Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

A Metal- and Solvent-Free Synthesis of aminoalcohols under Continuous Flow Conditions

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Section S1: Polymer dope composition and creation of polyamide-imide hollow fibers.

The porous polyamide-imide hollow fiber (i.e., PAI) was synthesised in this study. Torlon 4000T-HV, a commercially available polyamide-imide (PAI) (Solvay Advanced Polymers, Alpharetta, GA), and polyvinylpyrrolidone (PVP) (average Mw≈ 1300 K, Sigma-Aldrich) were used for the correspondence of the composite hollow fiber catalysts. The PVP was dried at 80 °C for 24 h under vacuum to release pre-sorbed water vapor. After that, Torlon was dried at 110 °C for 24 h proceed using De-ionized (DI) water that was added as a nonsolvent into the fiber dope. N-Methyl-2-pyrrolidone (NMP) was embedded as the solvent to form the spinning dope, which could attribute to its strong solvent power, low volatility, and good water miscibility. Therefore, all solvents and nonsolvents were used as-received with no purification or modification. Methanol and hexane were used for solvent exchange after fiber catalyst spinning. Besides, the methanol was used to remove excess water from the fibers. Namely, spinning dope to create a 10/90 (weight ratio) catalyst/Torlon contains the polymer PAI, zirconia particles, NMP (solvent), water (nonsolvent), and additives (PVP). The optimized polymer dope compositions and spinning conditions are tabulated in Table S1.

Table S1: Optimized spinning conditions for corresponding of polyamide-imide hollow fibers.

Dope composition (PAI/PVP/NMP/H_2O) (wt %)	24/7/64.5/4.5
Dope flow rate	600 mL/hr
Sheat fluid (NMP/H_2O)	50/50 wt%
Sheat flow rate	50 mL/hr
Bore fluid (NMP/H_2O)	88/12 wt%
Bore fluid flow rate	200 mL/hr
Air gap	10 cm
Take up rate	8.5 m/min
Operating temperature	60 °C
Quench bath temperature	60 °C

Figure S1 is a schematic representation of the hollow fiber creation process. A standard bore fluid involved in this work consists of NMP and water with the weight ratio of 88:12.¹ An appropriate Torlon core dope composition (determined by cloud point method and rheology measurements) was fed to the middle spinneret compartment.

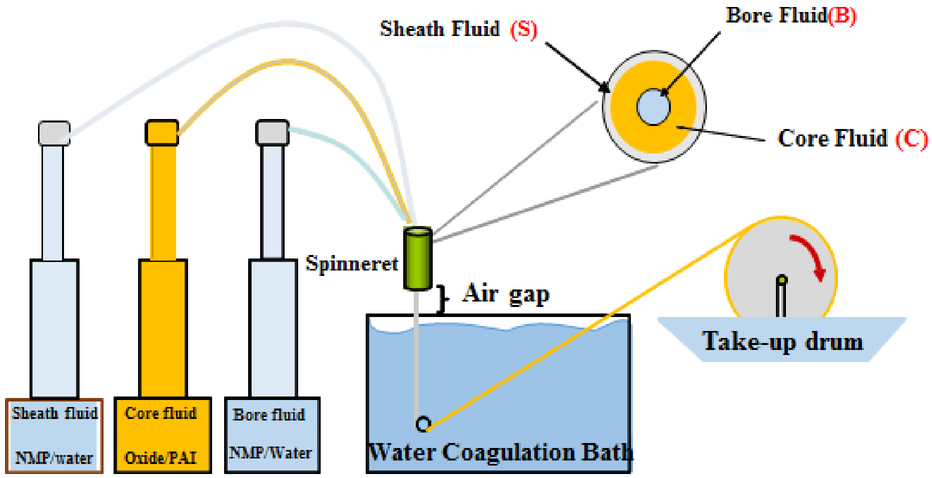


Figure S1: Schematic diagram of polyamide-imide hollow fibers spinning apparatus.

Section S2: Post spinning infusion and amine grafting of polyamide-imide hollow fibers.

The 3-Aminopropyltriethoxysilane (APS) was used as the grafting agents for grafting zirconia-Torlon fiber catalysts.[2–4] The amine grafting was performed in a mixture of a non-polar solvent (toluene) and a polar protic solvent (water). The water content of the mixture was kept within the range 0.01- 1.00 wt%. Additionally, water has played a vital role for protonating APS and hydrolyzing methoxy groups in dry liquid. As shown, exposure of APS to moisture obstructs strong hydrogen bonds leads to the formation of polysiloxane. It was clearly that a water content of 1.00 wt% caused the rise to highest amine loading. As a mentioned above, after the PAIHFs composites were formed, they were subjected to a methanol solvent exchange process demonstrated by exposure to different APS/toluene/water (ratio 9.9:90.0:0.1 wt%) solution mixtures with varying immersion times, from 1 to 6 h. As a result the PAIHFs catalysts were removed from the amine solution and rinsed with hexane for 30 min at ambient temperature to wash away the ungrafted APS deposited onto the fiber surface. Finally, APS-grafted PAIHF catalysts were placed in a preheated vacuum oven and cured for 1 h at 60 °C. The APS aminosilane can form a durable bond with the PAIHFs in this post-spinning immersion step. The optimum infusion condition was determined by soaking 0.15 g of PAIHF catalysts in a 100 g solution of different concentrations of APS in toluene/water mixture (i.e., 5, 10, 15, and 20 wt% APS) at room temperature for 1-8 h. For 10 wt% APS/toluene/water solution and an infusion time of 2 h, the fibers exhibited an optimum amount of amine loading.

The APS grafted PAIHFs were further modified by reaction with 1,3-dibromopropane in dry toluene at 80 °C for 2 h to give the ammonium bromide derivatives. Finally, the fibers were solvent exchanged with toluene and dried under vacuum (30 mTorr) at 85 °C to remove the residual solvent from the pores, yielding the Br-immobilized APS-grafted PAIHFs (Br/APS/PAIHFs).

Section S3: Hollow fiber trifunctional catalyst cheracterization

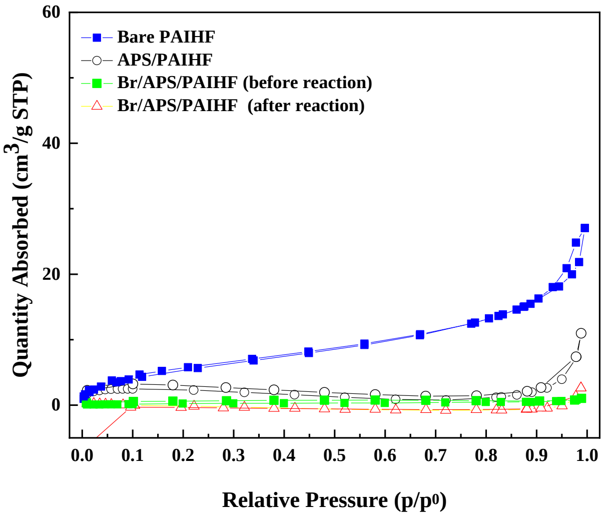


Figure S2. Nitrogen adsorption/desorption isotherms for bare PAIHFs, APS/PAIHF and Br/APS/PAIHF before and after reaction.

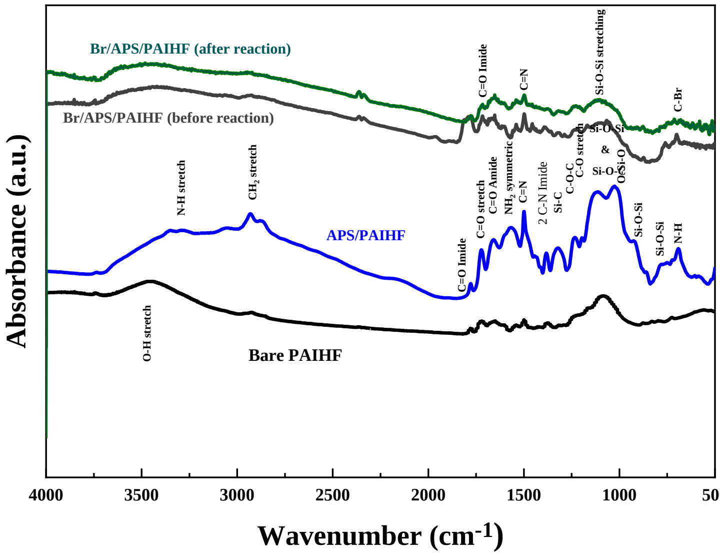
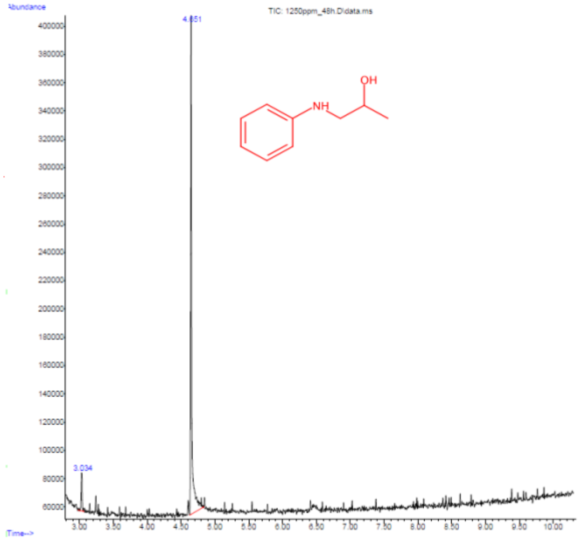


Figure S3. IR spectra of bare PAIHF, APS/PAIHF and Br/APS/PAIHF before and after reaction.

Section S4: Product characterization



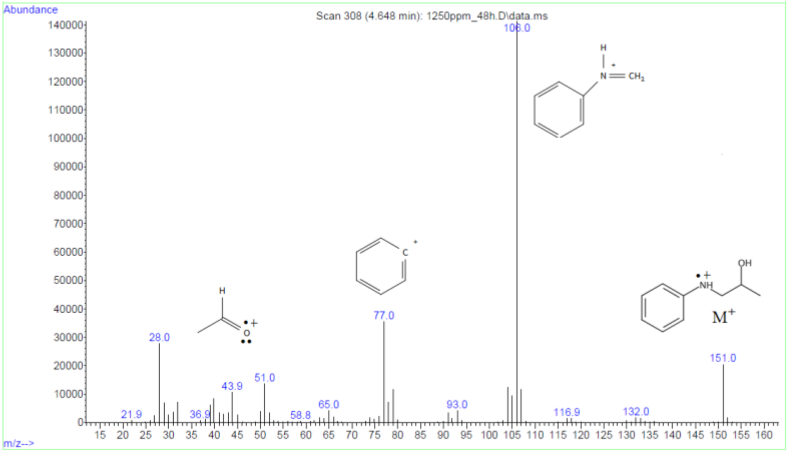


Figure S4. GC-MS spectra for the 1-(phenylamino) propan-2-ol

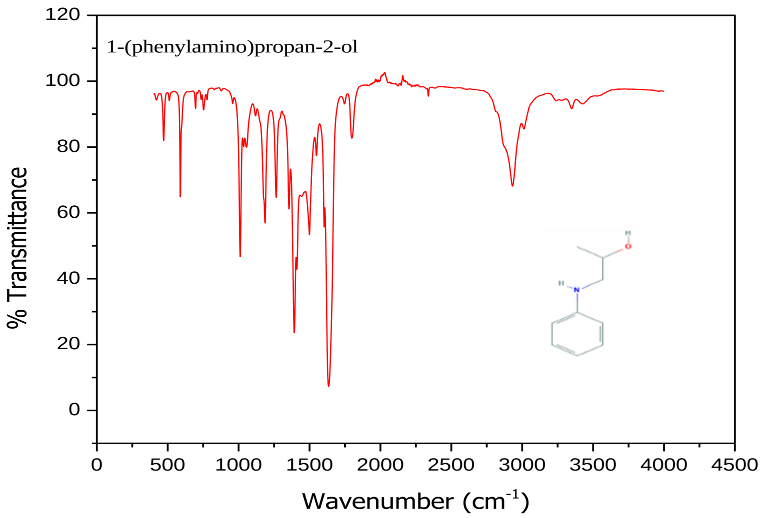


Figure S5. FTIR spectra of 1-(phenylamino) propan-2-ol.

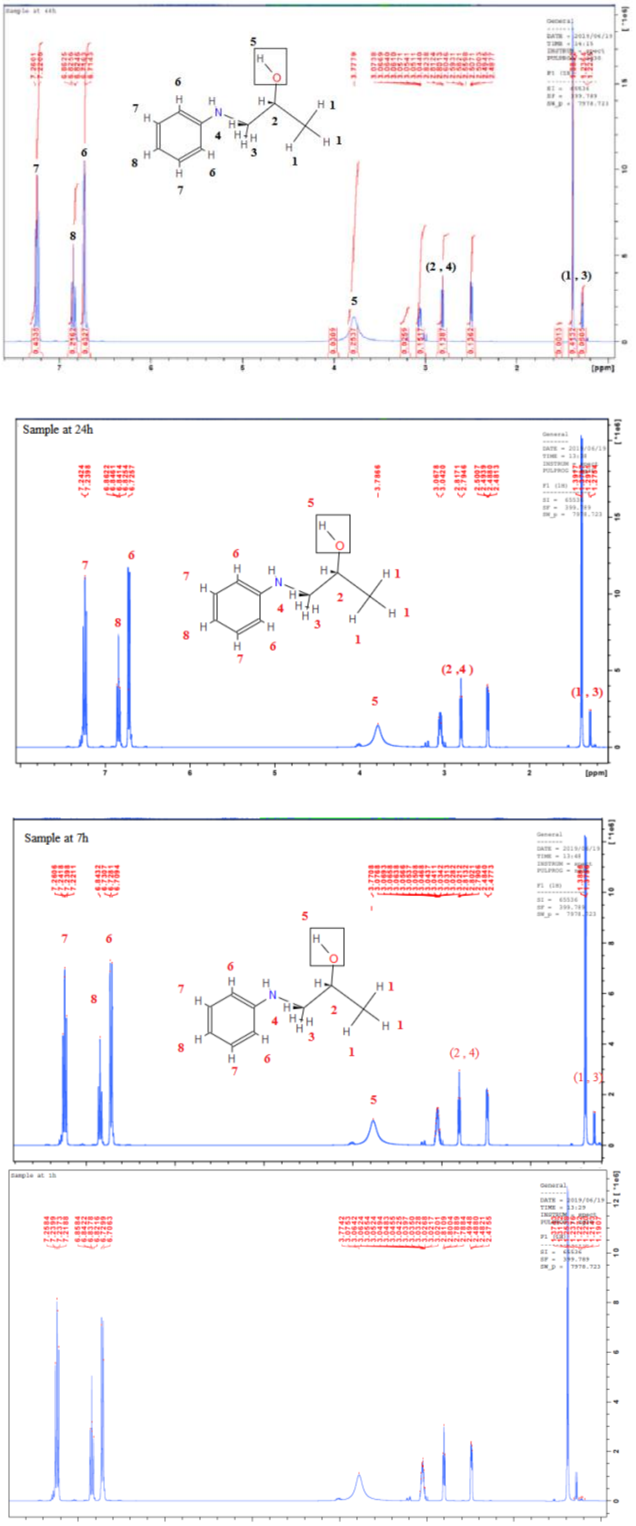


Figure S6. 1H NMR spectra of the 1-(phenylamino) propan-2-ol, at 1, 7, 24 and 48 h.

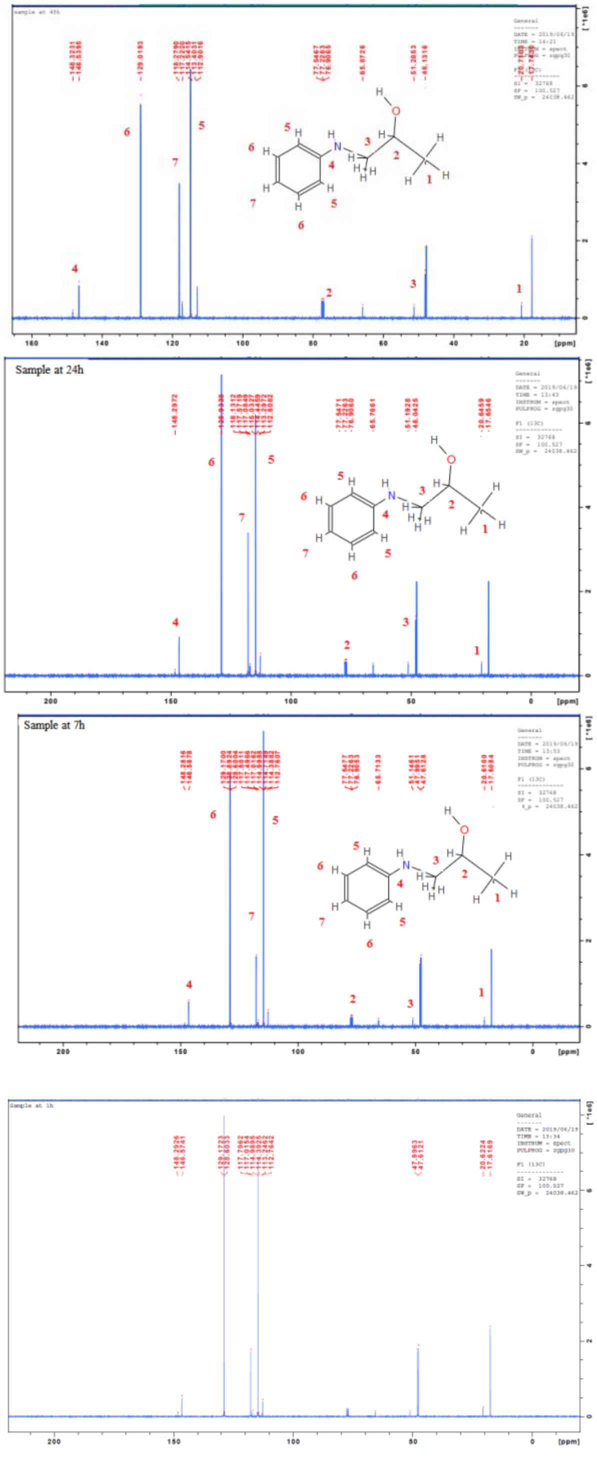
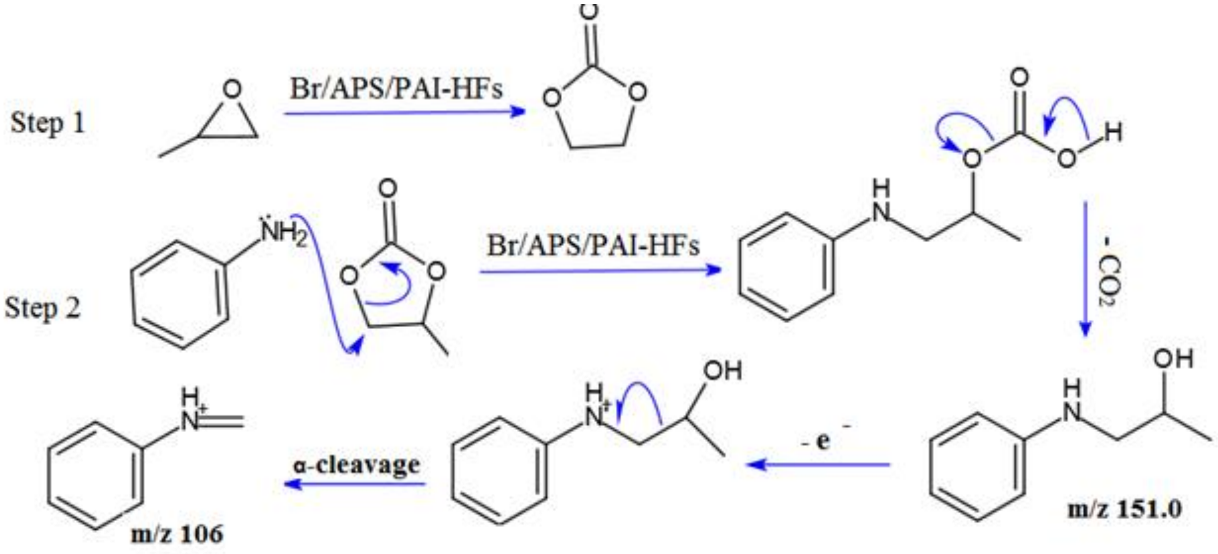


Figure S7. 13C NMR spectra of the 1-(phenylamino) propan-2-ol, at 1, 7, 24 and 48 h.



Scheme S1: the proposed reaction mechanism

References:

[1] A.A. Rownaghi, D. Bhandari, S.K. Burgess, D.S. Mikkilineni, J. Appl. Polym. Sci. 134 (2017) 1–10.
[2] A.A. Rownaghi, A. Kant, X. Li, H. Thakkar, A. Hajari, Y. He, P.J. Brennan, H. Hosseini, W.J. Koros, F. Rezaei, ChemSusChem 9 (2016) 1166–1177.
[3] Y. He, A. Jawad, X. Li, M. Atanga, F. Rezaei, A.A. Rownaghi, J. Catal. 341 (2016) 149–159.
[4] Y. He, F. Rezaei, S. Kapila, A.A. Rownaghi, ACS Appl. Mater. Interfaces 9 (2017) 16288−16295.