## Supporting information

## Catalyst Characterization techniques

The TEM (transmission electron microscopy) images of the material was recorded on Philips Technai operating at 200 Kv. The powder was suspended in ethanol by ultrasonic method. A drop of this solution is placed on a grid with a holey carbon copper film and then allowed to dry, covered by a watch glass. The size distribution of the particles was determined using Image J software and the mean particle diameters were calculated as number average values for at least 250 particles. For FTIR, all the spectra were taken at room temperature on a Horiba spectrometer FT-720. Before measurement, samples were grounded with KBr and pressed into thin wafers. XPS spectra were recorded on an Ulvac PHI 5601ci spectrometer. All the powder mineral samples were fixed onto a copper sample holder using double-sided sticky tape, which was then placed into a vacuum chamber attached with a turbo molecular pump. The samples were outgassed for 1 day under vacuum ($10^{-5}$ Pa) and then introduced into the analysis chamber, where the pressure was kept around 1 x $10^{-7}$ Pa. To ensure the accuracy of the data, the XPS system was calibrated using the peaks of Cu ($2P_{3/2}$) and Cu ($3P$) whose binding energies are 932.67 and 75.14 eV, respectively. The binding energy scales were adjusted to the highest C ($1s$) peak position equal to 284.8 eV. To calculate the chemical composition of the samples, empirical sensitivity factors were obtained from the relative area intensities of the photoelectron spectra of compounds of known chemical composition. Monochromatised Al $K\alpha$ X-ray (14 kV, 200 W) was used in place of a conventional X-ray source to obtain high-quality spectra to avoid overlapping of the satellite peaks; thus, uncertainty in the determinations of the peak position and peak area was nullified. An electron flood gun was used as a neutralizer, and the number of acquisitions was maintained at 12 for each analysis. For the used catalysts, additional cautions are taken to avoid the air exposure using glove box before subjected to XPS analysis.

## Analytical method

After separation from the solid catalyst, all products were first identified by GC-MS (Varian CP3800) against a standard, which was also used for qualitative analysis. Quantification of the products was obtained by a multi-point calibration curve for each product. The selectivity to each product was calculated by the following expression $S_i = C_i / \sum Cp$, where $C_i$ is the concentration of the product ‘i’ and $\sum Cp$ is the total concentration of the product. Quantitative analysis was carried out using a GC (HP 6890) equipped with Innowax capillary column (Agilent, 30 m x 0.32 mm, 0.25 μm) and a flame ionization detector. The GC method used was as follows: An initial oven temperature of 50 °C was held for 3 minutes. In the next step, the temperature was ramped at 10 °C/min. until it reached 100 °C and held for 2 minutes followed by the increase in temperature to 230 °C ramped at 7.5 °C/min. and held for 20 minutes. For, pyrrole and Indole aldehyde GC analysis were conducted using HP-5MS column. Due to the technical difficulties, calculation of carbon balance[1] including gaseous product was difficult (large volume of $CO_2$ was in the system), however, considering the liquid product ~ 95 % carbon balance can be obtained. The gas samples were collected and analyzed by a GC-TCD (Shimadzu GC-8A) analyzer equipped with one molecular sieve column and one Porapack Q column.

*Description of FTIR spectra of the fresh catalyst*

The spectrum of the fresh catalyst (Figure S2a) shows a band corresponds to the presence of hydroxyl groups at 3455 $cm^{-1}$. In addition, band appears at 562 $cm^{-1}$ and 750 $cm^{-1}$ attributed to the Al-O stretching and Al-O bending vibration, respectively.[2] The band at 1650 $cm^{-1}$ corresponds to H-O-H bending vibrations because of the possible presence of water, whereas, the other bands at 1520 $cm^{-1}$ and 2350 $cm^{-1}$ represents some undesired impurities.[3]

*FTIR band assignment of HMF in the fingerprint region*

Figure S4 shows a comparison between fingerprint region FTIR spectra of HMF and the used catalyst, which confirmed that the peaks at 1190, 1280, 1397, 1520, 1560, 1580 and 1665 $cm^{-1}$ belongs to HMF. The band at 1280 and 1190 $cm^{-1}$ are assigned to the C-O stretching mode of vibration of alcohol, whereas, the band at 1397 $cm^{-1}$ represents $CH_3$ mode. [4a, b] A series of band in the region of 1510 to 1580 $cm^{-1}$ are due to the aromatic skeleton of HMF. [4c]

*XPS spectra related to the support material*

The XPS spectra of the support materials revealed that the Al 2p and O1s spectra maintained their corresponding binding energies exhibiting a slight shift in the used catalyst as displayed in the Figure S5c to S5f. Figure S5c and S5d representing the Al2p spectra of fresh and used catalyst confirmed the shifting of binding energy from 74.5 eV to 74.1 eV. On the other hand, the O1s peak (Figure S5e and S5f) also shifted from 531.3 eV (fresh) to 531.8 eV (used), attributing a metal support interaction.[5, 6] No additional peaks related to the different O containing moieties were observed in the C1s spectrum of the used catalyst.

## Reference

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**Figure S1**: Recycling of $Pd/Al_2O_3$ catalyst after separation.

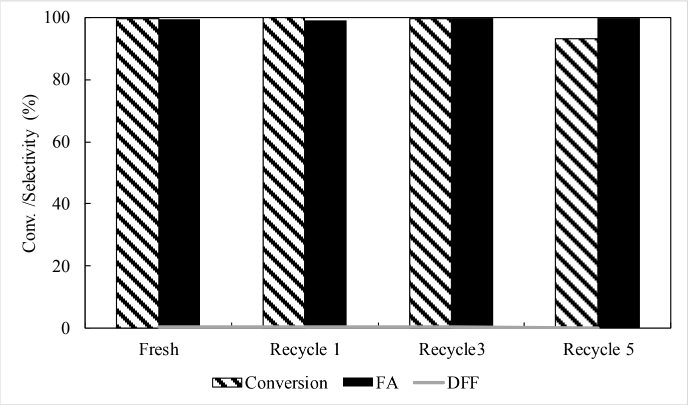

**Figure S2:** FTIR spectra of Pd/$Al_2O_3$ catalyst: (a) fresh and (b) spent catalyst (5th cycle). Dotted rectangle represents the region assigned to adsorbed CO on metallic Pd.

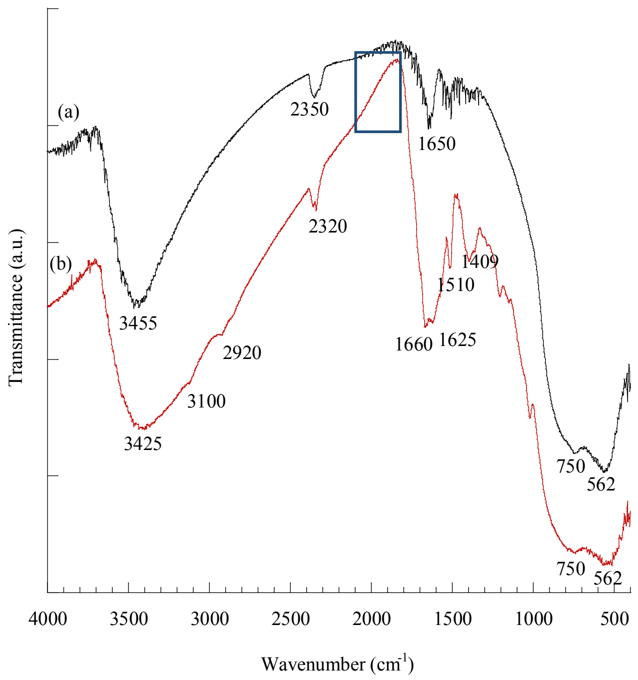

**Figure S3**: Gas chromatogram of the liberated gas.

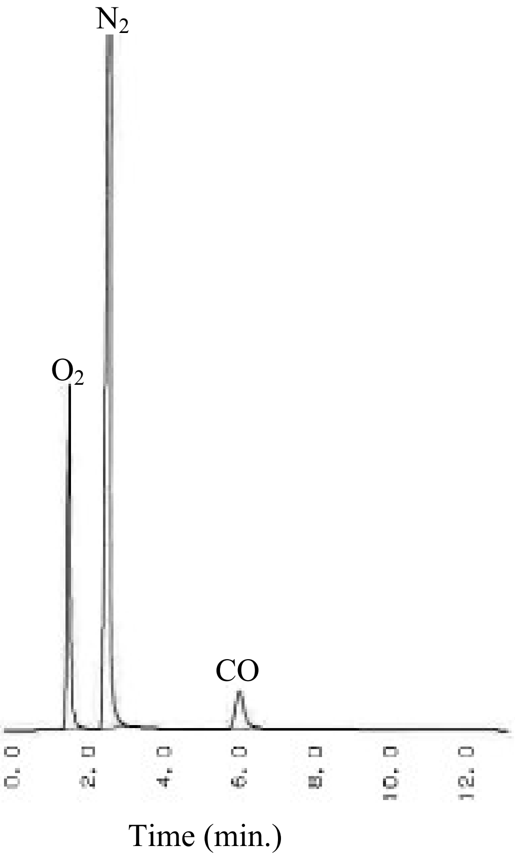

**Figure S4**: FTIR spectra of (a) used Pd/$Al_2O_3$ catalyst and (b) HMF in the fingerprint region.

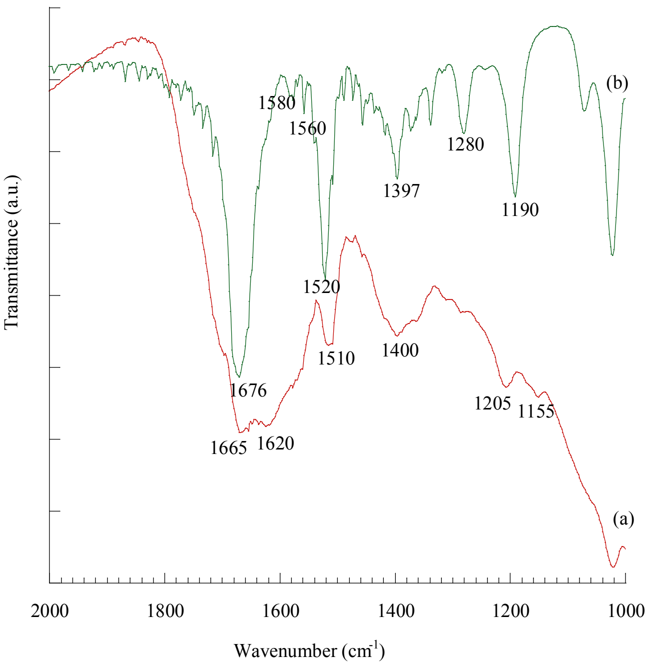

**Figure S5:** XPS of Pd/$Al_2O_3$ catalyst before and after the HMF decarbonylation. Pd 3d: (a) fresh, (b) used ; Al 2p: (c) fresh, (d) used ; O 1s: (e) fresh, (f) used.

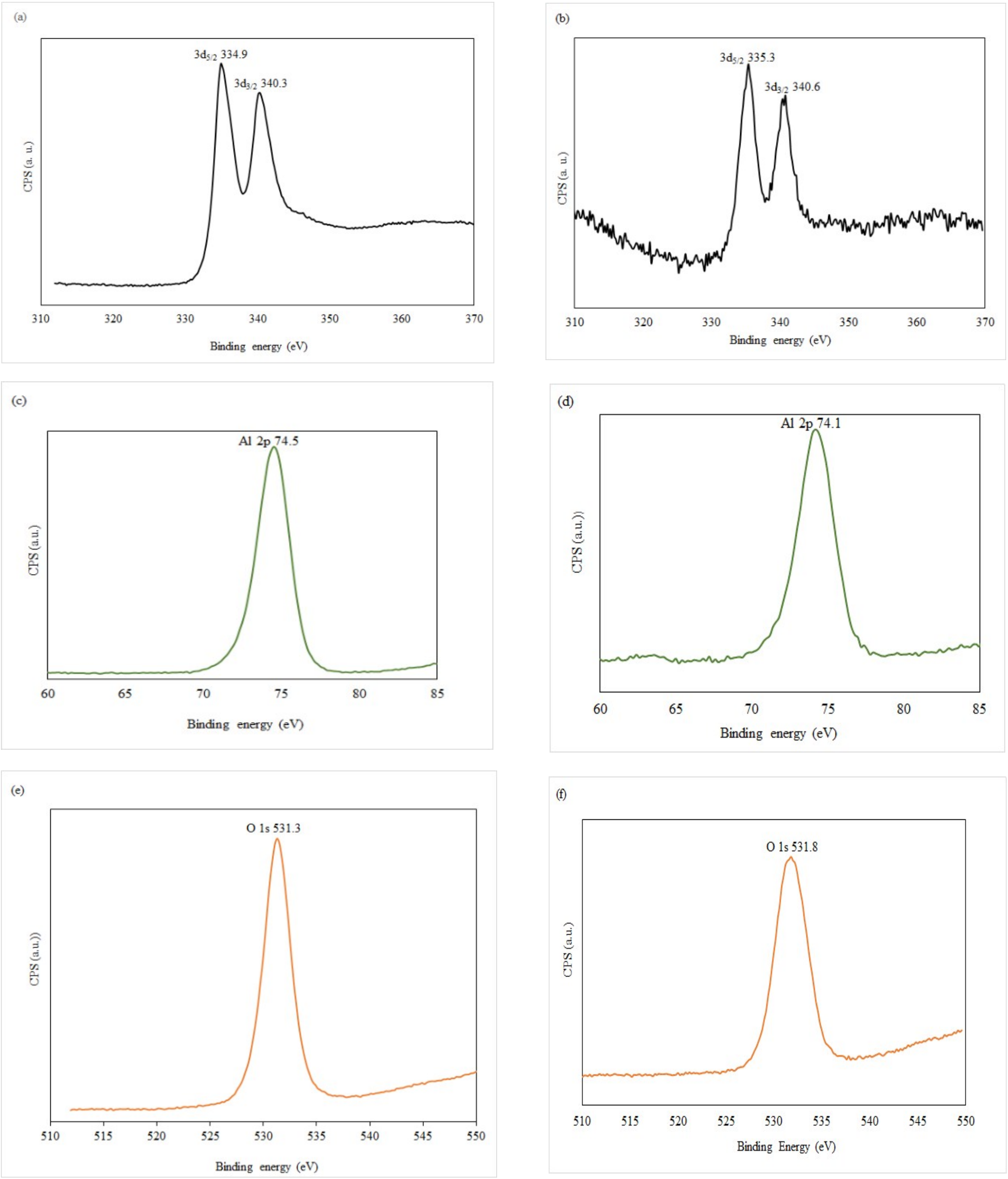

**Figure S6:** TEM images and particle size distribution of Pd catalysts supported on different support materials. (a) Pd/MCM-41, (b) Pd/Al-MCM-41, (c) Pd/C and (d) Pd/hydrotalcite