

Supporting information for:

Aerobic Oxidation of Alcohols Catalyzed by *in Situ* Generated Gold Nanoparticles inside the Channels of Periodic Mesoporous Organosilica with Ionic Liquid Framework

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Table of contents:

1. Experimental Section

1.1. Synthesis of ionic liquid 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride (BTMSPIC).....	S4
1.2. Synthesis of periodic mesoporous organosilica with ionic liquid framework (PMO-IL).....	S4
1.3. Preparation of Au@PMO-IL.....	S5
1.4. Preparation of Au-catalyst-(1).....	S5
1.5. Preparation of Au-catalyst-(2).....	S6
1.6. General procedure for aerobic oxidation of alcohols by Au@PMO-IL in the presence of Cs ₂ CO ₃	S6
1.7. General procedure for aerobic oxidation of alcohols by Au@PMO-IL in the presence of K ₂ CO ₃	S6
1.8. General procedure for recycling of Au@PMO-IL in aerobic oxidation of benzyl alcohol	
1.9. General procedure for the hot filtration test.....	S7
1.10. References.....	S7

2. Schemes

Scheme S1: Synthetic pathway for preparation of ionic liquid.....	S8
Scheme S2: Synthetic pathway for synthesis of the surfactant extracted PMO-IL.....	S8
Scheme S3: Schematically presentation of synthesis of Au-based catalysts	S9

3. Table:

Table S1. Textural properties of the Au-Catalyst-(1) and Au-Catalyst-(2).....	S10
Table S2. Aerobic oxidation of alcohols catalyzed by Au-Catalyst-(1)	S10

4. Figures:

Figure S1: DRIFT-IR spectrum of PMO-IL support.....	S11
Figure S2: DRIFT-IR spectrum of Au@PMO-IL catalyst.....	S12
Figure S3: TGA analysis of PMO-IL support.....	S13
Figure S4: N ₂ adsorption-desorption isotherms for Au-Catalyst-(1).....	S13

Figure S5: BJH Pore size distributions for Au-Catalyst-(1).....	S14
Figure S6: TEM image for Au-Catalyst-(1).....	S14
Figure S7: N ₂ adsorption-desorption of Au-Catalyst-(2)	S15
Figure S8: BJH Pore size distributions for Au-Catalyst-(2b).....	S15
Figure S9: TEM image for Au-Catalyst-(2).....	S16
Figure S10: Nitrogen adsorption-desorption isotherms for recovered Au@PMO-IL catalyst after 7 th run from the oxidation of benzylalcohol.....	S16
Figure S11: BJH Pore size distributions for recovered Au@PMO-IL catalyst after 7 th run from the oxidation of benzylalcohol.....	S17
Figure S12: Recycling data for Au@PMO-IL during aerobic oxidation of benzylalcohol.....	S17
Figure S13: TGA pattern of recovered Au@PMO-IL catalyst after 7 th run from the oxidation of benzylalcohol.....	S18

1. Experimental Section

1.1. Synthesis of ionic liquid 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride

(BTMSPIC): The ionic liquid BTMSPIC precursor was synthesized by few modifications of our last synthetic reports (Scheme S1).¹ In a typical experiment, a suspension of sodium imidazolid in dry THF was prepared from the direct reaction of freshly dried imidazole (2 g) and NaH 95% (0.77 g) at a flame-dried two necks flask containing dry THF (60 ml) under argon atmosphere. 3-chloropropyltrimethoxysilan (CPTMS) (5.4 ml) was added to the mentioned stirred suspension and the resulting mixture was refluxed for 30 h. Then, the reaction mixture was allowed to cool to room temperature followed by the solvent removal under reduced pressure until an oily mixture containing NaCl obtained. To this end, CPTMS (5.4 ml) and dry toluene (60 ml) were then added and the resulting mixture was refluxed for 48h until a two phase mixture comprising toluene and ionic liquid (BTMSPIC) obtained. Then, toluene phase was removed and dry CH₂Cl₂ (60 ml) was added to remove the precipitated NaCl. In the next stage, CH₂Cl₂ phase was transferred to the well-dried/two-necks flask and the volatiles removed by reduced pressure until the ionic liquid (BTMSPIC) and unreacted starting materials obtained. Finally, ionic liquid was washed by dry toluene (5×50ml) for removal of unreacted starting materials to give almost pure BTMSPIC.

1.2. Synthesis of periodic mesoporous organosilica with ionic liquid framework (PMO-IL)

(PMO-IL): PMO-IL was also synthesized according to our previously reported method (Scheme S2).¹ In a typical procedure, Pluronic P123 (1.67g) was dissolved in a mixture of H₂O (10.5g), HCl, (2M, 46.14g), and KCl (8.8 g), and the mixture was stirred at 40 °C until a homogenous solution obtained. To this end, a pre-mixed of BTMSPIC (2 mmol, 0.86g) and TMOS (18 mmol, 2.74 g) in dried methanol were immediately added to the above-mentioned solution and

stirred at 40 °C for 24 h. The resulting mixture was posed in hydrothermal treatment without stirring at 100 °C for 72 h. The obtained solid materials containing surfactant was filtered and carefully washed with deionized water. The surfactant residue was then extracted from the materials through a Soxhlet apparatus by using ethanol (100 ml) and concentrate HCl (37%, 3 mL). In a typical extraction, as-synthesized PMO (1g) washed four times with acidic ethanol over 12 h, dried under vacuum for 24 h, to afford PMO-IL as a bright yellow powder.

1.3 Preparation of Au@PMO-IL: Au@PMO-IL was prepared via simple ion exchange technique according to our procedure (Scheme S3).² In this regard, the resulting PMO (0.5 g, 1 mmol IL g⁻¹) was then dispersed in deionized water (20 mL) and sonicated for at least 15 minutes to obtain a homogeneous dispersion of PMO particles in water. This suspension was then mixed with solution of NaAuCl₄·2H₂O (0.020 g, 0.050 mmol) in water (2 mL) at room temperature for 2 h. After filtration, the resulting mixture was washed with deionized water (3 × 10 mL) and acetone (2 × 10 mL), respectively. The resulting material was then dried at room temperature under vacuum.

1.4. Preparation of Au-catalyst-(1): Au-catalyst-(1) was prepared according to our literature procedure with a slight modification (Scheme S3).³ The resulting PMO (0.5 g, 1 mmol IL g⁻¹) was first dispersed in deionized water (20 mL) and sonicated to obtain a homogeneous dispersion of PMO particles in water for at least 15 min. This suspension was then mixed with solution of NaAuCl₄·2H₂O (0.020 g, 0.050 mol) in water (2 mL) at room temperature for 2 h. Gold nanoparticles was obtained by addition of solution of NaBH₄ (1M) to related suspension at room temperature. After filtration, the resulting mixture was washed with deionized water (3 × 10 mL) and acetone (2 × 10 mL), respectively. The resulting material was then dried at room temperature under vacuum.

1.5. Preparation of Au-catalyst-(2): Au-catalyst-(2) was obtained according to a literature procedure with a slight modification (Scheme S3).³ The resulting PMO (0.5 g, 1 mmol IL g⁻¹) was then dispersed in deionized water (20 mL) and sonicated to obtain a homogeneous dispersion of PMO particles in water for at least 15 min. This suspension was then mixed with solution of NaAuCl₄·2H₂O (0.020 g, 0.050 mmol) in water (2 mL) at room temperature for 2 h. Then, the obtained suspension reacted with excess amount of benzyl alcohols at 80 °C for 12 h to give gold nanoparticles supported on PMO-IL. After filtration, the resulting mixture was washed with deionized water (3 × 10 mL) and acetone (2 × 10 mL), respectively. The resulting material was then dried at room temperature under vacuum.

1.6. General procedure for aerobic oxidation of alcohols by Au@PMO-IL in the presence of Cs₂CO₃: A mixture of alcohol (0.5 mmol), Au@PMO-IL (0.4–2 mol%, depending on alcohol) and Cs₂CO₃ (1.5 mmol) in toluene (0.7 mL) was prepared in a two-necked flask. The flask was then evacuated and filled with pure oxygen. The resulting mixture was stirred at 35 °C under an oxygen atmosphere. Reaction process was monitored by TLC and GC techniques.

1.7. General procedure for aerobic oxidation of alcohols by Au@PMO-IL in the presence of K₂CO₃: A mixture of alcohol (0.25 mmol) and catalyst (0.2–5 mol%, depending on alcohol) in toluene (0.7 mL) was prepared in a two-necked flask. The flask was then evacuated and filled with pure oxygen (1 bar). The resulting mixture was stirred at 60 °C under an oxygen atmosphere. Reaction process was monitored by TLC and GC techniques.

1.8. General procedure for recycling of Au@PMO-IL in aerobic oxidation of benzyl alcohol: After completion of the oxidation of benzyl alcohol (0.5 mmol) catalyzed by Au@PMO-IL (0.4 mol%, 0.020 g) in toluene (0.7 mL) under 1 atmospheric of oxygen at 35 °C, reaction mixture was centrifuged and solid catalyst was washed with water and ethyl acetate

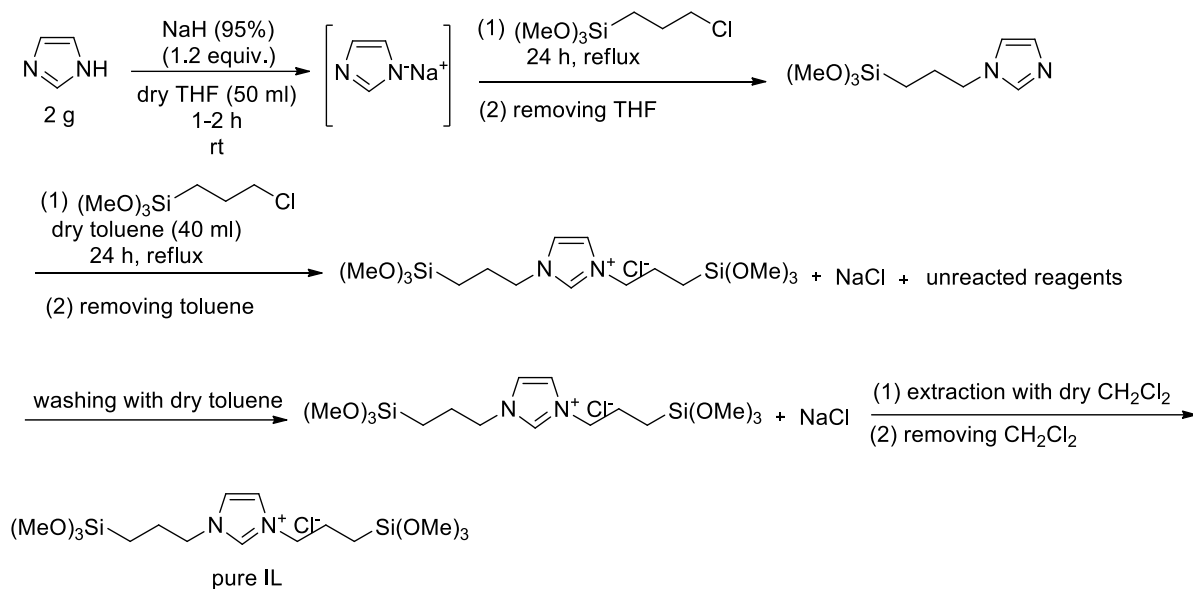
(2×5 mL) and dried with acetone and vacuum. The recycled catalyst was used in a new cycle of reaction with fresh reactants under the same conditions. Moreover, the catalyst could be recycled and reused 7 times with a constant decrease in catalytic activity of the recovered catalyst (Figure S10).

1.9. General procedure for the filtration test: For this purpose, the aerobic oxidation of benzyl alcohol (0.5 mmol) by using Au@PMO-IL (0.4 mol%, 0.02 g), Cs₂CO₃ (1.5 mmol) carried out under O₂ (1 atm.) in toluene (0.7 mL) at 35 °C for 1.5 h (benzaldehyde 45%). Then, the reaction mixture was filtered and filtrated solution was added 1.5 mmol of Cs₂CO₃ and allowed to continue to react under oxygen atmosphere (1 bar) at 35 °C for 12h. The reaction progress was analyzed by TLC and GC.

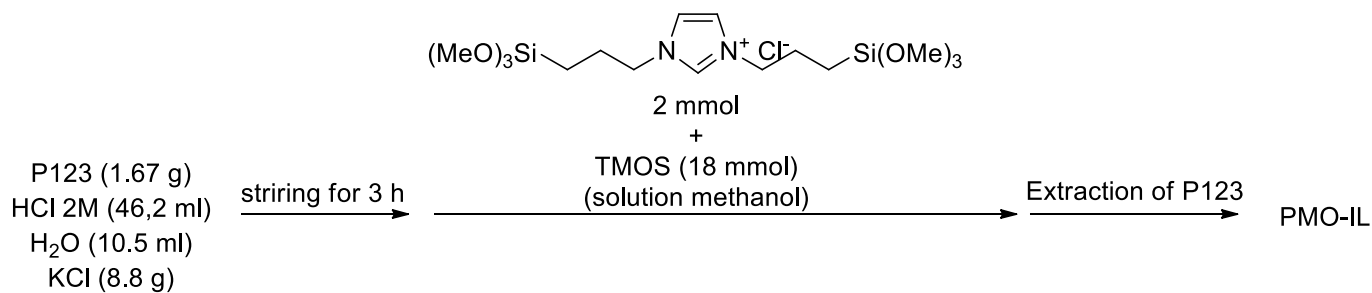
1.10. References

- [1] Karimi, B.; Elhamifar, D.; Clark, J. H.; Hunt, A. J. Ordered Mesoporous Organosilica with Ionic-Liquid Framework: An Efficient and Reusable Support for the Palladium-Catalyzed Suzuki–Miyaura Coupling Reaction in Water, *Chem. Eur. J.* **2010**, *16*, 8047-8053.
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- [3] Karimi, B.; Naderi, Z.; Khorasani, M.; Mirzaei, H. M.; Vali, H. Ultrasmall Platinum Nanoparticles Supported Inside the Nanospaces of Periodic Mesoporous Organosilica with an Imidazolium Network: An Efficient Catalyst for the Aerobic Oxidation of Unactivated Alcohols in Water, *ChemCatChem* **2016**, *8*, 906-910.

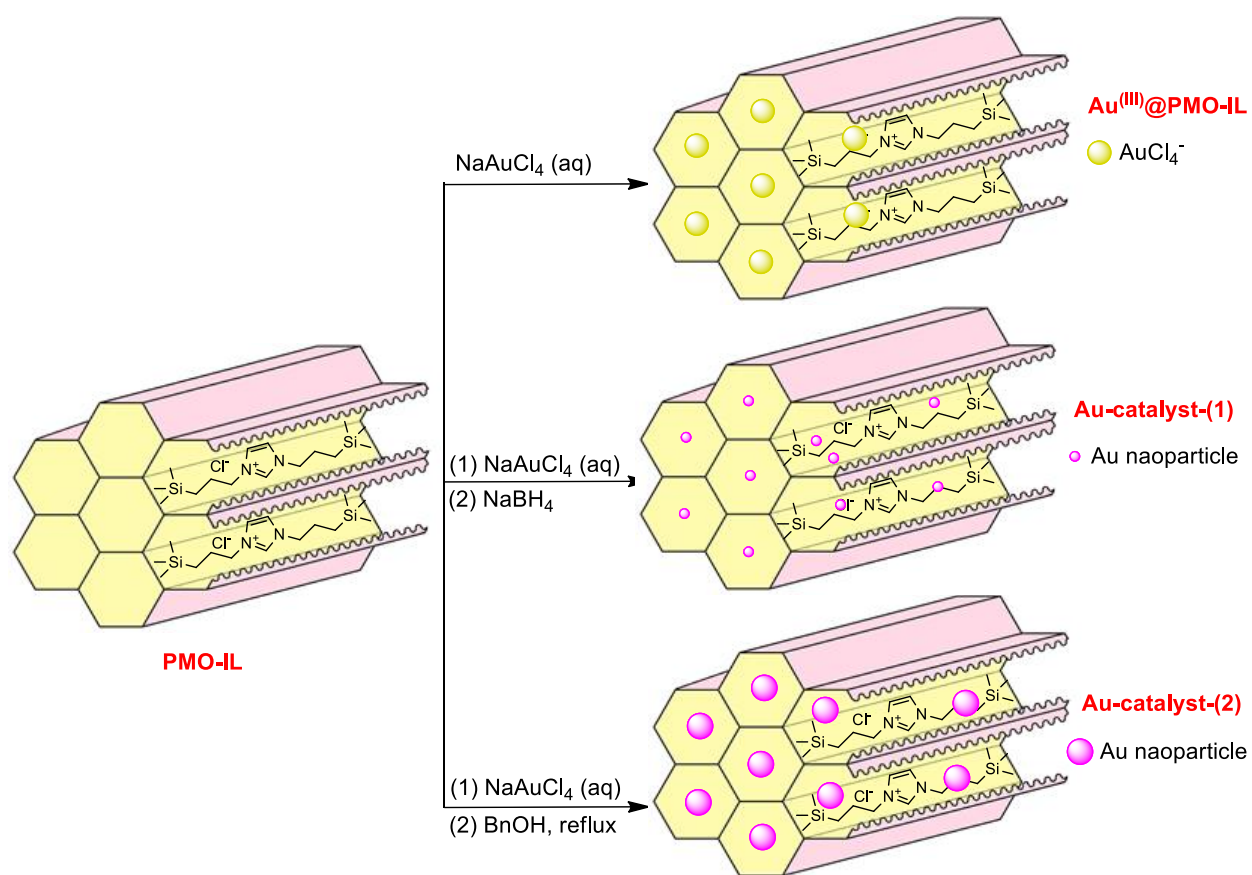
2. Schemes:



Scheme S1: Synthetic pathway for preparation of ionic liquid.



Scheme S2: Synthetic pathway for synthesis of the surfactant extracted PMO-IL.



Scheme S3: Schematically presentation of synthesis of Au-based catalysts

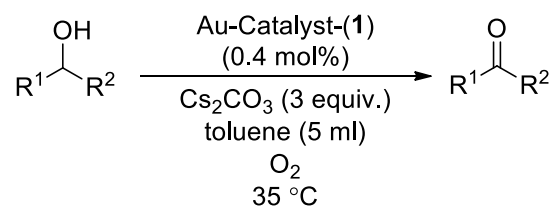
3. Tables

Table S1. Textural properties of the Au-Catalyst-(1) and Au-Catalyst-(2).

Material	$S_{\text{BET}}^{[a]}$ (m^2g^{-1})	$V_t^{[b]}$ (cm^3g^{-1})	$D_{\text{BJH}}^{[c]}$ (nm)	F.G. ^[d] (mmol g^{-1})
Au-Catalyst-(1)	424	0.71	9.21	Au (0.091)
Au-Catalyst-(2)	318	0.64	9.2	Au (0.088)

[a] S_{BET} : specific surface area, [b] V_t : total pore volume, [c] D_{BJH} : average pore size diameter calculated from the adsorption branch using BJH method. [d] Loading of Au estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Table S2. Aerobic oxidation of alcohols catalyzed by Au-Catalyst-(1) ^[a]



Entry	Alcohol	Time (h)	Yield (%) ^[b]
1	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	6	98
2	4-isopropyl- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	24	88
3	4- NO_2 - $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	24	61
4	3-Cl- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	24	30
5	α -Tetralol	24	69
6	2-octanol	24	73
7	cycloheptanol	24	63

[a] Reaction conditions: alcohol (0.5 mmol), Au-Catalyst-(1) (0.4 mol%) Cs_2CO_3 as base (1.5 mmol) in toluene (0.7 ml) at 35°C under O_2 atmosphere (1 bar). [b] GC yield

4. Figures

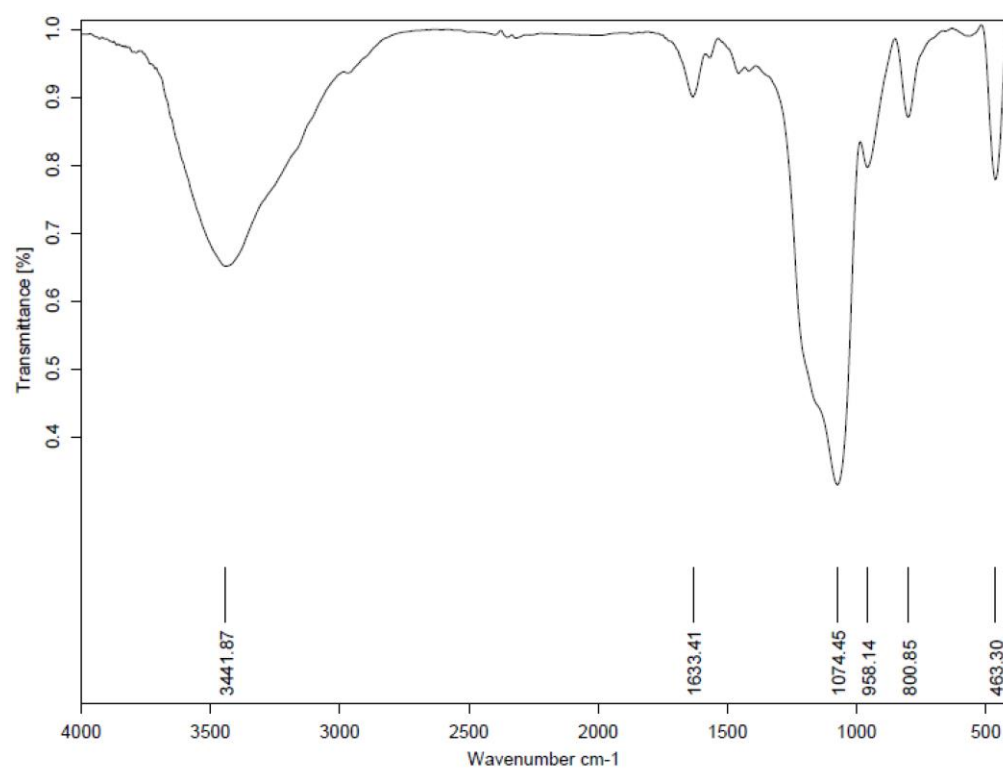


Figure S1: DRIFT-IR spectrum of PMO-IL support

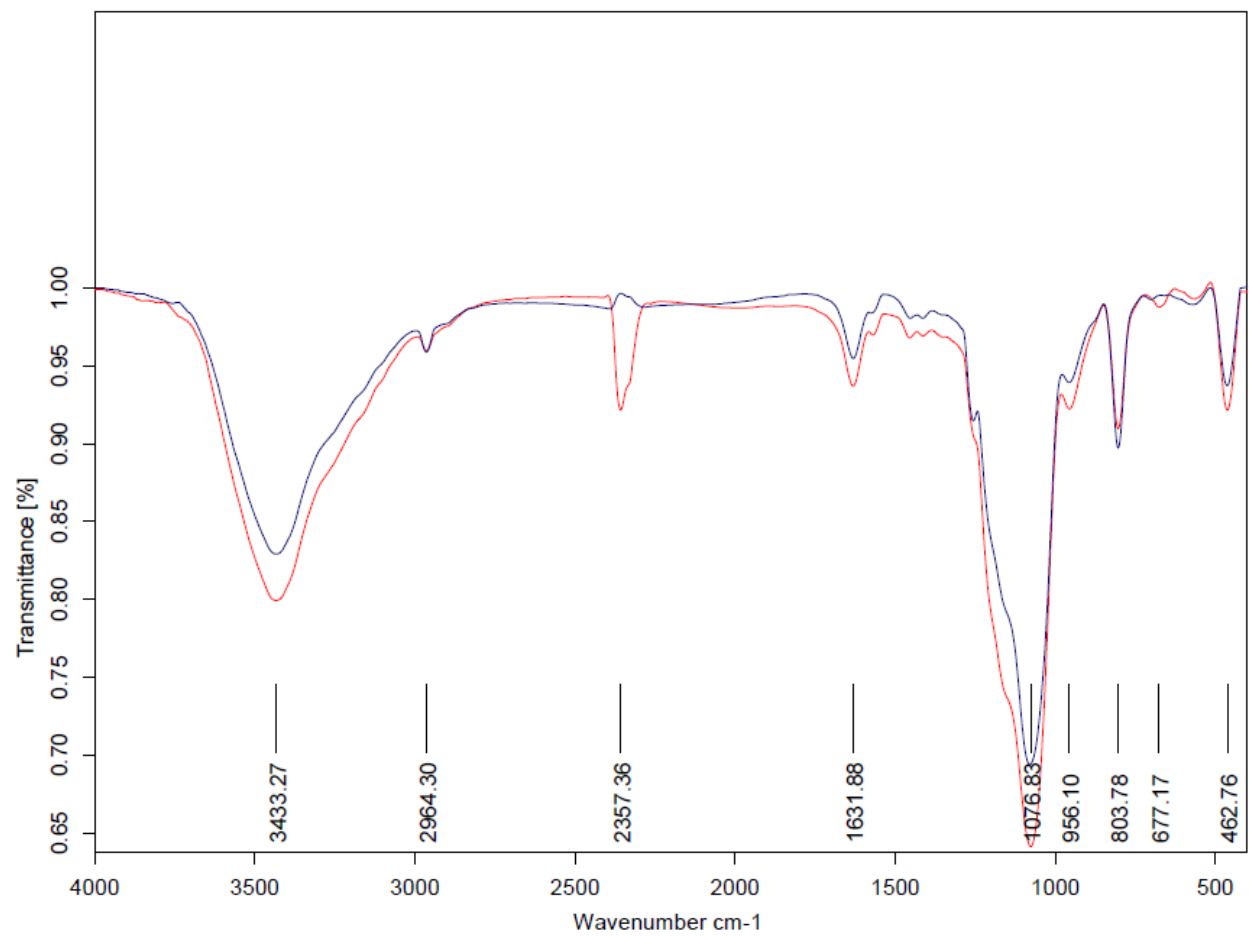


Figure S2: DRIFT-IR spectrum of Au@PMO-IL catalyst (red) and PMO-IL (blue)

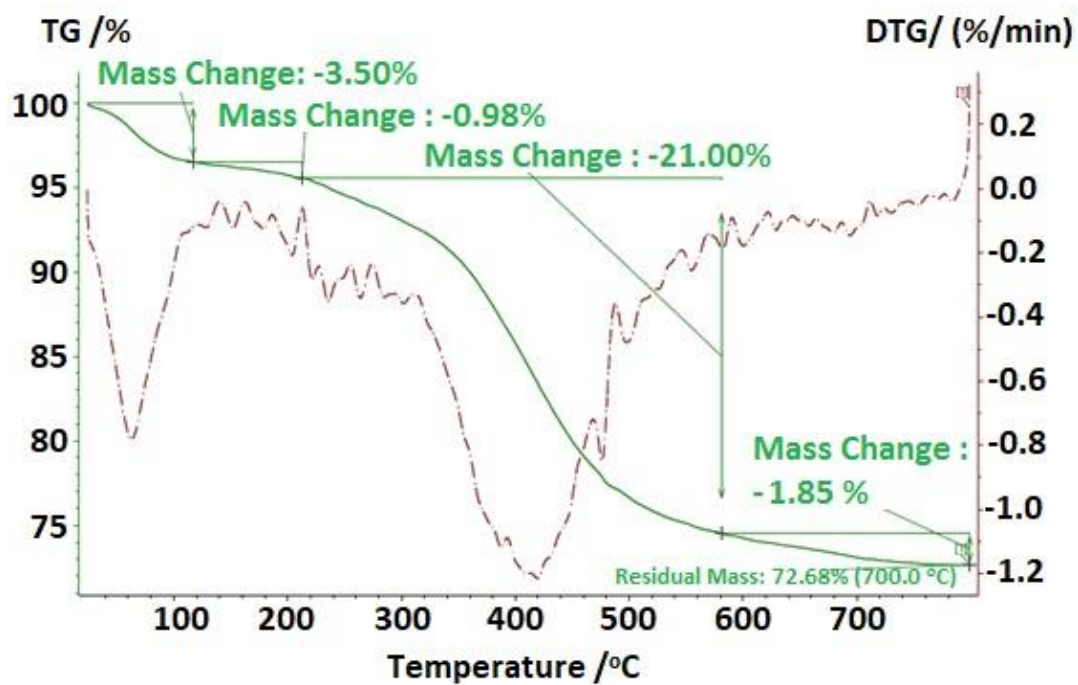


Figure S3: TGA analysis of PMO-IL support

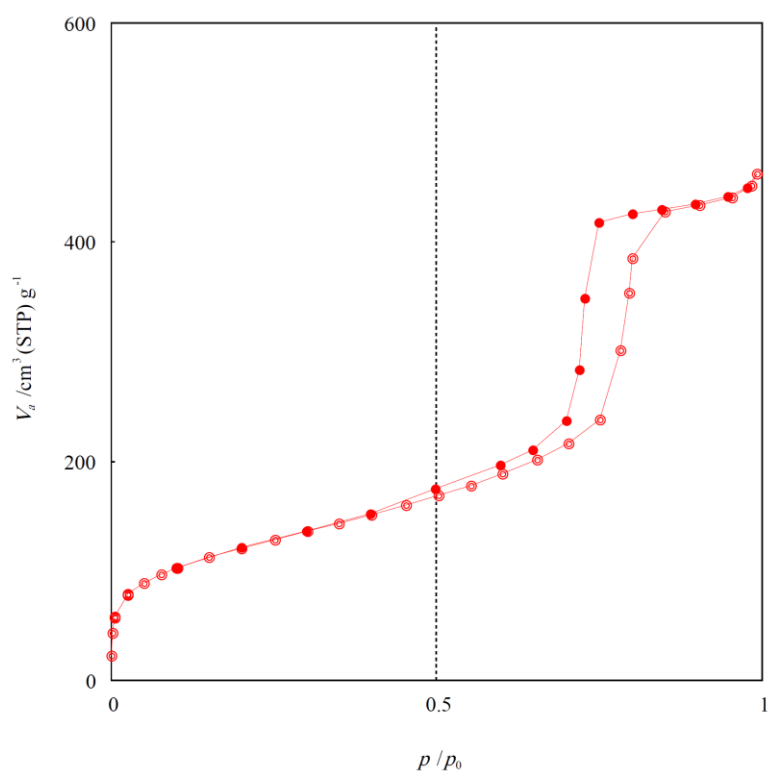


Figure S4: N₂ adsorption-desorption isotherms for Au-Catalyst-(1)

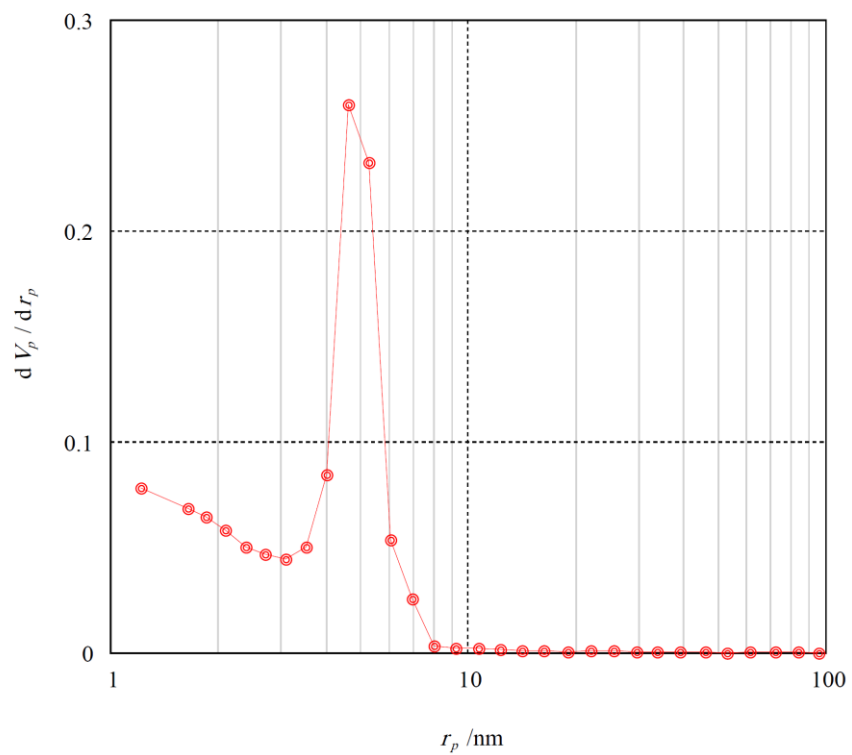


Figure S5: BJH Pore size distributions for Au-Catalyst-(1)

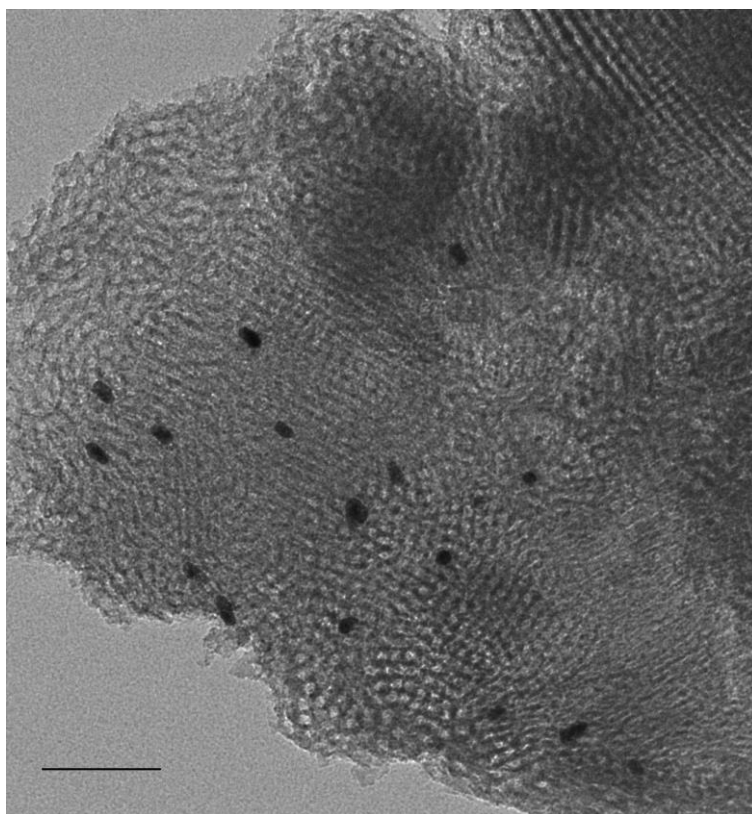


Figure S6: TEM image for catalyst Au-Catalyst-(1)-Scale bar: 100 nm

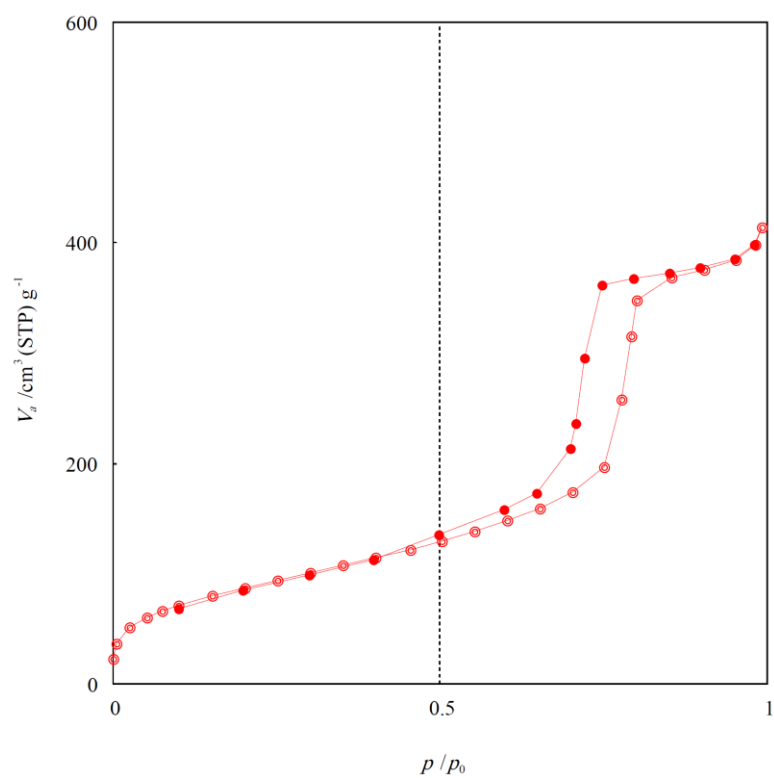


Figure S7: N_2 adsorption-desorption of Au-Catalyst-(2)

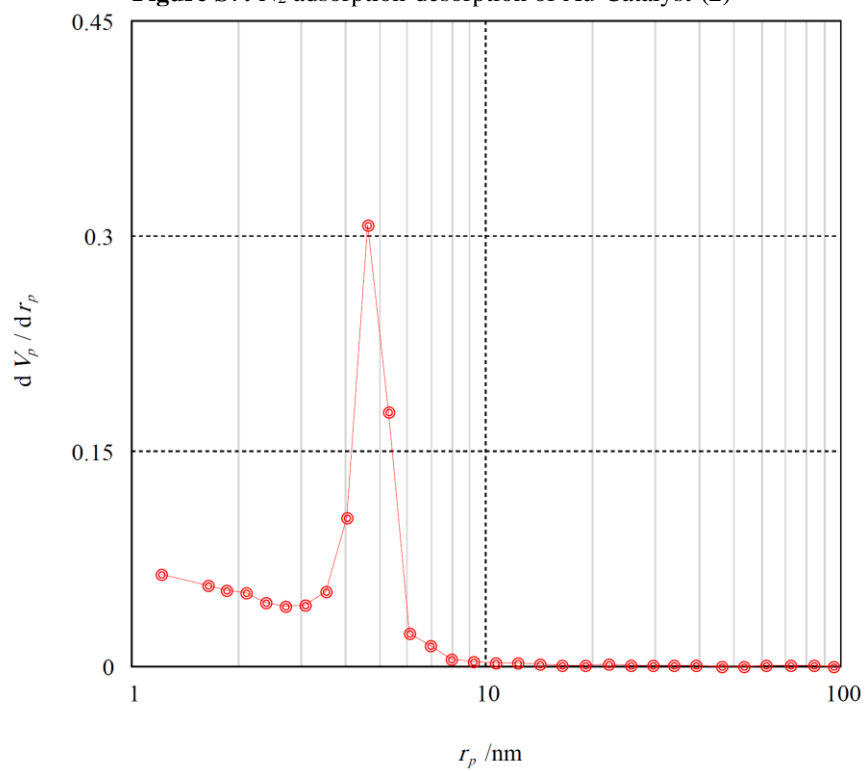


Figure S8: BJH Pore size distributions for Au-Catalyst-(2)

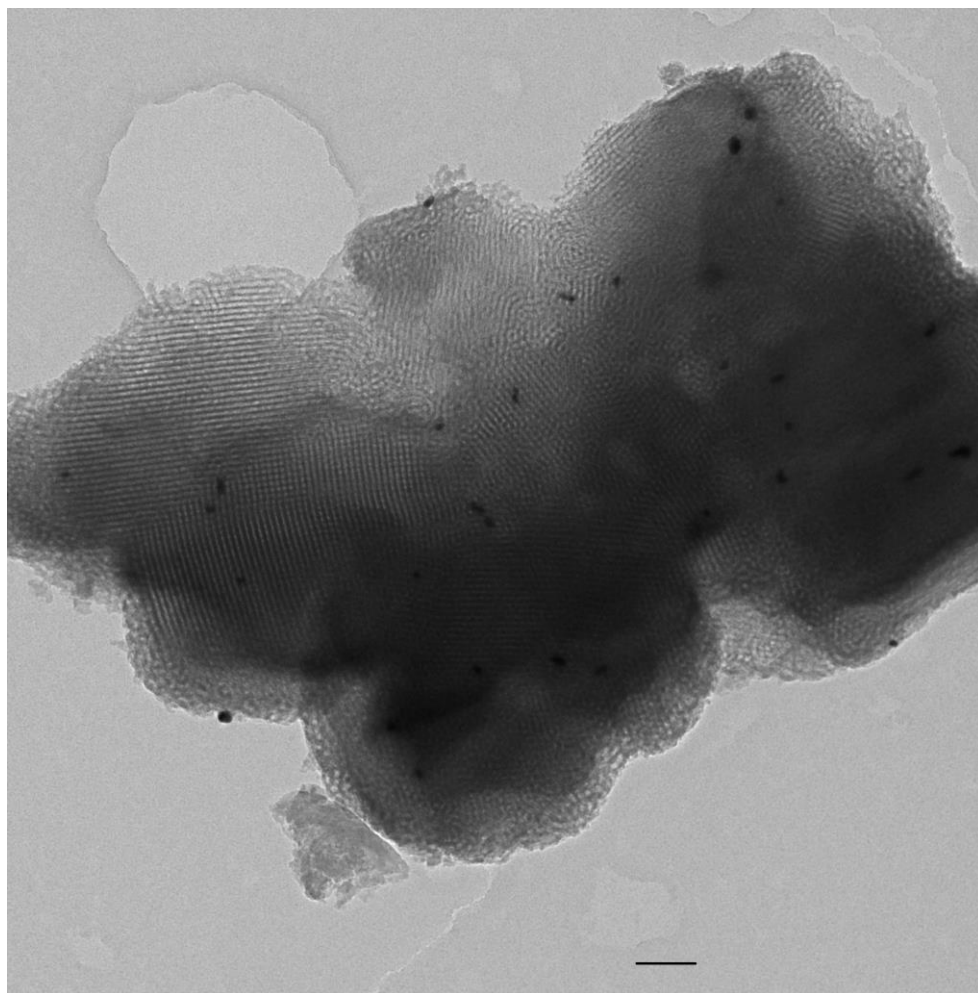
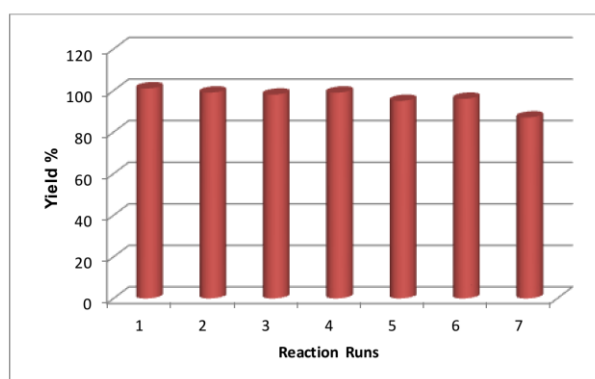


Figure S9: TEM image for Au-Catalyst-(2)-Scale bar: 100 nm



	1	2	3	4	5	6	7
Yield(%)	100	97	95	95	90	90	80
Time(h)	4	6	6	6	6	6	6

Figure S10: Recycling data for Au@PMO-IL during aerobic oxidation of benzylalcohol. (Total TON : 3225)

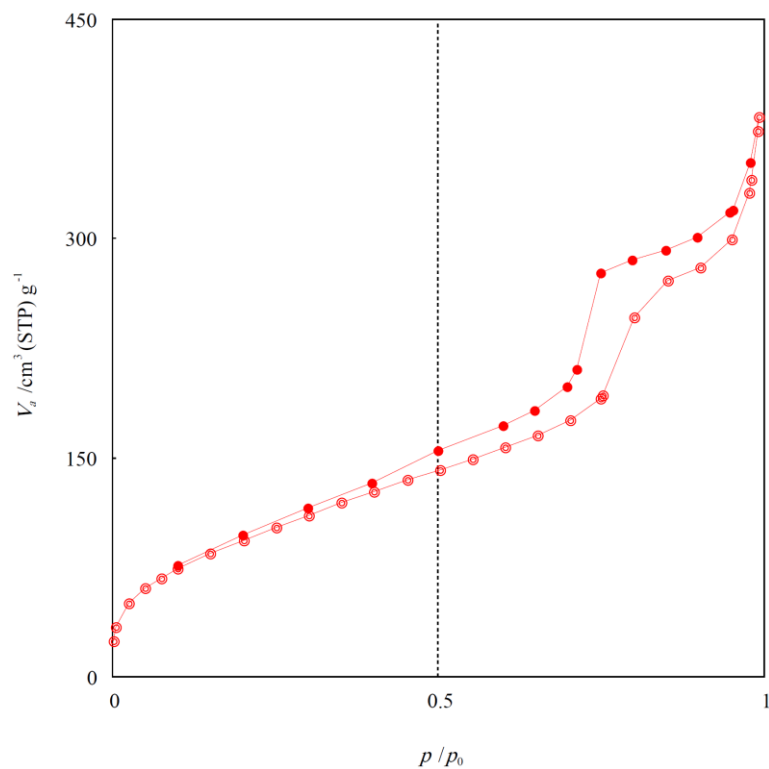


Figure S11: Nitrogen adsorption-desorption isotherms for recovered Au@PMO-IL catalyst after 7th run from the oxidation of benzylalcohol

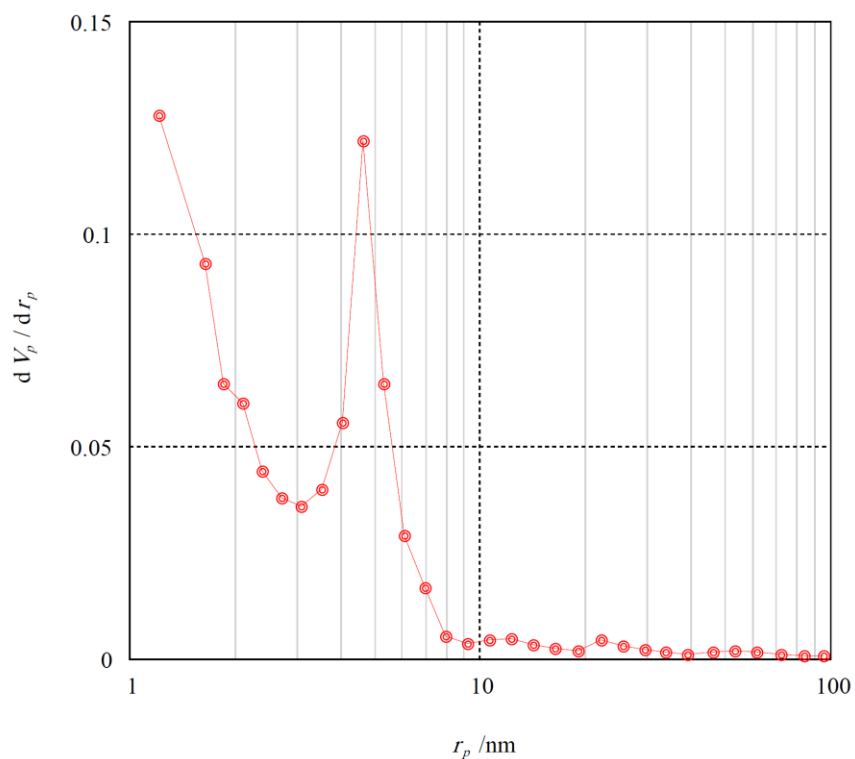


Figure S12: BJH Pore size distributions for recovered Au@PMO-IL catalyst after 7th run from the oxidation of benzylalcohol

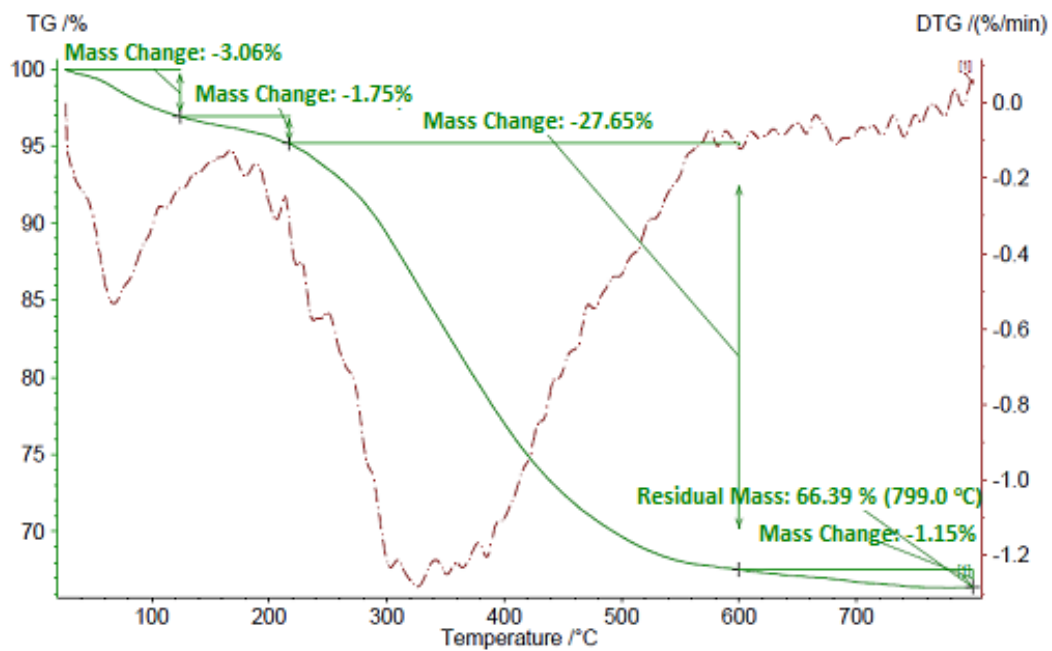


Figure S13: TGA analysis of recovered Au@PMO-IL catalyst after 7th run from the oxidation of benzylalcohol