Supporting Information for:

Aerobic Oxidation of Alcohols Using Various Types of Supported Palladium Catalyst: The Synergistic Role of Functionalized Ligands, Morphology of Support and Solvent in Generating and Stabilizing Nanoparticles

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CONTENT:

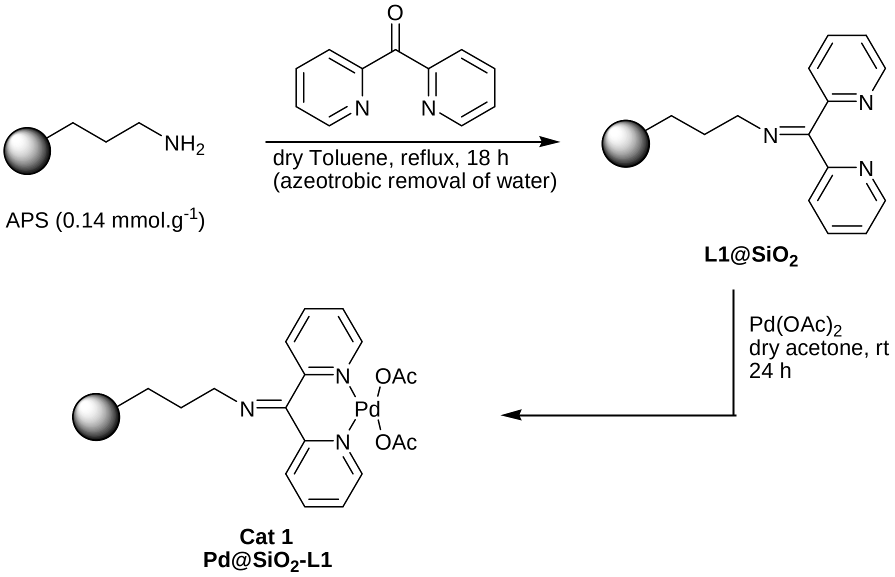
1) Experimental Procedures,

2) Characterization of the Catalysts

1.1.1) Preparation of Aminopropyl silica (APS) ***:*** Mesoporous silica gel (average pore diameter 60 Å) was activated by refluxing in concentrated hydrochloric acid (6 M) for 24 h and then washed thoroughly with the deionized water and dried before undergoing chemical surface modification. Refluxing the activated silica gel (10 g) with 3-aminopropyltrimethoxysilane (1.5 mmol) in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 110 ºC overnight to give the surface bound amine (APS) group at a loading *ca.* 0.14 mmol g^{-1} (by elemental analysis and back titration).

1.1.2) ***Preparation of surface bound bipyridyl ligand (L1@SiO$_2$):*** The resulting AMPS (0.14 mmol.g^{-1}, 5 g) was allowed to react with 2,2'-dipyridyl ketone (1 mmol, 0.184 g, Aldrich) in refluxing toluene with continuous removal of water using a Dean-Stark trap. The solid was filtered off and was washed thoroughly with hot toluene and ethanol to remove unreacted ketone. It was dried in air at 110 ºC overnight to furnish the corresponding surface bound bidentate ligand **1** at a loading *ca.* 0.13 mmol g^{-1} (Determined by TGA analysis).

1.1.3) ***Preparation of Pd@SiO$_2$-L1 (Cat 1):*** The catalyst was prepared by stirring a mixture of surface bound ligand **1** (4 g) and palladium acetate (0.52 mmol, 0.117 g, Merck) in dry acetone (100 mL) at room temperature for 24 h. After stirring the white brown solid was filtered, washed with large volume of acetone, ethanol and ether. It was then dried in an oven at 95 ºC overnight to furnish the corresponding catalyst **1** at a loading *ca.* 0.12±0.01 mmol g^{-1} (Determined by TGA analysis and atomic absorption spectroscopy (AA)).

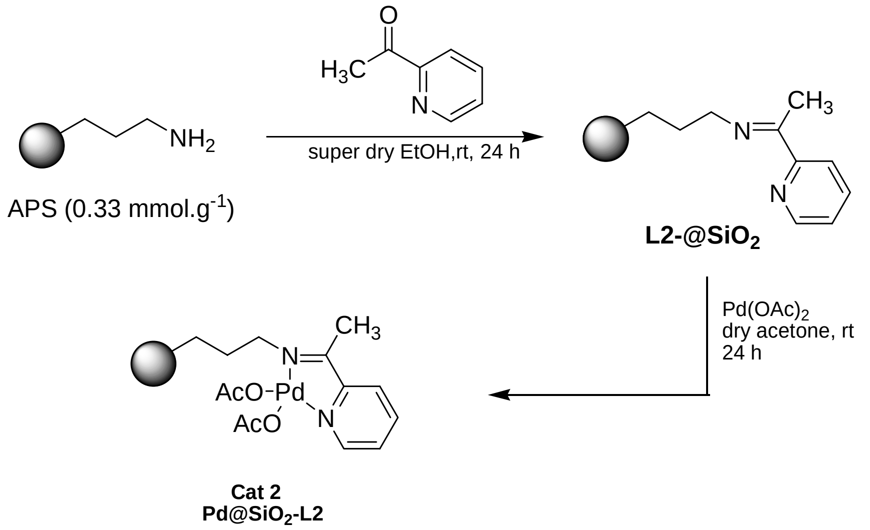


Scheme 1S. Preparation of Pd@SiO$_2$-L1 (Cat **1**)

1.2) Preparation of Catalyst 2:

1.2.1) ***Preparation of (L2@SiO$_2$):*** 2-acetylpyridine (0.605 g, 5 mmol) was added to a mixture of the oven dried AMPS (0.33 mmol.g^{-1}, 5 g) in super dry ethanol (150 mL) in a 250 mL round bottomed flask. The reaction mixture was stirred at 60 °C for 24 h. The ligand-grafted silica was filtered at the reaction temperature and the resulting solid and was washed thoroughly with hot toluene and ethanol to remove un-reacted ketone. It was dried in air at 95 ºC overnight to furnish the corresponding surface bound bidentate ligand **L2@SiO$_2$** at a loading *ca.* 0.28 mmol g^{-1} (Determined by TGA analysis).

1.2.2) ***Preparation of Pd@SiO$_2$-L2 (Cat 2)****:* The catalyst was prepared by stirring a mixture of surface bound ligand **L2@SiO$_2$** (4 g) and palladium acetate (0.50 mmol, 0.112 g, Merck) in dry acetone (100 mL) at room temperature for 24 h. After stirring the yellow solid was filtered, washed with large volume of acetone till washing were colourless. It was then dried in an oven at 95 ºC overnight to furnish the corresponding catalyst **2** (Scheme 2S) at a loading *ca.* 0.080±0.001 mmol g^{-1} (Determined by TGA analysis (Figure 5Sb) and atomic absorbtion spectroscopy (AA)). This indicates that more about 29% of the surface bound ligands were complexed with palladium

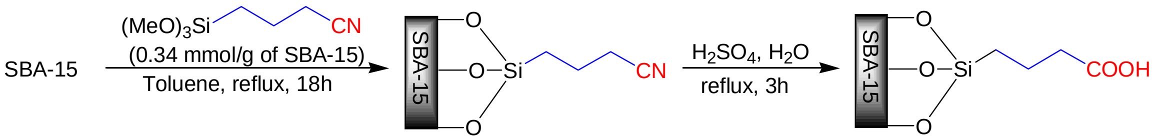


Scheme 2S. Synthesis of Pd@SiO$_2$-L2 (Cat **2**)

1.3) Preparation of Catalyst 3:

1.3.1) ***Preparation of SBA-15 :*** The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers (see reference 10b of the manuscript). In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw ≅ 5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 °C. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 °C for 20 h. The mixture was aged at 80 °C overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhelet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 ºC overnight.

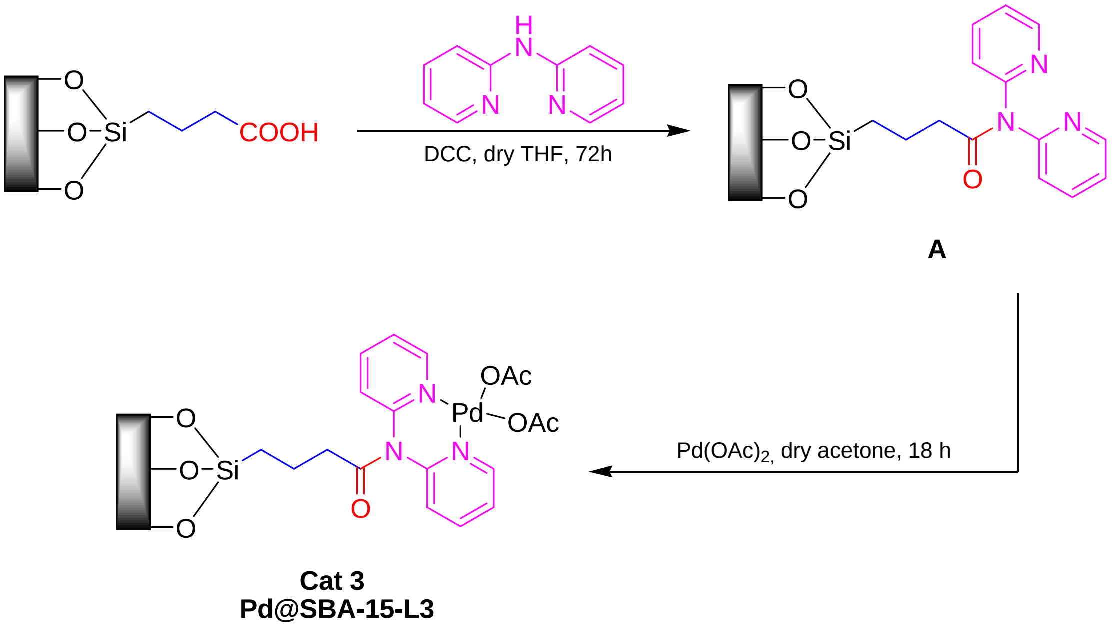
1.3.2) *Preparation of SBA-15 surface bound carboxylic acid*: The preparation of SBA-15 surface bound carboxylic acid was achieved according to the known procedure described by Clark *et. al.* (*Chem. Commun* **1996**, 1859 and *Chem. Commun.* **1998**, 2707): The resulting SBA-15 (6 g) was allowed to react with 3-cyanopropyltriethoxysilan (2 mmol, 0.462 g, Fluka) in refluxing dry toluene (150 mL) under nitrogen for 24 h. The solid was filtered off and was washed thoroughly with hot toluene and ethanol. It was dried in air at 90 ºC overnight to furnish the corresponding surface bound cyanopropyl group at a loading *ca.* 0.33 mmol g^{-1} (Determined by elemental analysis). The absorption band at 2256 cm^{-1} along with bands 2900-3000 cm^{-1} clearly indicates the attachment of cyanopropyl group onto the surface of SBA-15 (Figure 6S). The CN-SBA-15 was hydrolyzed by heating in 50% (v/v) aqueous sulfuric acid at 150 °C for 3h. After cooling to room temperature, the resulting solid was filtered off and filter cake was washed with an excess of deionized water. Drying in an oven at 110 °C overnight furnished the corresponding SBA-15-COOH with approximately the same loading.



Scheme 3S. Preparation of surface-bound propionic acid onto SBA-15

1.3.3) *Preparation of palladium complex covalently anchored onto silica* (Cat 3): The ligand **A** was first prepared by stirring a mixture of surface-bound carboxylic acid (5 g), 2, 2’-

bipyridylamine (1.7 mmol, 0.291 g, Aldrich) and dicyclohexylcarbodiimide (1.7 mmol, 0.350 g, Merck) in dry THF (150 mL) at reflux temperature for 72 h. The solid was filtered off and washed thoroughly with hot ethanol using a Soxhelet apparatus for 18 h to remove both the urea by-products and unreacted starting materials. It was then dried in an oven at 110 ºC overnight to furnish the corresponding surface-bound bipyridyl amide **A** at a loading *ca.* 0.2 mmol g^{-1} (Determined by TGA and elemental analysis, Figure 7S). The catalyst was then prepared by stirring a mixture of surface bound ligand **A** (4 g) and palladium acetate (0.11 mmol, 0.025 g, Merck) in dry acetone (100 mL) at room temperature for 24 h. After stirring the white brown solid was filtered, washed with large volume of acetone, ethanol and ether in order to remove any adsorbed palladium on the surface. It was then dried in an oven at 95 ºC overnight to furnish the corresponding catalyst **3** at a loading *ca.* 0.022±0.001 mmol g^{-1} (atomic absorption spectroscopy (AA)).



Scheme 4S. Synthesis of Pd@SBA-15-L3 (Cat **3**)

1.4) ***Typical experimental procedure for oxidation using catalyst 3:*** A mixture of K_2CO_3 (1 mmol) and Catalyst **3** (0.18 g, ~0.4mol% of Pd) in toluene (5 mL) was prepared in a two-necked flask. The flask was then evacuated (water aspirator) and refilled with pure oxygen for three times (balloon filled). To this solution the alcohol (1 mmol, in 1 mL toluene) was then injected and the resulting mixture was stirred at 80 ºC under an oxygen or air atmosphere (for the indicated time in the Table 1). After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed twice with CH_2Cl_2 (5 mL) the excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds.

2) Characterization of the Catalysts:

2.1) *Characterization of the Catalyst* 1: The catalyst **1** was characterized by atomic absorption spectroscopy (AA), FT-IR spectroscopy (Figures 1S, 2S), and thermo-gravimetric analysis (TGAm Figure 3S) and. From the TGA analysis of **1**, it is calculated that the loading of the bipyridyl ligand bound to the silica surface was 0.13 mmol. g^{-1}. TGA analysis of anchored palladium **1** shows a first weight loss due to the desorption of water below 100 ºC. This is followed by a second weight loss centered at 325 °C, corresponding to the loss of the surface bound bipyridyl ligand. The loading of palladium was determined using AA and shows a loading at 0.12 ± 0.01 mmol.g^{-1}. This indicates that more than 90% of the surface bound ligands were complexed with palladium.

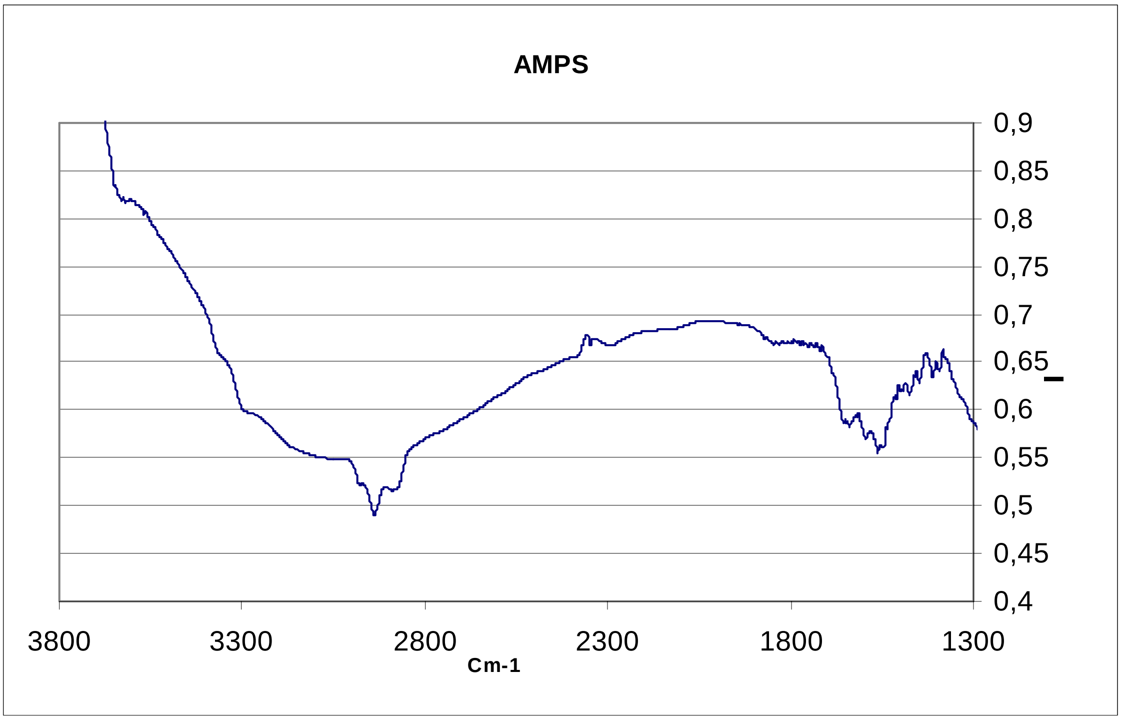


Figure 1S. DRIFT-IR of Aminopropylsilica (**APS**)

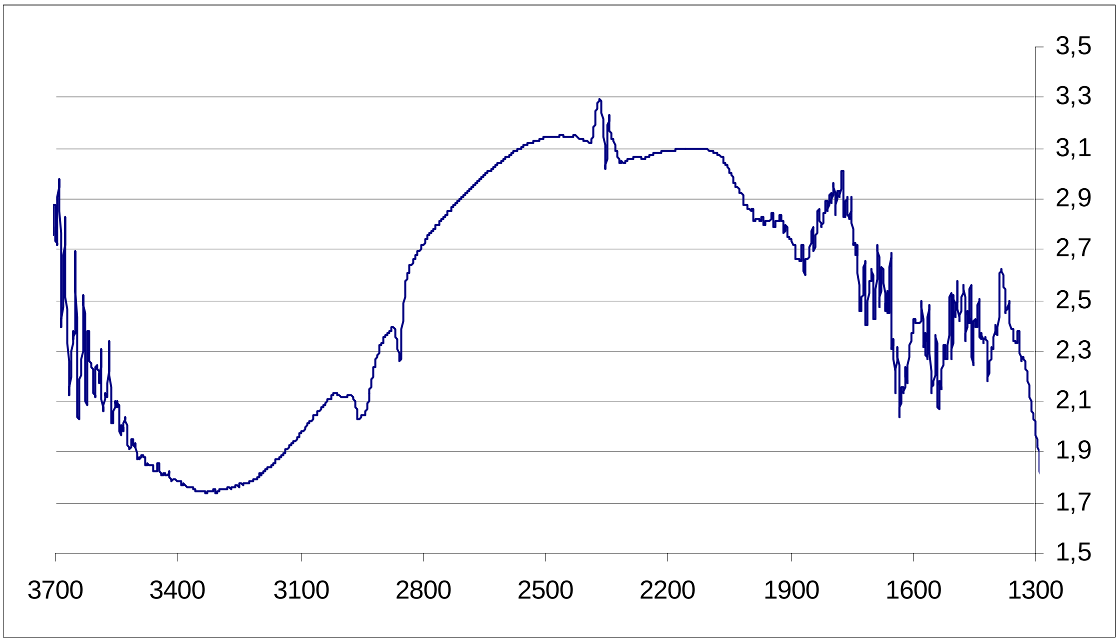


Figure 2S. DRIFT-IR of Pd@SiO_2-L1 (Cat **1**)

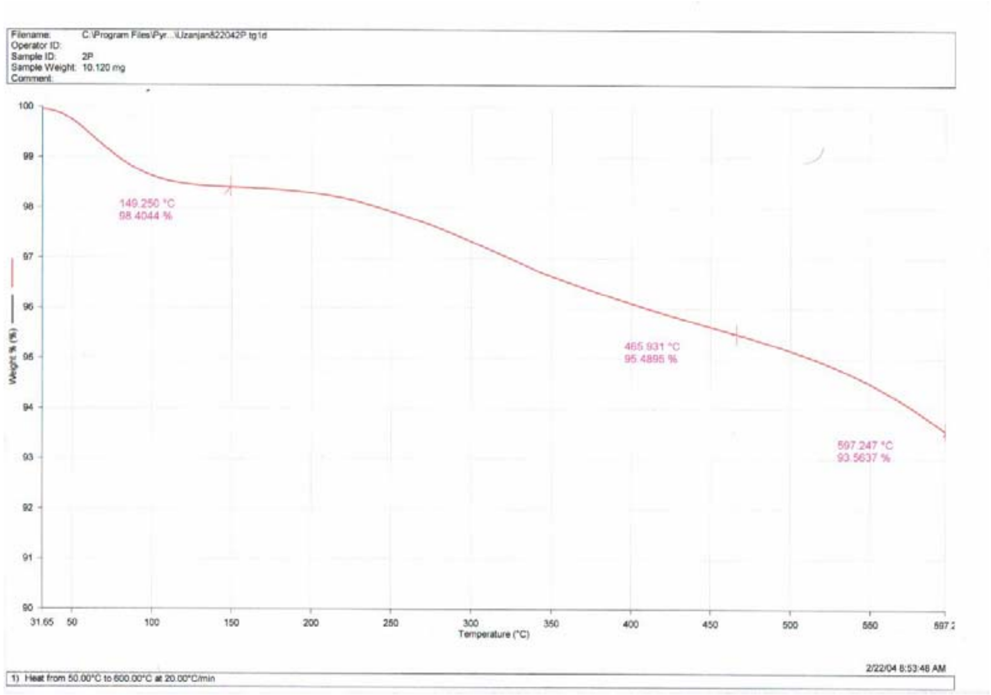


Figure 3S. TGA Diagram of Pd@SiO_2-L1 (Cat **1**)

Figure 4S shows a typical TEM image of **1** (in dark-field mode) after the third cycle of aerobic oxidation of benzyl alcohol. It can be seen that extensive agglomeration of palladium particles, with an irregular size distribution above 100 nm, has occurred. This result clearly shows that Pd-agglomeration is the major reason for deactivation of catalyst **1** just after the third cycle. The rapid increase in the size of palladium clusters observed is possibly a result of Ostwald ripening process.

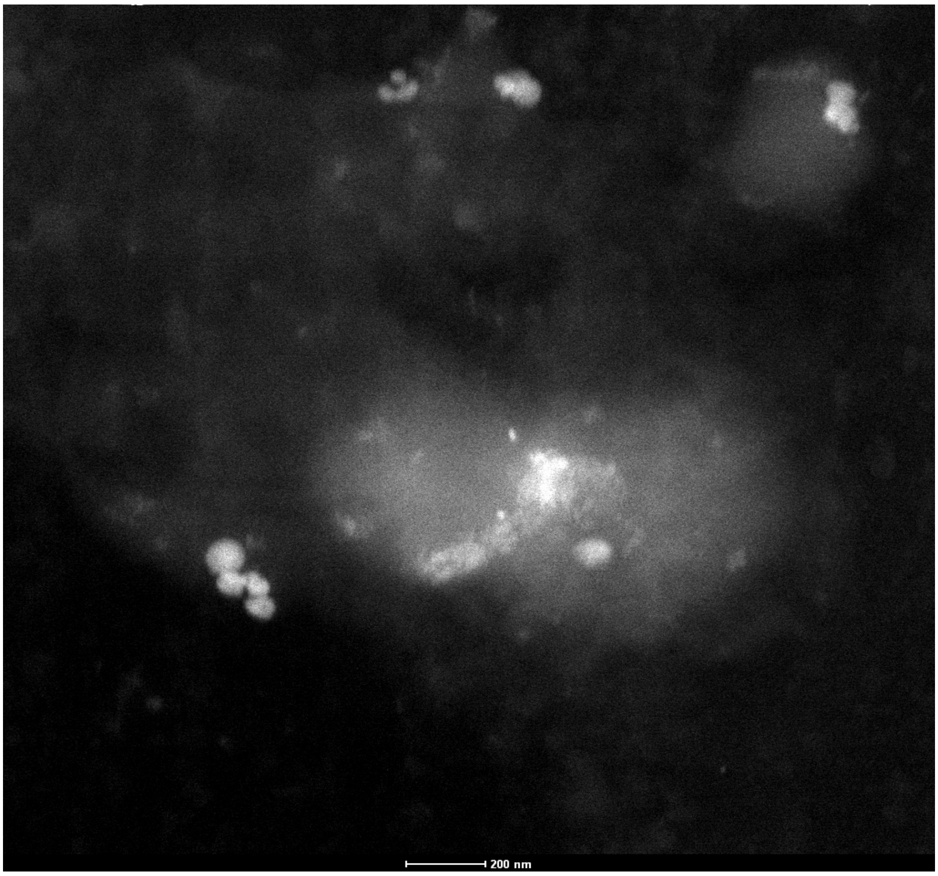
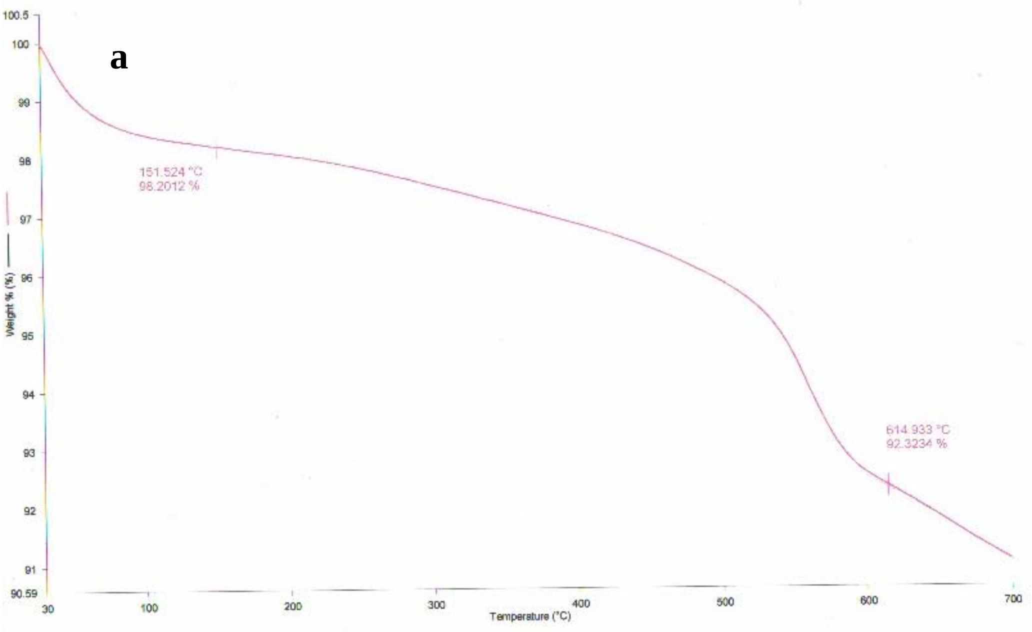


Figure 4S. Dark-field TEM image of catalyst **1** after the third reaction cycle



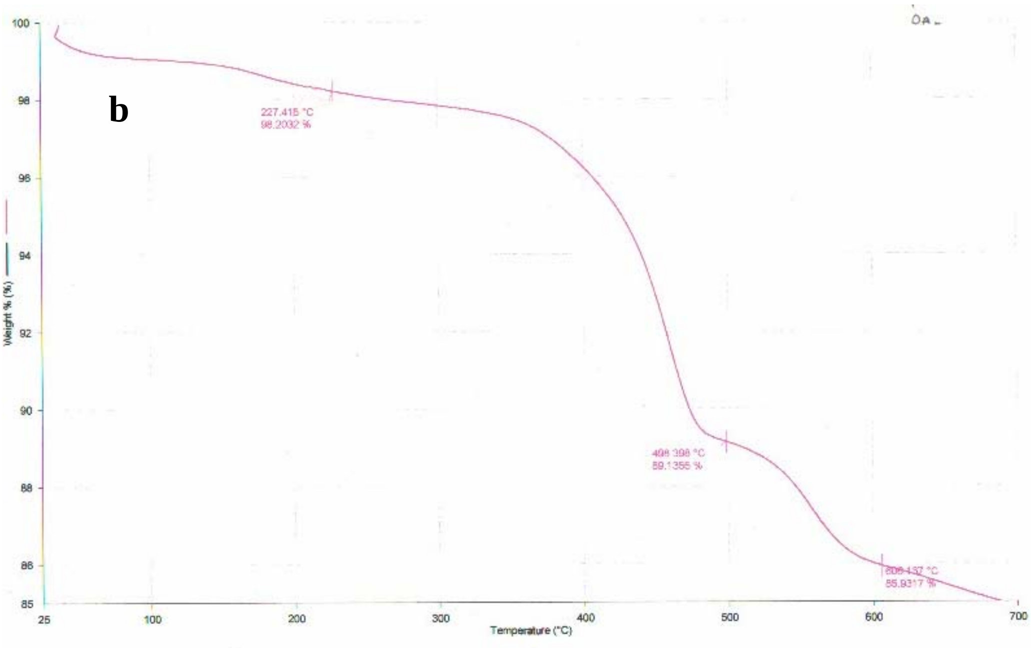


Figure 5S. TGA diagram of (a) L2@SiO$_2$; (b) Pd@SiO$_2$-L2 (Cat **2**)

2.2) *Characterization of the Catalyst* 3: The catalyst **3** was further characterized by atomic absorption spectroscopy (AA), elemental analysis, transmission electron microscopy (TEM) and surface pore analysis. From the AA analysis of **3**, it is calculated that the loading of palladium was 0.022±0.001 mmol. g^{-1}. We have used such a low loading in order to minimize the catalyst's leaching. Typically, a nitrogen adsorption desorption type IV with a very sharp hysteristis loop, which is characteristic of the ordered mesoporous materials, was obtained (Figure 8S).

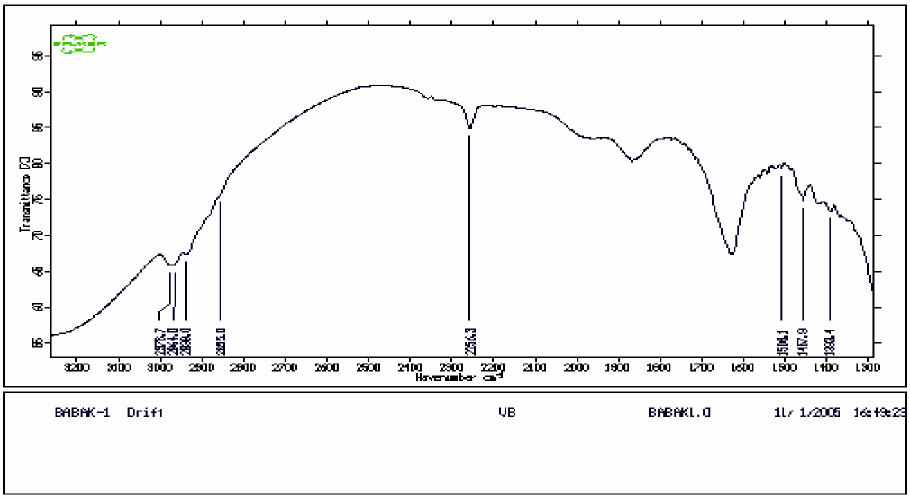


Figure 6S. DRIFT-IR of surface-bound Cyanopropyl onto SBA-15

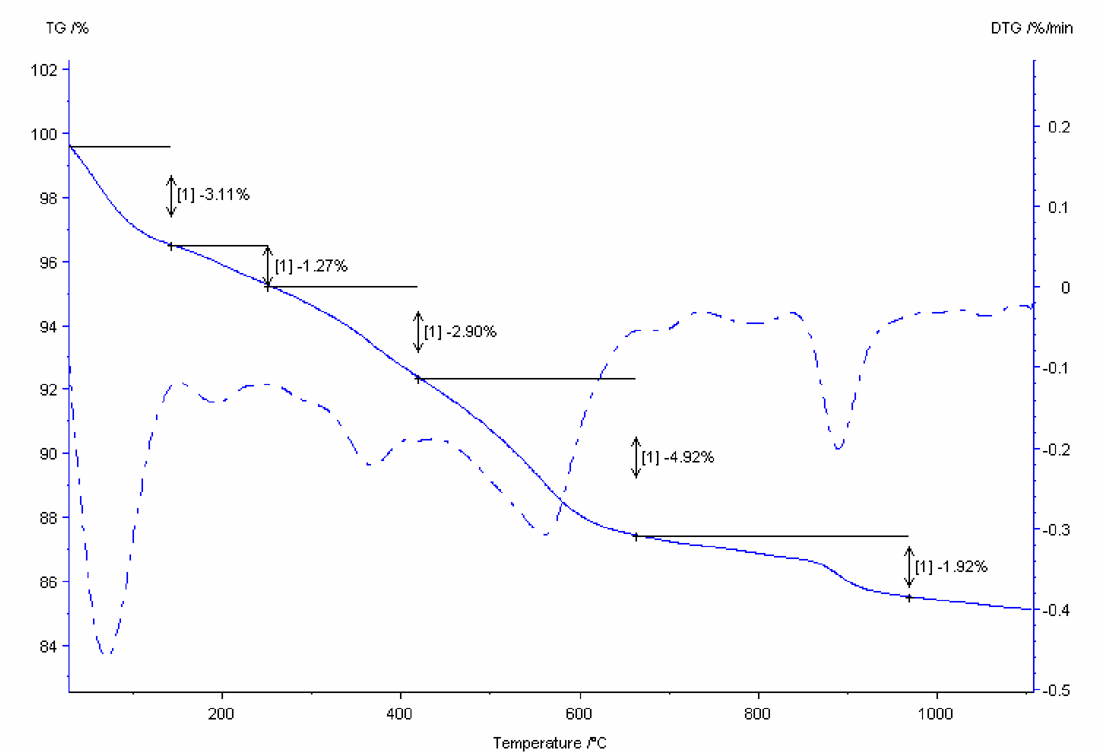


Figure 7S. TGA/DTA diagram of functionalized material **A**

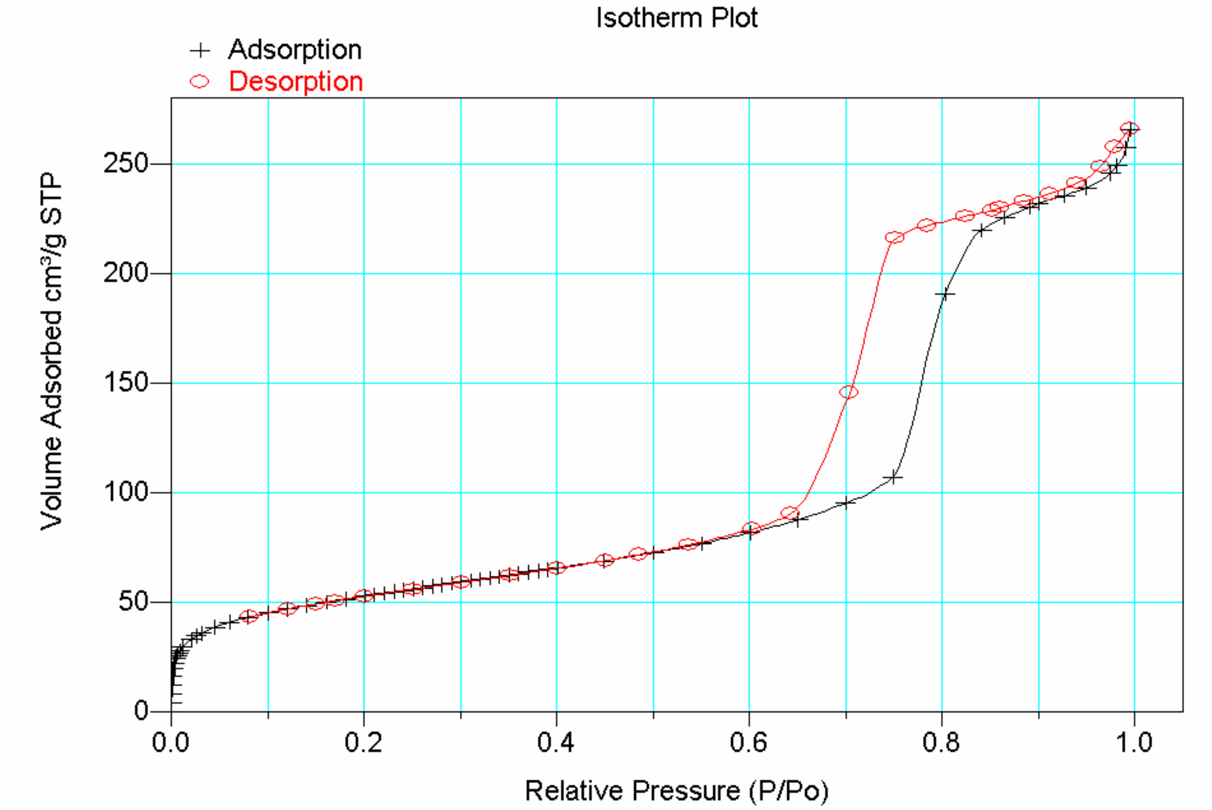


Figure 8S. The isotherm plot of a sample of Catalyst **3**

BET surface area 455 m^2/g and a total pore volume 0.76 cm^3/g were measured for the first sample of the catalyst, respectively. BJH calculations showed an average pore size 76 Å (7.6 nm) for this catalyst, which is in good agreement with the pore diameter estimated by TEM (Figure 9S, 10S). The TEM images interestingly showed that the nano-architecture of the catalyst (SBA-15 channels) survived even after prolonged refluxing at 150 °C in concentrated sulphuric acid (stage 2, Scheme 3S).

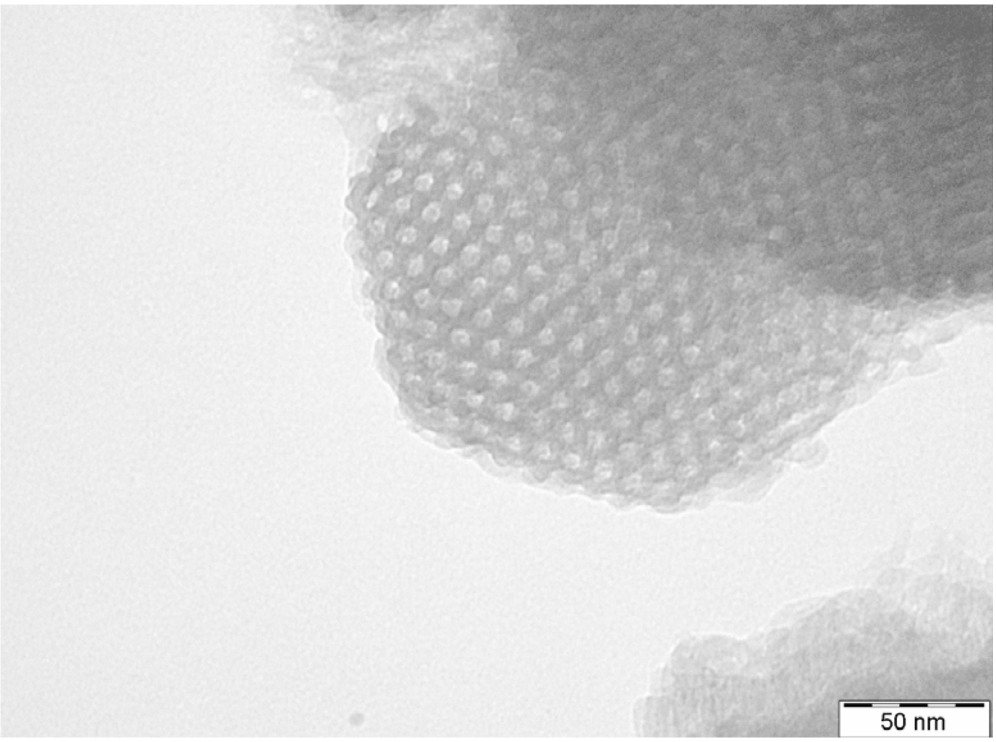


Figure 9S. TEM image of SBA-15 based catalyst **3** Perpendicular to the channel

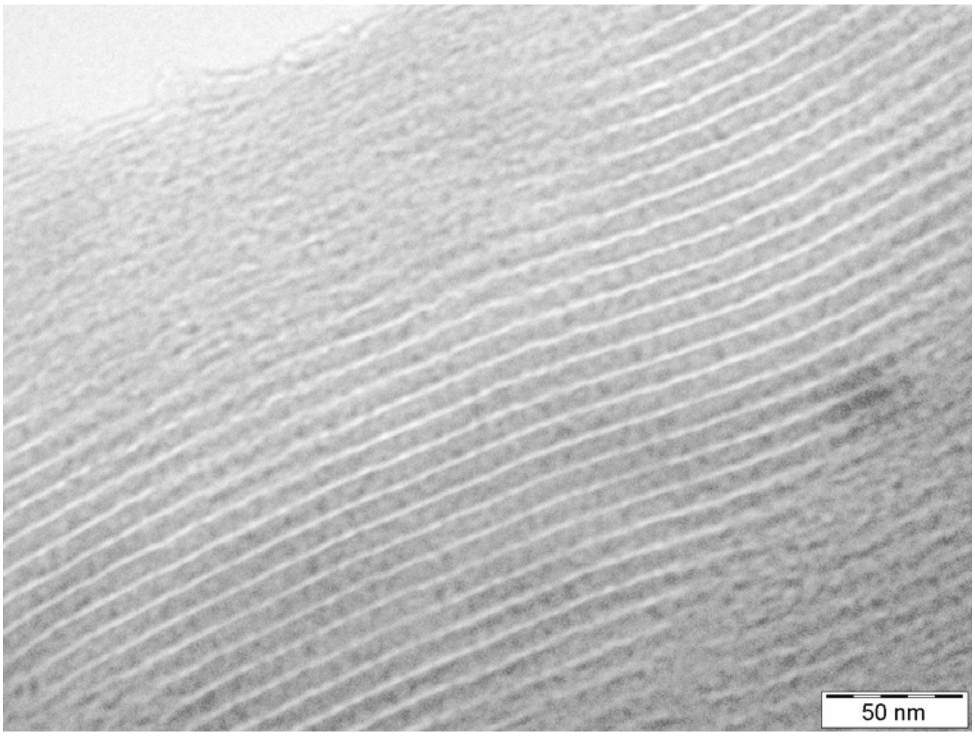


Figure 10S. TEM image of SBA-15 based catalyst **3** across to the channel

General experimental procedure for oxidation using molecular oxygen: A mixture of K_2CO_3 (1 mmol) and Catalyst **2** (0.18 g, ~0.4mol% of Pd) in toluene (5 mL) was prepared in a two-necked flask. The flask was then evacuated (water aspirator) and refilled with pure oxygen for three times (balloon filled). To this solution the alcohol (1 mmol, in 1 mL toluene) was then injected and the resulting mixture was stirred at 80 ºC under an oxygen or air atmosphere (for the indicated time in the Table 1). After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed twice with CH_2Cl_2 (5 mL) the excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds.

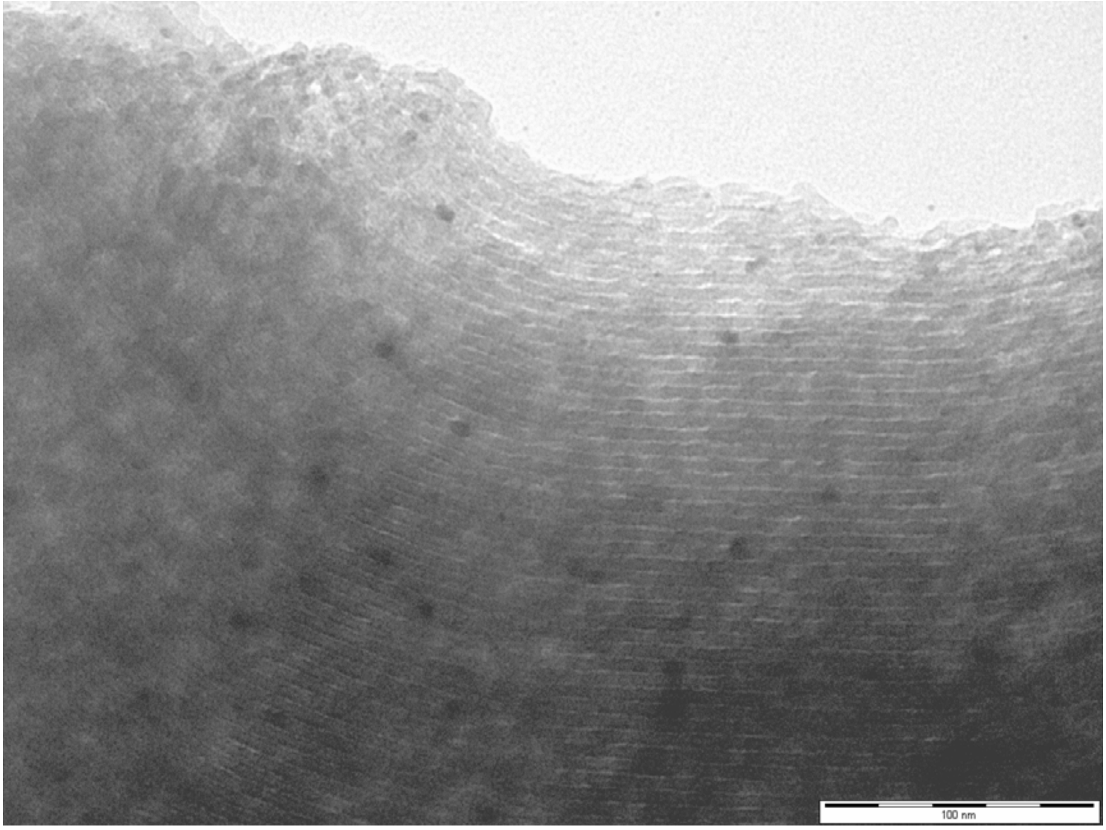


Figure 11S. TEM image of the recovered catalyst **3** across to the channels, the palladium nanoparticles with a relatively regular size clearly can be seen inside the channels.

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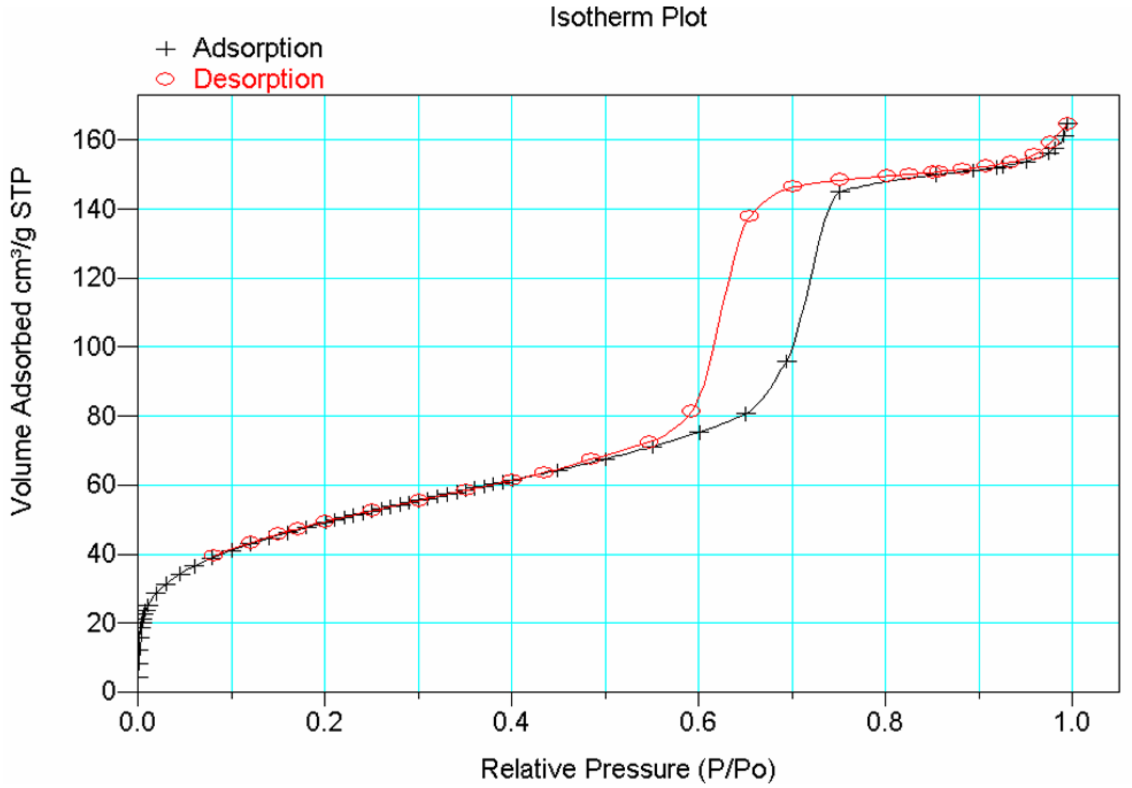

Figure 12S. Isotherm plot of the recovered catalyst **3**