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Hydrogenation of cyclohexene in aqueous solvent mixture over a Sustainable Recyclable Catalyst Comprising Palladium and Monolacunary Silicotungstate Anchored to MCM-41

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Abstract: An efficient, highly stable and ligand free catalyst comprising of Pd and monolacunary silicotungstate anchored to MCM-41 was synthesized and characterized by various techniques. The synthesized catalyst was used for hydrogenation reaction of cyclohexene as model substrate and various reaction parameters were studied in order to optimize the parameters for maximum conversion, 95% under mild conditions. The catalyst was regenerated by simply washing with methanol and reused up to three cycles without significant loss in the activity. The viability of the catalyst was evaluated for the different alkenes and ketones and in all cases the conversion was found to be in the range of 92-99%. It was also found that the sustainability arises from SiW₁₁, which binds the palladium very strongly and thus does not allow its leaching into the reaction mixture.

Introduction

Catalytic hydrogenation using heterogeneous transition-metal catalysts, especially supported palladium, is industrially very important and widely used over several years.¹⁻³ Supported Pd catalysts can be synthesized by grafting Pd on solid supports, viz., carbon,⁴⁻⁵ zeolites,⁶⁻⁷ mesoporous silica⁸⁻⁹ and metal oxides^{7,10} which comprises the ligand-free systems owing to economic synthesis and high stability in air.¹¹⁻¹²

However, in all cases, the limited accomplishment of anchored Pd catalysts is mainly responsible to the in situ formation of Pd (0) from Pd (II) during the reaction. It is known that the Pd (0) species are more prone to leaching into the reaction mixture than the Pd (II).¹³ The leaching and redeposition of Pd (0) species on the surface result in the agglomeration of Pd (0) species into large Pd nanoparticles or Pd black, causing a loss of metal dispersion and surface area.¹⁴ Hence, the development of a heterogeneous catalyst for aqueous phase hydrogenation of organic compound, free of Pd leaching and agglomeration, is still a challenging task. The applications of polyoxometalates as (POMs) heterogeneous catalyst is becoming an important topic of research over the past decade and most of the studies have been centred on the acidcatalysed or oxidation transformations. At the same time, the use of POMs as catalysts in reductive transformations has been less explored and few reports do exist which include the use of metal clusters stabilized POMs for the hydrogenation reaction. In 2002,

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Neumann has synthesized palladium R. substituted (K₅PdPW₁₁O₃₉/C) polyoxometalate as pre-catalyst for hydrogenation of arene, aldehyde, ketone and vicinal ketone.¹⁵ In 2012, K. M. Parida et al. have reported the synthesis of palladium based lacunary phosphotungstate supported mesoporous silica (50LPdPW₁₁O₃₉/MCM-41) for hydrogenation of p-nitrophenol to paminophenol at room temperature.16 In 2013, Kortz and coworkers have prepared Pd nanoclusters stabilized by tetrabutylammonim salts of phosphotungstates with the wellknown Keggin $[\alpha$ -PW₁₂O₄₀]³⁻, Wells-Dawsons $[P_2W_{18}O_{62}]^{6-}$ and their lacunary derivatives $[\alpha - PW_{11}O_{39}]^{7-}$ and $[P_2W_{15}O_{56}]^{12-}$ and utilized them for the hydrogenation of 1-Hexene at 30 °C under 5 bar continuous H₂ pressure.¹⁷

A literature survey shows that neither of any reports describe hydrogenation of cyclohexene even though it is one of the important organic transformations. Cyclohexane has immense importants for its uses as solvent and as an intermediate for the synthesis of cyclohexanol and cyclohexanone which are the chemical commodities to produce adipic acid, caprolactam, nylon 6 and nylon 6,6. It also shows that all reported catalysts are based on lacunary phosphotungstate, no studies were carried out on lacunary silicotungstate even though it is more stable due to its anionic nature.¹⁸

In the present work, an attempt has been made to design a new heterogeneous catalyst comprising Pd and monolacunary silicotungstate (SiW₁₁) anchored to MCM-41. The catalyst, Pd-SiW₁₁/MCM-41, was synthesized by anchoring SiW₁₁ onto MCM-41 support followed by exchange of the counter cations of SiW₁₁ with Pd(II). The Pd-SiW₁₁/MCM-41 was characterized by various physicochemical techniques and its catalytic activity for hydrogenation of cyclohexene was evaluated in aqueous phase by varying different reaction parameters. Recovery and recycling of the catalyst was also evaluated under optimized conditions. The selectivity of the catalyst was further evaluated for different substrates. In order to see the role of the SiW₁₁, Pd was also supported onto MCM-41 (Pd/MCM-41) and its catalytic activity was evaluated under optimized conditions.

Results and Discussion

Catalyst characterization

The EDX elemental analysis shows that, in the case of Pd/MCM-41, the % of Pd found was 6.25 wt%, while for Pd-SiW₁₁/MCM-41 it was 3.26 wt%. In the case of Pd/MCM-41, all the available protons on the surface of MCM-41 take part in the exchange with Pd, as a result the % of Pd was high. In the case of Pd-SiW₁₁/MCM-41, if the protons of SiW₁₁ and of MCM-41 are expected to be exchanged with Pd, the % of Pd would be

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significantly high. But on the contrary, Pd was found to be only 3.26 wt%. This indicates the replacement of protons of SiW₁₁ by Pd in Pd-SiW₁₁/MCM-41. EDX elemental mapping of the catalyst is shown in Figure 1.



Figure 1. EDX elemental mapping of Pd-SiW₁₁/MCM-41.



Figure 2. TGA curve of (a) SiW11/MCM-41 and (b) Pd-SiW11/MCM-41.

The TGA curves of SiW₁₁/MCM-41 and Pd-SiW₁₁/MCM-41 are shown in Figure 2. The TGA of SiW₁₁/MCM-41 showed weight loss of 6% up to 180 °C attributed to the removal of adsorbed water molecules followed by 2% weight loss up to 250 °C was observed because of loss of water of crystallization. No notable weight loss was observed after this up to 500 °C. The Pd-SiW₁₁/MCM-41 showed initial weight loss of 1.6% up to 130 °C due to the loss of adsorbed water. After this, gradual weight loss observed up to 300 °C due to the removal of water of crystallization of SiW₁₁ as well as removal of water via condensation of silanol groups of the MCM-41. The gradual weight loss after 320 °C suggests that the catalyst is stable up to 320 °C.

The textural properties such as surface area and pore diameter are presented in Table 1. The incorporation of SiW_{11} into the channels of the support is apparent here, as it leads to 19 % reduction in surface area as well as 17 % reduction in pore diameter. This gives first indication of chemical interaction between SiW₁₁ and MCM-41. Further, after exchange with Pd the surface area as well as pore diameter decreases significantly. This confirms the presence of Pd inside the channels of MCM-41. The nitrogen sorption isotherms of support and catalyst are shown in figure 3. All the isotherms show type IV behavior and exhibits H1 hysteresis loop which is a characteristic of mesoporous solids. ¹⁹ The adsorption branch of each isotherm displayed a sharp inflection, which suggests a typical capillary condensation inside the uniform pores. The position of the inflection point is obviously related to the diameter of the mesopore, and the sharpness of this step designates the uniformity of the mesopore size distribution. In addition, narrow pore size distribution was observed for the samples indicating long range order over large scales. The decrease in pore diameter in of Pd-SiW₁₁/MCM-41 is due to the presence of Pd inside the channels of the support. Further, the interaction of Pd with SiW₁₁ was confirmed by FT-IR analysis.

Table 1. Surface area and pore diameter of support and the catalyst.			
Sample	Surface area (m²/g)	Pore diameter (nm)	
MCM-41	659	4.79	
SiW ₁₁ /MCM-41	536	3.96	
Pd-SiW ₁₁ /MCM-41	452	3.34	



Figure 3. Nitrogen adsorption isotherms of MCM-41, SiW_11/MCM-41 and Pd-SiW_11/MCM-41.

The FT-IR spectra of MCM-41, SiW₁₁/MCM-41and Pd-SiW₁₁/MCM-41 are presented in figure 4. FT-IR of MCM-41 (Figure 4a) shows a broad band around 1000-1300 cm⁻¹, corresponding to the asymmetric stretching of Si-O-Si. The bands at 460 cm⁻¹ and 808 cm⁻¹ are attributed to the bending vibration of the Si-O-Si bonds and free silica. The band at 966 cm⁻¹ corresponds to symmetric stretching vibration of Si-OH. The FT-IR of SiW₁₁/MCM-41 (Figure 4b) shows characteristic bands of SiW₁₁ at 960 cm⁻¹ (W=O_d), 900 cm⁻¹ (Si-O_a) and 795 cm⁻¹ (W-O_b-W) in good agreement with the reported one. ²⁰ The FT-IR of Pd-

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SiW₁₁/MCM-41 shows the characteristic bands of SiW₁₁ at 970 cm⁻¹ (W=O_d), 897 cm⁻¹ (Si-O_a) and 790 cm⁻¹ (W-O_b-W) (Figure 4c). The presence of these bands confirms that lacunary SiW₁₁ remains intact even after exchange with the Pd. Further, the observed shift in the bands as compared to SiW₁₁/MCM-41 confirms the interaction of Pd with SiW₁₁.



Figure 4. FT-IR spectra of (a) MCM-41, (b) SiW11/MCM-41 and (c) Pd-SiW11/MCM-41.



Figure 5. XRD patterns of (a) MCM-41 and (b) Pd-SiW₁₁/MCM-41.

XRD patterns of MCM-41 and Pd-SiW₁₁/MCM-41 is shown in figure 5. The XRD pattern of the MCM-41 shows a sharp reflection around 20=2° corresponding to (100) plane indicating well-ordered hexagonal structure of MCM-41. The comparison of the XRD pattern of MCM-41 and Pd-SiW₁₁/MCM-41 reveals that the mesoporous structure of MCM-41 is rather intact even after

exchange with the Pd. Further the absence of characteristic reflections of SiW_{11} as well as Pd in the catalyst indicates that Pd-SiW₁₁ species are highly dispersed inside the hexagonal channels of MCM-41.



Figure 6. SEM images of a) MCM-41 and b) Pd-SiW₁₁/MCM-41.



Figure 7. TEM images of Pd-SiW $_{11}/MCM\text{-}41$ at (a) 100 nm and (b) 200 nm resolution.

Figure 6 shows the SEM images of MCM-41 and Pd-SiW₁₁/MCM-41. The surface morphology of the catalyst is almost identical to that of MCM-41. No change in surface morphology of the catalyst and no separate crystallites of bulk phase of Pd or SiW₁₁ were

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found in the catalyst indicating well dispersion of the species inside the channels of the support.

TEM images (Fiagure 7a and 7b) of Pd-SiW₁₁/MCM-41 clearly shows porous channels spread uniformly through entire surface as well as presence of Pd(0). Absebsce of separate crystallites of Pd-SiW₁₁ indicates well dispersion of Pd-SiW₁₁ on the surface of the catalyst. Further the presence of Pd (0) is confirmed by XPS.



Figure 8. XPS spectrum of Pd-SiW₁₁/MCM-41

The XPS of Pd-SiW₁₁/MCM-41 is displayed in Figure 8. A high intense peak at 532 eV $(3p_{3/2})$ with broad peak at 558 eV $(3p_{1/2})$ are in good agreement with the available reports ²¹ and confirms the presence of Pd(0).

Catalytic activity



Scheme 1. Reaction scheme for cyclohexene hydrogenation.

The catalytic activity of Pd-SiW₁₁/MCM-41 was evaluated for hydrogenation of cyclohexene (Scheme 1) and effect of various reaction parameters like effect of solvent, catalyst concentration, reaction temperature and hydrogen pressure were studied in order to obtain maximum conversion. In all the experiments, cyclohexane was the only product observed.

Effect of solvent on the hydrogenation of cyclohexene was evaluated and results are presented in Figure 9. While as low as ~15% conversion was observed when water was used as solvent, the use of acetonitrile/water mixture resulted in ~4.5-fold increase in the conversion of cyclohexene in 2 h of reaction time mainly due to solubility of cyclohexene in the reaction medium. When, methanol/water was used as solvent, 95% conversion of cyclohexene was achieved in 2 h resulting in ~1.4-fold increase in

the conversion as compared to acetonitrile/water mixture. This may be due to the increased competitive adsorption of coordinating solvent on the Pd surface.



Figure 9. Effect of solvent on hydrogenation of cyclohexene. Reaction conditions: catalyst amount= 100 mg, temperature= $80 \text{ }^{\circ}\text{C}$, $p(H_2) = 10$ bar.

Table 2. Effect of catalyst concentration on cyclohexene conversion.				
Catalyst amount	Concentration of Pd, mmol×10 ⁻³	% Conversion		
25	7.65	22		
50	15.31	73		
100	30.63	95		

Reaction conditions: Cyclohexene= 10 mmol, $p(H_2)$ = 10 bar, time= 2 h, temperature= 80 °C, water: methanol= 30:20 mL.

The effect of catalyst concentration on hydrogenation of cyclohexene was studied by taking 25 mg to 100 mg of the catalyst containing 7 mg to 31 mg of Pd (Table 2). The results showed that with increase in the concentration of Pd, the conversion of cyclohexene was increased. The higher catalyst concentration would mean a higher number of active sites for adsorption of the substrate and hence higher conversion. This suggests that Pd functions as active site for the hydrogenation reaction. The maximum cyclohexene conversion of 95% was achieved by using 100 mg of the catalyst.

The influence of hydrogen pressure was studied for hydrogenation of cyclohexene as shown in figure 10. The conversion was increased linearly with increasing H₂ pressure from 2 to 12 bar and optimum conversion of 95 % was achieved at H₂ pressure of 10 bar, while it was about 29% at 2 bar, suggesting the reaction rate depends on the concentration of hydrogen.

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Figure 10. Effect of hydrogen pressure on cyclohexene conversion. Reaction conditions: cyclohexene= 10 mmol, time= 2 h, temperature= 80 °C, water: methanol= 30: 20 mL.



Figure 11. Effect of temperature on cyclohexene conversion. Reaction conditions: Cyclohexene= 10 mmol, $p(H_2) = 10$ bar, temperature= 80 °C, water: methanol= 30:20 mL.

Figure 11 shows the influence of reaction temperature on the catalytic hydrogenation of cyclohexene. It was found that with increase in the reaction temperature, the conversion of cyclohexene was increased. At 80 °C, maximum conversion was achieved.

The optimized conditions for maximum conversion of cyclohexene over Pd-SiW₁₁/MCM-41 are, catalyst amount: 100 mg, reaction time: 2 h, $p(H_2)$: 10 bar, temperature: 80 °C, water/ methanol= 30/20 mL.

Control experiments, Heterogeneity and Recycling test

The hydrogenation of cyclohexene was carried out using SiW_{11}/MCM -41, PdCl₂, Pd /MCM-41 and Pd-SiW_{11}/MCM-41 under optimized conditions. It can be seen from Table 3 that SiW_{11}/MCM -41 was inactive towards the hydrogenation of cyclohexene, indicating that the catalytic activity is due to only Pd. To confirm, the same reaction was carried out by taking an

equivalent active amount of Pd in form of $PdCl_2$ in homogeneous medium (89 % conversion) as well as Pd/MCM-41 and Pd-SiW₁₁/MCM-41 in heterogeneous medium (98 % and 95 % conversion respectively) was obtained. The obtained results show that we are succeeded in heterogenizing Pd onto SiW₁₁/MCM-41 without any loss in the catalytic activity.

Table 3. Control experiments for hydrogenation of cyclohexene.				
Material	% Conversion	TOF, h ⁻¹		
SiW ₁₁ /MCM-41 ^[a]	4	-		
PdCl ₂ ^[b]	89	158		
Pd/MCM-41 ^[a]	98/75/52	83		
Pd-SiW ₁₁ /MCM-41 ^[a]	95/92/89	155		

Reaction conditions: Cyclohexene= 10 mmol, catalyst amount= ${}^{[a]}100$ mg, ${}^{[b]}3$ mg, $p(H_2) = 10$ bar, time= 2 h, temperature= 80 °C, water: methanol= 30:20 mL.

Heterogeneity test was carried out by filtering the catalyst from the reaction mixture at 80 °C after 1 h and the filtrate was allowed to react up to 2 h. The reaction mixture after 2 h and the filtrate were analysed by GC. The results of the test showed no change in the % conversion for Pd-SiW₁₁/MCM-41 indicating the present catalyst was truly heterogeneous (Figure 12). Also, in Pd-SiW₁₁/MCM-41, the Pd showed no tendency to agglomerate even after 2 h. i.e. no undesired Pd-black was formed. In contrast, the heterogeneity test (Figure 12b) showed that homogeneous catalysis contributes significantly to the coupling reaction due to leaching of Pd into reaction medium from Pd/MCM-41. These studies confirm that SiW₁₁ plays an important role in stabilizing the palladium and do not allow the leaching of the palladium during the reaction. Also, because of the higher loading of Pd in Pd/MCM-41, the formation of palladium black is visible during the reaction. The found observations are in good agreement with the reported ones.17, 22-23



Figure 12. Heterogeneity test for hydrogenation of cyclohexene over (a) Pd-SiW₁₁/MCM-41 and (b) Pd/MCM-41. Reaction conditions: catalyst amount=100 mg, $p(H_2) = 10$ bar, temperature= 80 °C, water: methanol= 30:20 mL.

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The catalyst was recycled in order to test its activity as well as stability. The obtained results are presented in Table 3. The recycled catalyst, Pd-SiW₁₁/MCM-41 did not show any appreciable change in the activity up to three cycles, indicating that the catalyst is stable and no leaching of Pd was found from the catalyst. At the other side, Pd/MCM-41 shows that there is a significant loss in the activity, suggesting the leaching of Pd during the reaction. This was further supported by elemental analysis of the regenerated catalyst by EDX and product mixture by AAS, suggesting no appreciable loss of Pd content.

Characterization of regenerated catalyst

In order to check the constancy, the regenerated catalyst was characterized for EDX, FT-IR, TEM and XPS.

EDX value of Pd (3.23 wt%) in regenerated Pd-SiW₁₁/MCM-41 is in good agreement with value of fresh catalyst (3.26 wt% of Pd) confirming no emission of Pd from Pd-SiW₁₁/MCM-41. This indicates that SiW₁₁ plays an important role as a stabilizer to keep the Pd active and also prevent it to leach from the support.



Figure 13. FT-IR spectra of (a) Fresh Pd-SiW_11/MCM-41 and (b) Regenerated Pd-SiW_11/MCM-41.

The FTIR spectra of the fresh and regenerated catalyst are shown in Figure 13. It can be seen that almost identical spectrum was obtained without any significant shift in the bands of regenerated catalyst in comparison with fresh catalyst indicating that catalyst structure remains intact even after the regeneration. However, the spectrum intensity was found low in case of regenerated catalyst, may be due to the sticking of the substrates, although this might not be significant in the reutilization of the catalyst.²⁴

TEM images of regenerated catalyst Pd-SiW₁₁/MCM-41 are displayed in Figure 14 at various magnifications. Images (14a & 14b) show the presence of Pd (0) as well as its uniform dispersion inside the pores of MCM-41. Moreover, obtained images are almost identical with the fresh catalyst, show the stability and sustainability of the catalyst during the reaction without aggregate formation (Pd black).

The XPS of fresh and regenerated $Pd-SiW_{11}/MCM-41$ is displayed in Figure 15. The obtained spectra are identical with fresh one confirms that Pd(0) species are stabilized by SiW₁₁ and

catalyst is sustainable during the reaction. Here, the intensity of regenerated catalyst spectrum is low, may be due to the sticking of the substrates on the surface, although this might not be significant in the reutilization of the catalyst.



Figure 14. TEM images of Regenerated Pd-SiW11/MCM-41 at (a) 100 nm and (b) 200 nm resolution.



Figure 15. XPS spectrum of fresh and recycled catalysts.

 Table 4. Hydrogenation of different substrates over Pd-SiW11/MCM-41.



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Reaction conditions: substrate= 10 mmol, catalyst amount=100 mg, $p(H_2) = 10$ bar, time= 2 h, temperature= 80 °C, water: methanol= 30:20 mL.

In order to see the viability of the present catalyst, hydrogenation of different substrates was carried out over Pd-SiW₁₁/MCM-41 and the results are presented in Table 4. From the Table 4 it is clear that the catalyst was found to be active for hydrogenation of both alkenes as well as ketone. However, in the case of crotonaldehyde where hydrogenation of both C=C as well as C=O is possible, hydrogenation of only C=O was observed. Here, Lewis acid sites of SiW₁₁ plays important role in strengthening the interaction of the catalyst with C=O of crotonaldehyde and therefore enhance the selectivity of the crotylalcohol.

Conclusions

We have come up with a new heterogeneous catalyst comprising of Pd (0) nanoparticles and SiW₁₁ anchored to the MCM-41. The SiW₁₁ species stabilizes the Pd (0) and eliminates the possibility of formation of Pd black and hence leaching. The BET surface area measurements suggest that Pd-SiW₁₁ species are present inside the hexagonal channels of MCM-41. The FT-IR analysis confirms that SiW₁₁ remains intact even after anchoring on to the support. The slight shift in the bands confirms the strong interaction of Pd-SiW₁₁ with the support. XRD pattern confirms that MCM-41 retains its hexagonal framework structure and well dispersion of Pd-SiW₁₁ species. The present catalyst was found to be highly active showing 95% conversion of cyclohexene. Interestingly, the present catalyst was found to be selective for C=O hydrogenation in the presence of C=C. The catalyst could also be regenerated after simple centrifugation and reused up to three cycles with retention in the activity.

Experimental Section

The chemicals used were of A.R. grade. Acetonitrile, methanol, cyclohexene, palladium chloride, sodium tungstate, sodium silicate, tetraethyl orthosilicate, dichloromethane, n-butylamine and acetone were purchased from Merck.

MCM-41 was synthesized following the previously reported procedure. ²⁵ Surfactant, cetyltrimethylammonium bromide (1 g) was added to the dilute solution of NaOH (2 M, 3.5 mL NaOH in 480 mL distilled water) with stirring at 28 °C. Then, 5 mL tetraethyl orthosilicate was added drop wise and the gel was aged for 2 h at 60 °C. The resulting material was filtered, washed with distilled water, dried in oven and calcined in air at 550 °C for 5 h. The obtained material was designated as MCM-41.

The mono lacunary silicotungstate was synthesized by following the method reported by Brevard et al. ²⁶ 0.22 mol, 7.2 g sodium tungstate and 0.02 mol, 0.56 g sodium silicate were dissolved in 150 mL distilled water

at 80 °C. The pH was then adjusted to 4.8 by dilute nitric acid. The volume of the mixture was reduced to half and the resulting solution was filtered to remove unreacted silicates. The lacunary polyoxometalate anion was separated by liquid-liquid extraction with acetone. The extraction was repeated until the acetone extract showed the absence of nitrate ions. The extracted sodium salt of mono lacunary silicotungstate was dried at room temperature in air. The resulting material was designated as SiW₁₁.

A catalyst containing 30% of SiW₁₁ anchored to MCM-41 was synthesized by impregnation method. ²⁷ MCM-41 (1 g) was impregnated with an aqueous solution of SiW₁₁ (0.3/30 g/mL of distilled water) and dried at 100 °C for 10 h. The resulting material was treated with 0.1 N HCl, filtered, washed with double distilled water and dried at 100 °C for 2 h. The obtained material was designated as SiW₁₁/MCM-41.

Synthesis of Pd exchanged anchored SiW₁₁ was carried out by wet impregnation of 1 g of SiW₁₁/MCM-41 with 25 mL 0.05 M solution of PdCl₂ for 24 h with stirring. The solution was then filtered, washed with distilled water in order to remove the excess of Palladium and dried in air at room temperature. The resulting material was designated as Pd-SiW₁₁/MCM-41. The same procedure was followed for the synthesis of Pd supported MCM-41 and the resulting material was designated as Pd/MCM-41.

Elemental analysis was carried out using JSM 5910 LV combined with INCA instrument for EDX- SEM. TGA was carried out on METTLER TOLEDO STAR-SW 7.01 instrument. The BET surface area measurements were performed in a Micromeritics ASAP 2010 volumetric static adsorption instrument with N2 adsorption at 77 K. The pore size distributions were calculated by BJH adsorption-desorption method. For FT-IR spectra, samples pressed with dried KBr into discs were recorded by using a Perkin-Elmer spectrometer. The XRD pattern was obtained by using PHILIPS PW-1830. The conditions used were: Cu Ka radiation (1.5417 A°), scanning angle from 0° to 60°. The surface morphology of the support and supported catalyst was studied by scanning electron microscopy using a JEOL-SEM instrument (model-JSM-5610LV) with scanning electron at 15 kV. TEM was done on JEOL (JAPAN) TEM instrument (model-JEM 100CX II) with accelerating voltage 220kV. The samples were dispersed in ethanol and sonicated for 5-10 minutes. A small drop of the sample was then taken in a carbon coated copper grid and dried before viewing. X-ray photoelectron spectroscopy (XPS) measurements were performed with Auger Electron Spectroscopy (AES) Module PHI 5000 Versa Prob II.

The catalytic reaction was carried out using Parr reactor instrument having three major components: The batch type reactor of 100 mL capacity is made up of SS-316, H₂ reservoir and electronic temperature and pressure controller. For example, in typical reaction, 10 mmol of cyclohexene with 50 mL solvent (30/20 mL of methanol/water) and 50 mg of catalyst were charged to the reactor vessel. The reactor was flushed thrice with H₂ gas to remove the air present in the empty part of the vessel. Finally, 10 bar H₂ pressure was applied for the reaction. The reaction was set at 80 °C with the stirring rate of 1700 rpm for 4 hours. The continuous decrease in pressure inside the vessel was utilized for determination of the reaction progress. After reaction completion, the reaction mixture was cooled at room temperature and then H₂ pressure was released from the vent valve. The organic layer was extracted using dichloromethane, whereas catalyst was collected from the junction of the liquid phases and finally recovered by centrifugation. The organic phases were then dried with anhydrous magnesium sulfate and analyzed by a gas chromatograph (Shimadzu-2014) using a capillary column (RTX-5). The products were recognized by comparison with the standard samples.

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Keywords: Hydrogenation • Cyclohexene • Palladium • Monolacunary silicotungstate • MCM-41 • Heterogeneity test

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