amounts of small-sized metal nanoparticles (5–15 nm) were present in the clay/Pt (2.07 Å interplanar distance) and clay/Ni (2.31 Å interplanar distance) catalysts (see the Supporting Information). EDX mapping of the clay/Pd sample further supported a fine distribution of the Pd nanoparticles in the clay (see the Supporting Information for the clay/Pt and clay/Ni data).

The Brunauer–Emmett–Teller (BET) surface areas, pore-size distributions, and pore volumes of the metal-intercalated clay catalysts were determined. The surface area of the clay/Pd catalyst (62 m^2g^{-1}) was higher than that of the clay/Ni catalyst (37 m^2g^{-1}) and that of the clay/Pt catalyst (28 m^2g^{-1}) (Figure 3).

The X-ray diffraction (XRD) data of the clay and metal-intercalated clay catalysts are shown in Figure 4 (also see the Supporting Information). The XRD pattern of the clay revealed its crystalline nature, and characteristic peaks can be identified for montmorillonite clay with some quartz content[22] (see the Supporting Information). The XRD patterns of the clay/Pd and clay/Pt catalysts have a majority of the (111) plane. However, the intensity of the Ni(111) plane is low, and no clear peak is observed in the case of the clay/Ni sample. As observed earlier, a comparative XRD study revealed metal intercalation into the clay with suppression/disappearance of characteristic montmorillonite peaks (Figure 5). Noteworthy changes were observed for the {001}, {002}, and {003} planes of the montmorillonite clay during metal intercalation, as the intensities of the peaks were significantly reduced.[23] Such an observation indicated metal intercalation, facilitated by surface modification, in the clay during wet impregnation in dilute nitric acid, as determined during the SEM analysis.

Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere (nitrogen flow 19.8 mL$\min^{-1}$ and pressure 3 bar) at a heating rate of 10 °C$\min^{-1}$. The clay/Pd and clay/Pt catalysts were stable up to 900 °C. However, a higher degree of weight loss was observed in clay/Ni (see the Supporting Information). The FTIR spectra were recorded and analyzed (Figure 6).[3b] Bands for the O–H bonds in the clay are observed at $\tilde{\nu}=3622$ and 3415 cm^{-1}, and these can be attributed to the hydroxy groups of the clay and the interlayer water molecules, respectively. A band at $\tilde{\nu}=1636$ cm^{-1} is attributed to O–H bending. For the Si–O bonds, a broad and intense band is detected at $\tilde{\nu}=1036$ cm^{-1}. As expected, the bands are reduced to a single low-intensity band at approximately $\tilde{\nu}=3440$ cm^{-1} after metal intercalation. Other bands also followed similar trends.

Hydrotreatment of squalene (1 g) was performed in the presence of the metal-intercalated clay catalysts without any solvent. The catalysts were pretreated under a hydrogen atmosphere at 300 °C for 3 h. A mixture of squalene and the catalyst was taken in a high-pressure reactor and a nitrogen atmosphere was created. Hydrogen gas was purged to remove the

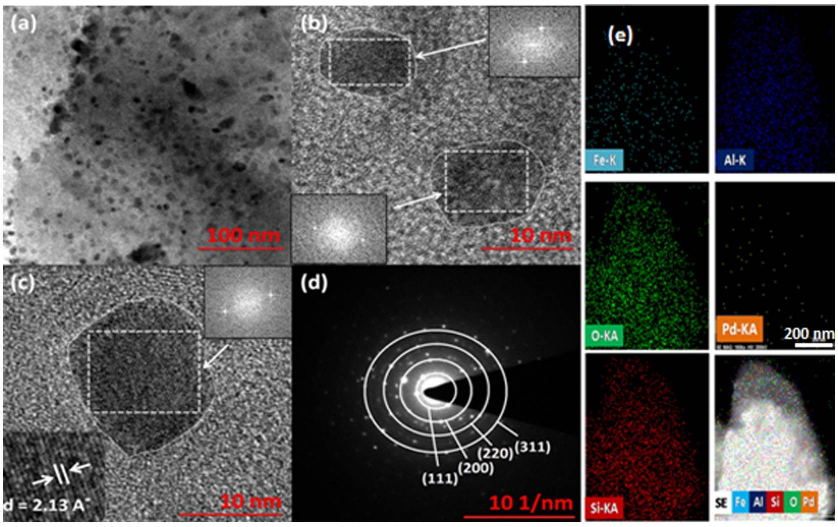

Figure 2. a–d) TEM and HRTEM images and e) EDS mapping of clay/Pd.

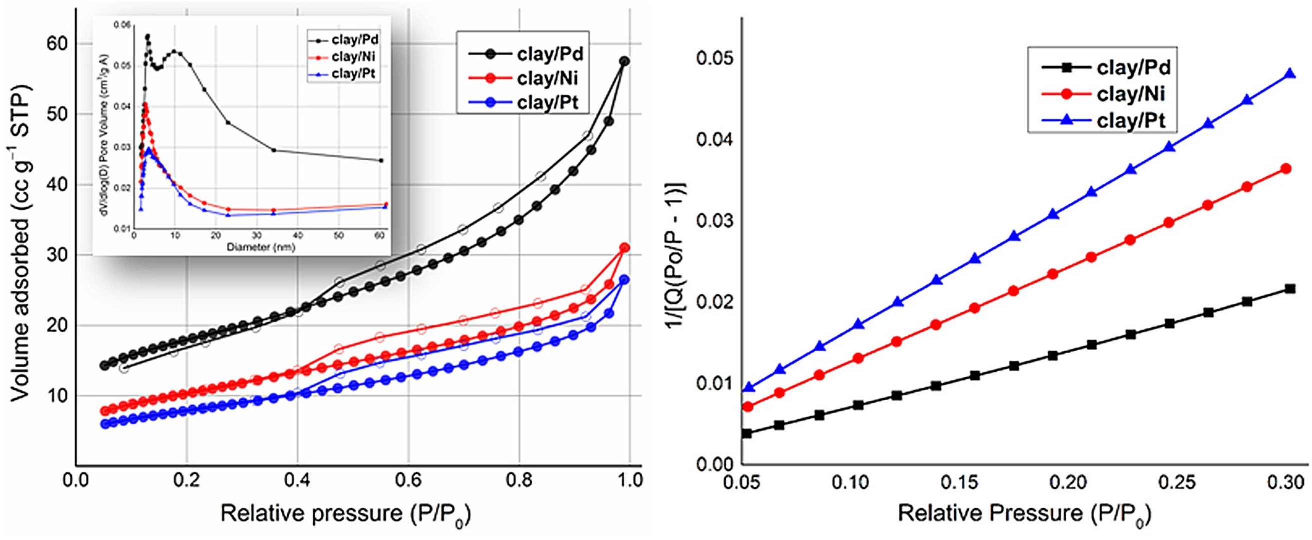

Figure 3. N_2 adsorption/desorption isotherms, BJH pore-size distribution plot, and BET adsorption plot of the catalysts.

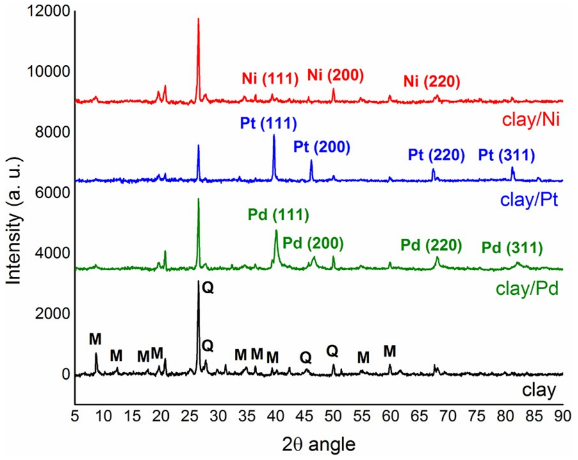

Figure 4. XRD patterns of clay and the metal-intercalated clays.

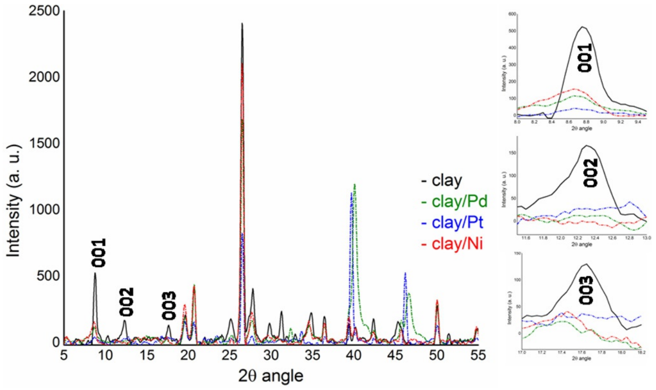

Figure 5. XRD study of clay before and after intercalation.

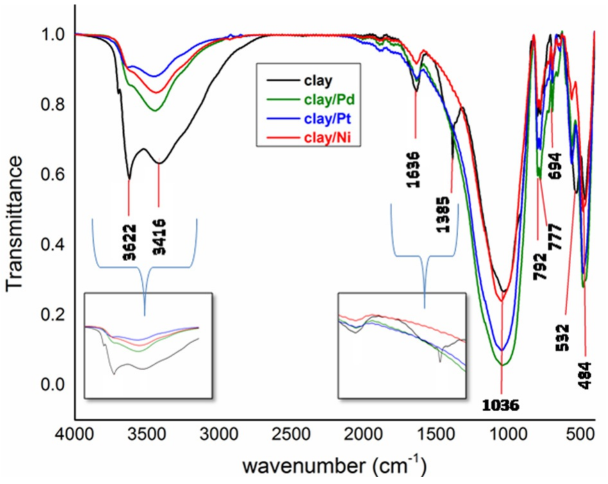

Figure 6. FTIR spectra of clay and the metal-intercalated clays.

nitrogen further, and the desired pressure was attained. The reaction was performed at 200/300 °C and 4–50 bar H_2 pressure (cold) for 6–16 h. The results are shown in Table 1. The reaction temperature was increased from 25 °C at a rate of 5 °C min^{-1} to reach the desired temperature. The overall reaction time is given in Table 1. After hydrotreatment, the reaction mixture was extracted with *n*-heptane (20 mL) and centrifuged. The liquid fraction thus obtained was used for GC and NMR spectroscopy analyses. Among these catalysts, the clay/Pd sample showed the highest reactivity and selectivity with a Pd loading of approximately 0.06 mmol per gram of squalene at 200 °C and 4 bar H_2 pressure (cold) for 6 h (Table 1, entry 6). Complete conversion and selectivity in the hydrogenation were achieved at lower Pd loadings (0.05 and 0.025 mmol per gram of squalene) at higher temperatures and pressures (Table 1, entries 9 and 11).

A comparison was made between the chromatograms of squalene, the product mixtures, and commercial squalane to quantify the conversion and selectivity. Identification and quantification of the products after hydrotreatment of squa-

Table 1. Catalytic hydrogenation of squalene.[a]

Entry	Catalyst[b]	Catalyst [wt %]	T[c] [°C]	H_2 pressure[d] [bar]	t[e] [h]	Conversion/ Selectivity[f] [%]	Yield[g] [%]
1	clay/$Pt_{6.18}$	20	300	50	16	95/50	–
2	clay/$Pd_{6.11}$	20	300	50	16	100/100	98.9
3	clay/$Pd_{6.11}$	10	200	30	16	100/100	99.1
4	clay/$Pd_{6.11}$	10	200	10	16	100/100	99.3
5	clay/$Pd_{6.11}$	10	200	4	10	100/100	99.0
6	clay/$Pd_{6.11}$	10	200	4	6	100/100	99.5
7	clay/$Pd_{6.11}$	10	150	4	6	85/70	–
8	clay/$Pd_{6.11}$	10	150	1	4	40/20	–
9	clay/$Pd_{6.11}$	5	200	6	10	100/100	99.2
10	clay/$Pd_{6.11}$	5	200	4	10	100/92	–
11	clay/$Pd_{6.11}$	2.5	300	10	10	100/100	99.4
12	clay/$Ni_{5.94}$	10	200	4	10	96/92	–
13	clay/$Pt_{6.18}$	10	200	4	6	15/3	–

[a] Catalysts were prepared with a metal loading of approximately 6 wt %. The reactions were performed with squalene (1 g) and catalyst under a H_2 atmosphere. [b] Final wt % metal loading is shown in the subscript. [c] Temperature was gradually increased from 25 °C at a rate of 5 °C min^{-1}. [d] Initial pressure. [e] Overall reaction time. [f] Conversion of squalene/squalane yield evaluated by GC analysis. [g] Yield of isolated squalene.

Table 2. Recyclability of the clay/Pd catalyst in the hydrogenation of squalene.[a]

Entry	Cycle	Conversion/Selectivity [%]
1	0	100/100
2	1	100/100
3	2	100/100
4	3	100/99
5	4	100/98
6	5	98/95

[a] The reactions were performed at 200 °C and 4 bar (cold) H_2 pressure with 10 wt % clay/Pd.

lene were performed by GC (see the Supporting Information). NMR spectra were recorded at 500 MHz in $CDCl_3$. The spectra of the crude material after hydrotreatment were compared with the standard data of squalane (see the Supporting Information).

Leaching and catalyst stability

The crude liquid product was analyzed by ICP-MS. Pd leaching in the isolated crude product was 0.0311 ppm for the reaction with 1 g squalene, clay/Pd [10 wt %, 0.06 $mmol_{Pd}\,g_{squalene}^{-1}$] at 200 °C and 4 bar (cold) H_2 pressure for 6 h (Table 1, entry 6).

Reusability test

The catalytic activity of the clay/Pd catalyst was tested over five cycles (Table 2). After each reaction run, the catalyst was isolated by centrifugation, dried, and reused. The high reactivity of the clay/Pd catalyst can be attributed to more abundant Pd(111) surfaces. Zheng and co-workers[24] studied facet-dependent catalysis by Pd nanocrystals. In this regard, a study of squalene-mixed catalysts was performed to support the higher reactivity of the clay/Pd catalyst further. Thus, an equal amount of squalene was mixed with the catalysts, and the mixtures were left for 2 h under 10 bar H_2 pressure at room temperature. The XRD patterns of the squalene-mixed clay/Pd (Figure 7) do not show the characteristic Pd peaks, which suggests strong absorption of squalene over the Pd surface even at room temperature. No change in the Pt peaks is observed for the clay/Pt catalyst. However, the observations for clay/Ni are not clear, owing to the presence of low-intensity peaks (see the Supporting Information). Analysis of the squalene-mixed catalysts by diffuse reflectance spectroscopy (DRS) was also undertaken, for which the absorption graphs follow an order with respect to the metal (Pd > Ni > Pt; see the Supporting Information). These observations are in agreement with the reactivity order of the catalysts during hydrogenation. After hydrotreatment, the Pd peaks in clay/Pd reappeared without any significant change in their intensities.

However, studies based on the Horiuti–Polanyi mechanism suggest preliminary adsorption of the C=C bonds on the catalyst to form two M–C chemical bonds, which induces carbon hybridization intermediate between sp^2 and sp^3.[25] Delbecq, Sautet, and co-workers[26] studied the surface chemistry of Pd

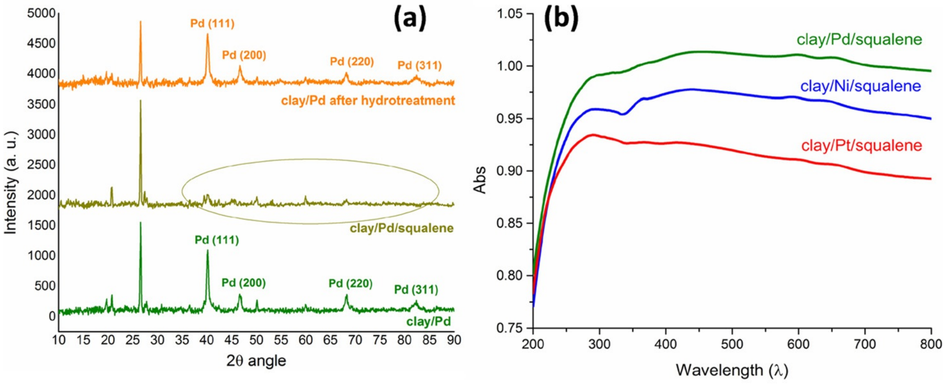

Figure 7. a) XRD patterns for clay/Pd, clay/Pd/squalene, and clay/Pd after the hydrogenation reaction. b) Diffuse reflectance spectra of the squalene-mixed catalysts.

and Pt for hydrogenation reactions and proposed that partial decoordination of unsaturated hydrocarbons from the metal–substrate species may allow hydrogenation with a low-energy barrier on the noninteracting olefinic bond with the catalyst.[26c] However, very low reactivity of the clay/Pt catalyst under the optimized reaction conditions (Table 1, entry 13) suggests the role of metal–substrate coordination for activation of double bonds by adsorption on the metal surface for effective hydrogenation, as supported by XRD analysis of the squalene-mixed clay/Pt. Substrate-dependent reactivity of the double bonds on the Pd(111) and Pt(111) surfaces and their interactions have already been investigated.[26a,27] Further studies will be undertaken to understand the role of the substrate on the adsorption and reactivity of these catalysts.

In conclusion, metal-intercalated clay catalysts with metal (Pt, Pd, and Ni) loadings of approximately 6 wt% were prepared, and their catalytic activity in the hydrogenation of squalene was tested. Simultaneous surface modification of the clay and metal intercalation were observed during wet impregnation in dilute nitric acid, which resulted in a change in the morphology of the clay. Highly faceted Pd(111) intercalated in the clay showed the highest catalytic activity and selectivity in the chemoselective full reduction of squalene under solvent-free conditions. The effectiveness of this catalyst was attributed to the formation of Pd nanoparticles with a dominating (111) plane, which promoted the reaction at a low Pd/squalene ratio ($0.06\ \mathrm{mmol_{Pd}\,g_{squalene}}^{-1}$). Clay/Pd was stable under the optimized reaction conditions, and a very small amount of Pd was leached (0.0311 ppm). The amount of Pd used in the hydrogenation reaction could be reduced further to 0.015 mmol if it was performed at higher temperatures and pressures.

Experimental Section

Materials

Natural montmorillonite clay was procured from a local source in Rajasthan, India.[3b] Squalene (98%), palladium nitrate hydrate (99.9%), and nickel nitrate hexahydrate (98%) were purchased from Alfa Aesar. Chloroplatinic acid hexahydrate was purchased from Sigma–Aldrich. Nitric acid was received from Fisher Scientific.

Preparation of the catalysts

The clay was successively treated with 1 N HNO_3 and 1 N NH_4OH for 12 h each at RT. The resulting clay was washed thoroughly with deionized water and was dried overnight in an oven at 120 °C to be used as the solid support. Metals were incorporated by using the wet impregnation method.

A solution of the metal salt in 3 N HNO_3 (10 mL) was added to the clay (1 g), and the mixture was dried at 120 °C with stirring. The powdered material was calcined at 500 °C for 5 h under a nitrogen atmosphere, which was followed by reduction of the metal at 300 °C for 3 h under a hydrogen atmosphere. This afforded the catalyst with a metal loading of approximately 6 wt%.

General procedure for the hydrogenation of squalene

Catalysts were prehydrogentated at 300 °C for 3 h under a hydrogen atmosphere. The hydrogenation reaction was performed in a Berghof HR-100 high-pressure vessel equipped with a steel container. The catalyst (100 mg) and squalene (1 g) were taken in an air-dried container. A vacuum was created in the container, which was followed by purging the hydrogen gas and the pressure was maintained. The reaction temperature was raised from 25 °C at 5 °C min^{-1} to attain the desired temperature and was maintained for several hours. The mixture was allowed to reach room temperature and was diluted with *n*-heptane (10 mL). The thus-obtained solution was centrifuged, and the liquid fraction was separated. The precipitated catalyst was diluted with *n*-heptane (2 × 10 mL), shaken, and centrifuged to remove most of the product. The thus-obtained liquid fractions were collected and used for analysis. Reaction conversion and selectivity were measured by GC. The formation of squalane was further supported by ^1H NMR spectroscopy.

Acknowledgements

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Keywords: chemoselectivity · clays · hydrogenation · nanoparticles · palladium

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