Montmorillonite Clay Supported Palladium Nanoparticle for the Catalytic Hydrogenation of Furfural to Tetrahydrofurfuryl Alcohol

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Abstract— **Palladium nanoparticles are incorporated into Montmorillonite (MMT) clay after treating MMT with APTES and heterogeneous catalyst (Pd@APTES-MMT) has been synthesized, characterized and evaluated for the hydrogenation of furfural. The highest yield 92 % of tetrahydrofurfuryl alcohol was observed by hydrogenation reaction of furfural using highly reactive Pd@APTES-MMT catalyst in the tetrahydrofuran (THF) solvent. The low Pd@APTES-MMT loading, easy recovery of the THFA and 4 times recyclability of Pd@APTES-MMT catalyst proved the great potential of Pd@APTES-MMT heterogeneous catalyst for the hydrogenation reaction of furfural.**

Keywords— Hydrogenation, Montmorillonite, heterogeneous catalyst, Pd nanoparticles, tetrahydrofurfuryl alcohol (THFA)

I. INTRODUCTION

Nowadays the biomass derived products and bio-refineries which can consume the biomass for valuable products are getting more attention due to the depletion of traditional fossil feedstock [1]. Furfural, an important compound is usually obtained by acidic hydrolysis of corn core or catalytically from the hemicellulose fraction of biomass [2]. Furfural, particularly found in one of the numerous oxygenates bio-oil is particularly undesirable as fuel components. Due to the high reactivity of furfural its catalytic hydrogenation helps to improve boiling range, storage and water solubility of bio-oil [3]. Hydrogenation can produce tetrahydrofurfuryl alcohol which is very useful as an eco-friendly solvent with thermal and chemical stability [4-8]. The desired product (THFA) is generally used for the preparation of 1, 5-pentanediol and an environmentally benign solvents. THFA is used extensively in various industries as a high purity water miscible solvent and as a chemical intermediate. The catalytic liquid phase hydrogenation using noble and non-noble metal catalyst for

the hydrogenation of furfural to furfural alcohol has been reported using. The tetrahydrofurfuryl alcohol is conventionally produced by two step process (1) hydrogenation of furfural over Cu-Cr catalyst and (2) further hydrogenation of furfuryl alcohol over supported noble metal catalyst [9].

Palladium metal based catalysts are widely used as homogeneous catalyst for various organic reactions but suffers from separation after the reaction, recovery, and reuse [10-14]. To overcome this palladium immobilized heterogeneous catalyst is an alternative. Palladium catalyst is generally immobilizes on supports such as activated carbon, alumina, silica or polymers [14-17]. Clay based catalysts are widely used in many industrial processes because of its low cost, abundance, recyclability, and excellent surface and exchange properties [18-21]. However, there are only a few reports on clay supported metal nanoparticles. The most reliable and easy method for preparing these type of materials is by the formation of metal nanoparticles supported on organophilic clay [22-24]. With this approach, clay supported Ag, Au, Pd and Pt metal nanoparticles have already been reported. Other kinds of nanoparticles such as Ni, Rh, Fe, and Sn have also been reported [25-28]. This supported metal nanoparticles show unique catalytic activity and stability as a heterogeneous catalyst [29, 30]. Natural clays are hydrophilic in nature. To convert hydrophobic or organophilic it is treated with organic moieties like cetyltrimethylammonium bromide, tetraoctylammonium bromide and silanes (aminopropyltrimethoxy silane, aminopropyltriethoxy silane) [31-34].

Montmorillonite clay is belonging to the Smectite group of clay which is environmentally benign material. It possesses some unique properties like cation exchange capacity,

intercalation and swelling, etc. which makes it suitable for the catalyst as well as catalysts supports [35-37]. MMT supported metals have been tested as a catalyst for several reactions like oxidation, reduction, trans esterification, and coupling reaction, but to achieve maximum metal exchange and high catalyst loading is still a challenge [38].

In this work we have prepared palladium nanoparticles in the montmorillonite interlayer as a support materials by simple cation exchange and reduction procedure. The as synthesized Pd@APTES-MMT was used for the catalytic hydrogenation of furfural to tetrahydrofurfuryl alcohol (THFA). Cost effectiveness, easy separation of catalyst, low catalyst loading and recyclability are the interesting features of the present work.

I.   MATERIALS AND METHOD

Indian Montmorillonite (MMT) clay was collected from the clay mineral from Kutch, Gujarat (India) and beneficiated as previously reported. The beneficiated clay has a cation exchange capacity (CEC) of 92 meq/100 g. Palladium Chloride (PdCl2) sodium borohydride (NaBH4) and Aminopropyltriethoxysilane (APTES) were purchased from Sigma Aldrich, USA. Furfural was obtained from sigma Aldrich, USA. Tetra hydro furan (THF) and acetone solvents were purchased from TCI Co. Ltd, Japan. All the chemicals and reagents were of high purity and were used without further purification. Maintaining the Integrity of the Specifications

SYNTHESIS OF PD@APTES-MMT CATALYST

in the first stage for the encasement of compatibility and uniform distribution of pd nanoparticles on the montmorillonite surface, the montmorillonite is modified by grafting it with aptes. in order to prepare the modified montmorillonite, 5 g of mmt was taken in 1000 ml round bottom flask with a mixture of 375 ml of methanol and 125 ml of water. 1 g of aptes was added slowly in the mmt suspension under continuous stirring. the stirring continued up to 12 h followed by centrifuging and drying at 70 °c overnight. the palladium nanoparticles could be easily prepared on mmt clay layers by cation exchange with aptes-mmt followed by treatment with palladium chloride in methanol and then the reduction with nabh4 in methanol (scheme 1). the as prepared 7.00 g of aptes-mmt was dispersed in 500 ml of methanol. to this was added pdcl2 (0.280 g) and the mixture was stirred at room temperature for 1 h. the product was filtered, washed with methanol, and treated with nabh4 (280 mg) in methanol (500 ml) at room temperature for 1 h, and dried in air. the palladium contents in synthesized pd@aptes-mmt catalyst were measured both by icp and sem-edx analysis.

HYDROGENATION OF FURFURAL BY PD@APTES-MMT CATALYST

12.07 mmol of furfural was taken in 100 ml of high pressure reactor (Amar reactor) with 40 ml of THF as a solvent and 100 mg of Pd@APTES-MMT catalyst. The reaction mixture was stirred at 150 °C and 30 bar pressure of H2 for 3 h. To know the effect of different parameters, the reaction was

carried out at a different temperature, pressure and time. To check the recyclability of catalyst, the catalyst was separated after the reaction, washed with acetone, dried and used up to 4 cycles. On completion of the reaction, the product was separated from THF solvent by rotary evaporator and then analyzed by GC-MS to identify the products conversion of reactants and selectivity of the products.

CHARACTERIZATION TECHNIQUES

X-ray diffraction (XRD) was carried out in a Rigaku - Miniflex II system using Cu Kα radiation (λ= 1.5406 Å) with a step size of 0.04˚ and a step time of 2 seconds. FT-IR absorption spectra of the samples were recorded on a Perkin-Elmer FT-IR spectrometer (FT-1730) by mixing the sample with KBr and spectra were recorded with a nominal resolution of 4 cm-1. Thermo gravimetric analyses (TGA) were performed on Mettler TGA/SDTA 851e and thermal experiments were carried out at a nitrogen flow rate of 50 ml min-1 at a heating rate of 10 °C/ min. Elemental analysis and Pd concentrations were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Perkin-Elmer, OES, and optical 2000DV). Ammonia-TPD experiment was carried out using "Autochem II 2920" instrument. Morphology of the material was observed by Field Emission Scanning Electron Microscope (FESEM - JEOL JSM 7100M, accelerating voltage of 15 kV and a working distance of a 17 mm, with magnification values up to 100,000x). X-ray Photoelectron spectroscopy was carried out using XPS, JEOL, Japan.

III. RESULTS AND DISCUSSION
CHARACTERIZATION OF SUPPORT MATERIALS (APTES-MMT) AND CATALYST (PD@APTES-MMT)
X-RAY DIFFRACTION

The PXRD analysis of parent Montmorillonite shows a basal reflection peak at a 2θ value of 3.44º corresponding to the d-spacing value of 25.64 Å. After the immobilization of Pd nanoparticles in Montmorillonite layers, the intensity of the basal reflection is decreased and the d-spacing is increased (25.90 Å) which confirmed the intercalation of Pd nanoparticles. As shown in figure 1(b) there are five distinct reflections in the diffractogram at 40.02° (111), 46.49° (200), 68.05° (220), 81.74° (311), 86.24° (222) [39]. These characteristic reflections can be indexed to the face centered cubic (fcc) structure of Palladium (JCPDS: 87-064, space group: Fm3m (225)) [40]. The high intensity of reflection peak at (111) in comparison with the other four, may indicate the preferred growth direction of the nano crystal.
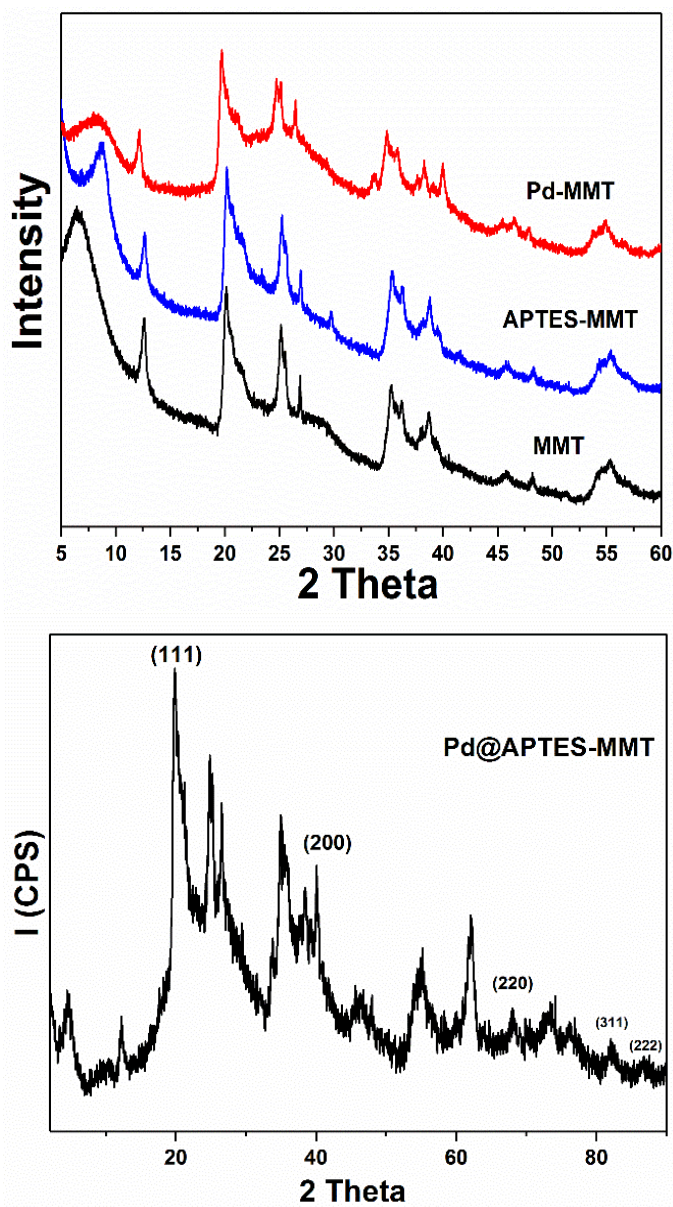
Figure 2. FT-IR spectra (b) of MMT, APTES-MMT, and Pd@APTES-MMT

Figure 1(a). PXRD pattern of MMT, APTES-MMT, Pd-MMT (b) Pd@APTES-MMT

NH3 TPD

The presence of the acid sites on the catalyst (Pd@APTES-MMT) was qualitatively evaluated by thermal desorption of ammonia, being a strong base, reacts even with extremely weak acid sites, which therefore makes NH3-TPD a useful techniques for the evaluation of the acid sites on a surface. The acid strength of Pd@APTES-MMT corresponded to a higher desorption temperature of ammonia adsorbed on acid sites. The NH3-TPD spectra of Pd@APTES-MMT, exhibits weak, medium and strong acid sites which are included in the region at 100-300 ℃ and 350-500 ℃. (Figure 3)

Figure 3. NH3-TPD profile of Pd@APTES-MMT, indicating the different acid sites on a surface

FT-IR ANALYSIS

The FT-IR spectra of MMT APTES-MMT and Pd@APTES-MMT are shown in figure 2. The band at 3698 cm-1 and 3619 cm-1 are due to the -OH stretching vibration of Al-OH and Si-OH of MMT structure. The overlaid absorption peak at 1647 cm-1 is due to -OH bending mode of the adsorbed water. The characteristic peak at 1035 cm-1 is due to the Si-O stretching mode of MMT. In addition to the CH2 group, the peaks at 1407 cm-1 are due to the H-C-H stretching vibration. The IR absorption band of the MMT and APTES-MMT in lower frequency region were largely comparable indicating that clay mineral matrix has not changed upon exchange of the interlayer ions of silylating agents and palladium.
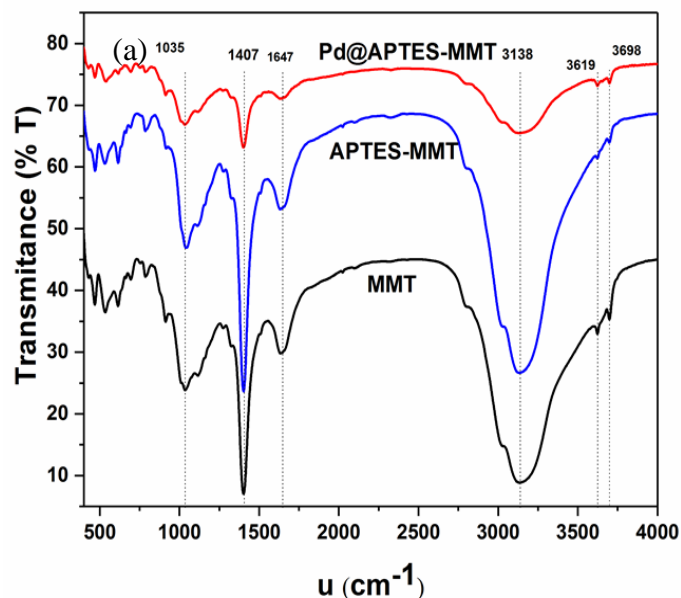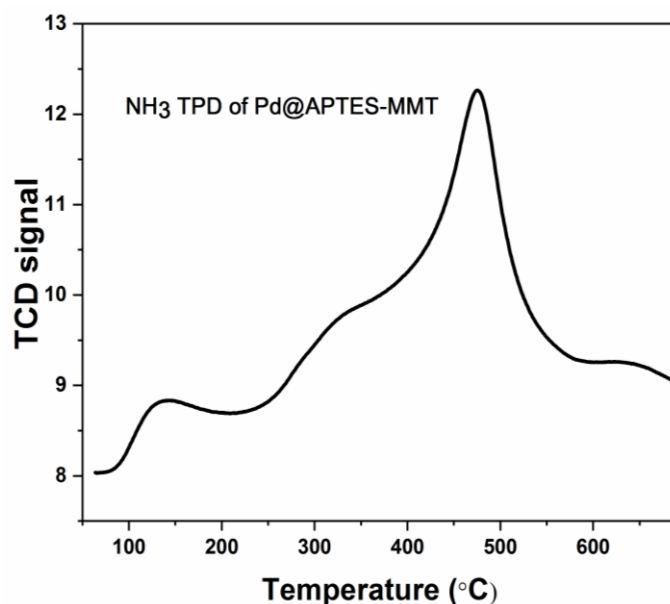
FE-SEM-EDX AND ICP-OES ANALYSIS

The FE-SEM and FE-SEM-EDX analysis also confirmed the formation of Pd nanoparticles on the layer of the montmorillonite. , along with other elements of clay. Likewise, the elemental mapping also clearly indicates the presence and distribution of Pd element and other elements of MMT in the support (Figure 4. a,b,c,d). The FE-SEM-EDX data shows 1.2 % loading of Palladium in Pd@APTES-MMT catalyst and the ICP-OES analysis shows 2.2 % loading of Palladium (Figure 4B).
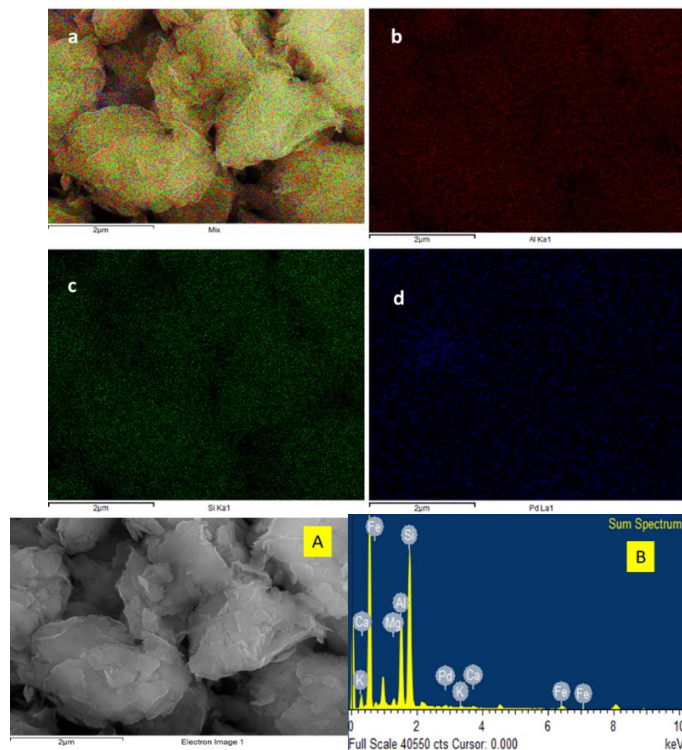

Figure 4. (1) FE-SEM image (A) and FE-SEM EDX of Pd@APTES-MMT (2) mapping of the elemental species on the surface of the Pd@APTES –MMT (a) Mix metal (Si, Al, Pd), (b) Al map, (c) Si map and (d) Pd map

TEM

The TEM images of Pd@APTES-MMT (Figure 5) catalyst indicate that the most Pd nanoparticles are well distributed on the surface of the montmorillonite layers and the wide range of particle size distribution from 5 nm to 70 nm.
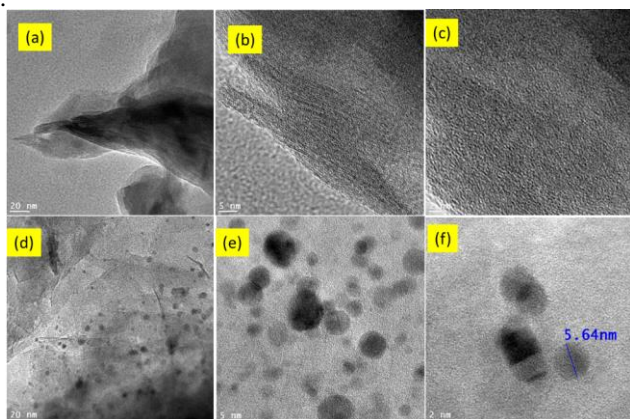

Figure 5. TEM images of APTES-MMT (a, b, c) and Pd@APTES-MMT ((d, e, f)

XPS

In order to confirm the presence of Pd nanoparticles in montmorillonite layers, the XPS studies were carried out. Figure 6 shows the XPS spectra for Pd@APTES-MMT powder. The XPS spectra of Pd metal shows that the Pd XPS spectrum was decomposed into four component. Two peaks detected at 335.6 eV and 340.7 eV are attributed to the Pd(0) species. [41-43]. This results indicate the reduction of Pd(II) to Pd(0) is correlate with the XRD analysis. Considering that XRD and XPS both showed the satisfactory reduction of Pd(II) to Pd(0), the amount of oxidized atom should be small and the oxidized atoms exist on the surface of MMT layers.
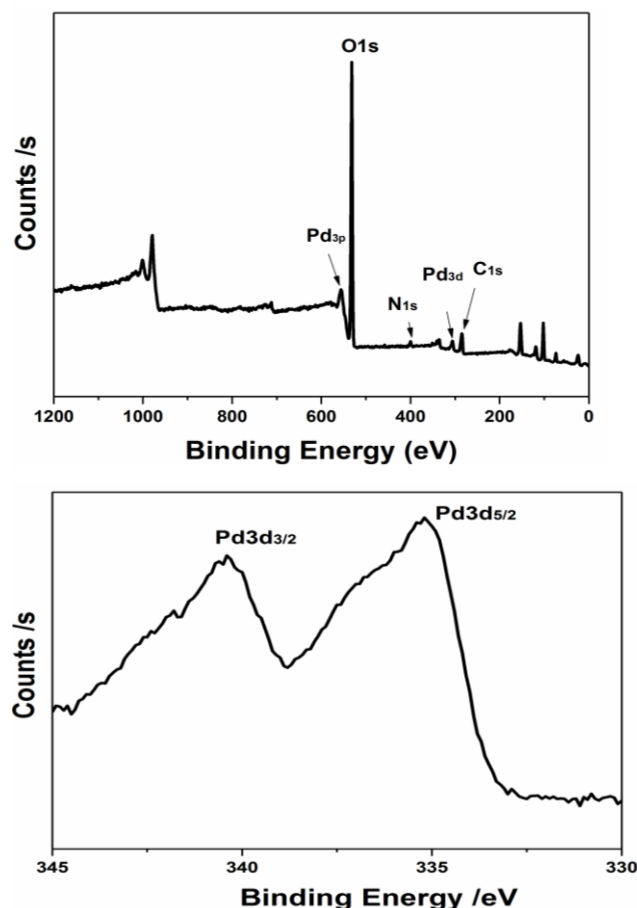

Figure 6. (a) XPS survey spectra obtained for Pd@APTES-MMT and (b) XPS spectra for Pd nanoparticles.

CATALYTIC PERFORMANCE OF PD@APTES-MMT

The catalytic activity of the Pd@APTES-MMT catalyst was evaluated by the catalytic hydrogenation of the furfural in a THF reaction medium. The furfural can be more easily hydrogenated to furfuryl alcohol (FA) because C-O group of furfural can be more easily hydrogenated than the C=C bond in furan ring. Hydrogenation of furfuryl alcohol (FA) gives tetrahydrofurfuryl alcohol (THFA). Nearly 100% conversion of furfural was achieved in the first 3 h, and selectivity of THFA was up to 71 %. A full transformation of FA to THFA could be achieved by extending the reaction time up to 6 h. The described results indicates that the catalytic system Pd@APTES-MMT could be used for the generation of THFA by hydrogenation of furfural.

EFFECT OF HYDROGEN (H2) PRESSURE ON FURFURAL HYDROGENATION

Figure 7 shows the enfluence of H2 pressure in the catalytic conversion of furfural to THFA. It is clearly observed that with the increase of H2 gas pressure in reactor from 1 MPa to 4 MPa was significantly increase the hydrogenation rate for furfural to THFA. . Furfural was completely hydrogenated and converted into THFA at 4 MPa H2 pressure and the 92 % selectivity of THFA was achieved simultaneously under the investigated reaction condition. After 4 Mpa H2 preesure there is no improvement in hydrogenation was observed which indicate that the H2 pressure has no dramatic influence on the catalytic hydrogenation of furfural under the present catalytic reaction system.
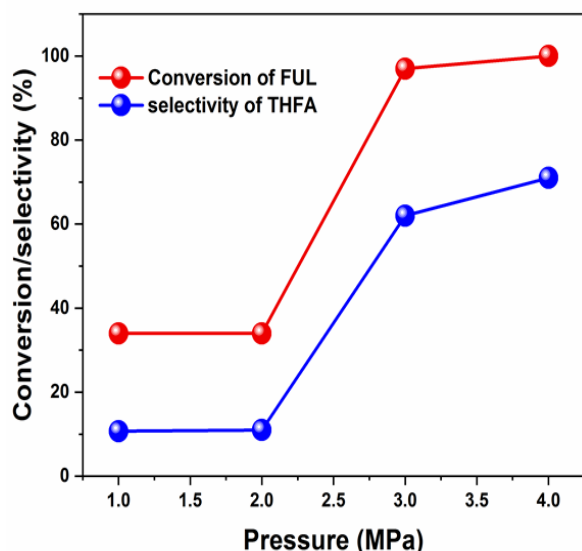

Figure. 7 Effect of H2 gas pressure on the THFA generation by hydrogenation of furfural. Reaction condition: Furfural (12 mmol), catalyst (0. 1 g), solvent (40 ml), 160 °C, 5 h

EFFECT OF REACTION TEMPERATURE ON FURFURAL HYDROGENATION

The temperature dependence of the THFA generation was carried out from 120 °C to 160 °C temperature (Figure 8). The hydrogenation of furfural and the THFA generation could be increased by increasing temperature up to 160 °C. Figure 8 shows that the selectivity of desired product (THFA) was increased when the reaction temperature was increased gradually. The results of temperature variation indicate that the temperature had a significant effect on the hydrogenation of furfural to generation of THFA. The high reaction temperature would increase the hydrogenation of furfural. The target product THFA could be obtained with high selectivity at 160 °C with 0.1 g catalyst, 5 h reaction time over the Pd@APTES-MMT catalyst.
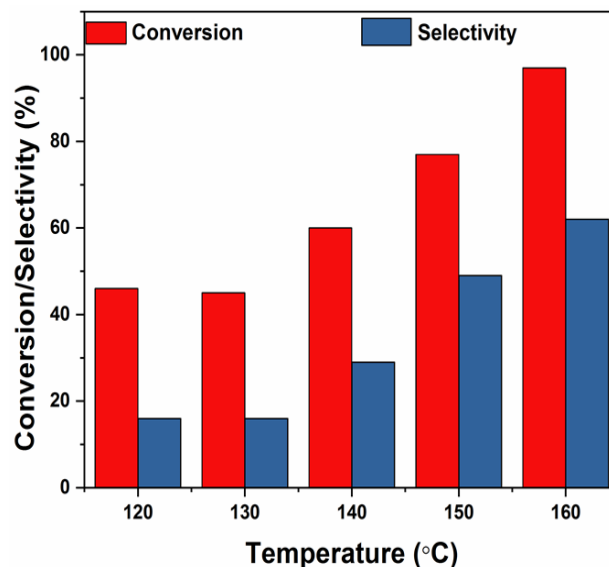

Figure 8. Influence of temperature on conversion of furfural and selectivity of THFA

EFFECT OF REACTION TIME ON FURFURAL HYDROGENATION

The effect of reaction time on catalytic activity and product distribution over Pd@APTES-MMT catalyst have been investigated at 160 °C and 40 bar of hydrogen pressure. The total conversion of furfural and THFA selectivity was increased with reaction time (Figure 9). As the reaction time increases furfural conversion reached 100 % at 3 h and THFA selectivity reached to 92 % at 5 h (Table S1). The results indicate that time has no dramatic effect beyond 3 h on the THFA generation.
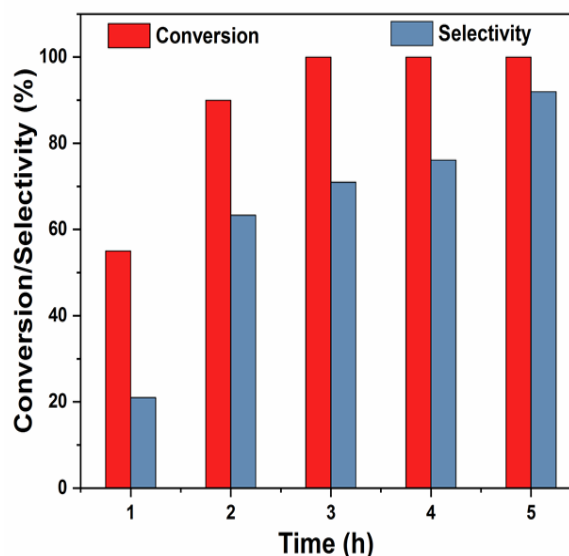

Figure 9. Influence of time on hydrogenation of furfural. Reaction conditions: Furfural (12 mmol), catalyst (0. 1 g), solvent (40 ml), 40 bar H_2, 160 °C

EFFECT OF CATALYST AMOUNT ON FURFURAL HYDROGENATION

To show the effect of Pd@APTES-MMT catalyst amount, catalyst loading was varied from 50 mg to 200 mg at 160 °C and 40 bar H2 pressure with a reaction time of 3 h (Figure 10). The conversion of furfural reached 100% using 100 mg of the catalyst with 70 % selectivity of THFA. The selectivity of THFA increased with an increasing amount of catalyst up to 200 mg. Results indicate that the selectivity of THFA can be increased with higher catalyst amount as shown in table S1.
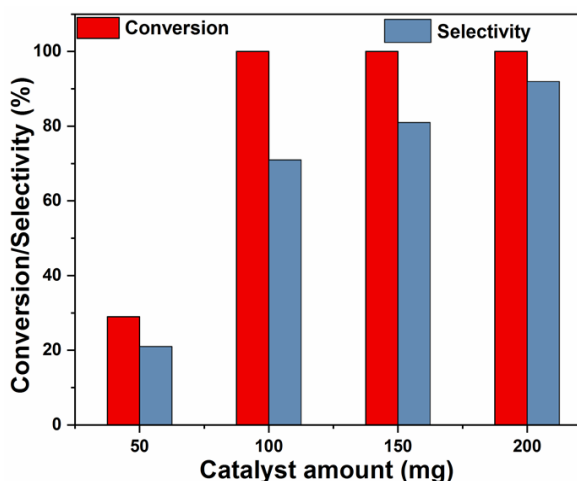

Figure 10. Influence of catalyst amount on hydrogenation of furfural and generation of THFA. Reaction conditions: Furfural (12 mmol), solvent (40 ml), 40 bar H_2, 160 °C, 5 h

RECYCLABILITY OF PD@APTES-MMT

The recyclability of the catalyst (Pd@APTES-MMT) was showed under the identical reaction parameters to evaluate the catalyst stability with continuous use. After each reaction the Pd@APTES-MMT was separated and washed thoroughly with acetone. The conversion rate of furfural slightly decreased after the first cycle. It indicates the slight decay in the catalyst activity. It should be noted that the activity of the Pd@APTES-MMT catalyst became stable during the next three cycle experiments (Figure 11).
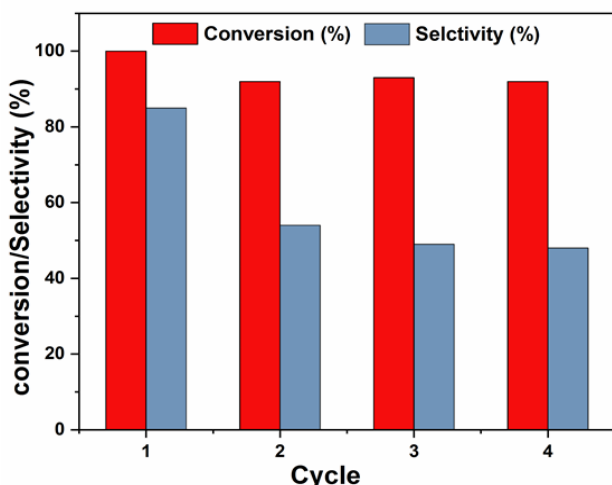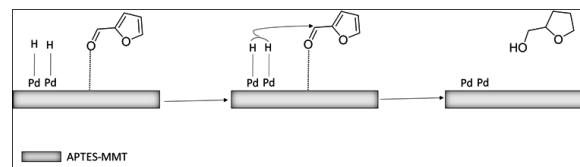

Figure. 11 Recyclability of Pd@APTES-MMT catalyst for hydrogenation of furfural. Reaction conditions: Furfural (12.07 mmol), catalyst (0. 1 g), solvent (40 ml), 40 bar H_2, 160 °C, 5 h

Scheme 1. Possible reaction pathways for the catalytic hydrogenation of furfural over Pd@APTES-MMT catalyst

IV. CONCLUSION

Palladium nanoparticles were successfully incorporated into APTES modified montmorillonite structure by direct cation exchange approach and reduction procedure respectively. The silyalation of montmorillonite make it more suitable for highly dispersed and uniform distribution of palladium nanoparticles into the support. Pd@APTES-MMT has been demonstrated as the efficient and reusable heterogeneous catalyst for the hydrogenation of furfural (FR) to tetrahydrofurfuryl alcohol (THFA). The catalyst shows good catalytic performance. The yield of THFA reach 92 % at 160 ℃ temperature, 40 bar hydrogen pressure and 5 h of reaction time. The Pd@APTES-MMT catalyst is recycled and reused up to four cycles for the hydrogenation of furfural.

V. ACKNOWLEDGMENT

VI. REFERENCES

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