

**SBA-15 Functionalized TEMPO Confined Ionic Liquid: An Efficient
Catalyst System for Transition-Metal-Free Aerobic Oxidation of
Alcohols with Improved Selectivity**

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Materials and Methods

Preparation of SBA-15: The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers (see reference 16b of the manuscript). In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw $\cong$ 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 Soxhlet apparatus for 18 h to remove the surfactant molecules. It was dried in air at 110 °C overnight.

Preparation of aminopropyl-SBA-15: Refluxing the activated SBA-15 (10 g) with 3-aminopropyltrimethoxysilane (3.5 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 (Soxhlet) and then dried in oven at 110 °C overnight to give the surface bound amine (AMP-SBA-15) group at a loading *ca.* 0.35 mmol g⁻¹ (by elemental analysis).

Preparation of SBA-15-Supported-TEMPO: To a mixture of aminopropyl functionalized SBA-15 (3 g, 1.1 mmol) in super dry CH₃OH (15 mL), 4-oxo-TEMPO (1.5 mmol, 0.281) was added, followed by NaBH₃CN (0.125 g, 2 mmol). The reaction mixture was then stirred vigorously for 3

days at ambient temperature. The solution was removed by filtration, and the remaining solid was finally extracted with methanol in a Soxhlet apparatus for 3 days, to remove any surface adsorbed materials. The degree of functionalization was determined to be 0.33 mmol g^{-1} by elemental analysis and kinetic measurement of NH_3 created using simultaneous thermal analysis (Fig 7S).

Preparation of SBA-15-Functionalized TEMPO Confined Butylmethylimidazolium bromide [BMIm]Br (IL@SBA-15-TEMPO, 2)

To prepare **2**, briefly, a dispersion of 4 g of SBA-15-TEMPO **1** in acetone (30 mL) was first sonicated to obtain a homogeneous distribution of **1** in acetone. The resulting dispersion were then subjected to mix under vigorous stirring with a solution of 2 g of butylmethylimidazolium bromide [BMIm]Br in 70 mL acetone. The mixture was stirred for further 3h at room temperature. To this end, the solvent was evaporated under reduced pressure to afford a very fine bright yellow and free-flowing solid denoted as IL@SBA-15-TEMPO **2**. Before the use in catalysis, the material was further conditioned at 50 °C under vacu over P_2O_5 as drying agent for 20 h.

General procedure for Aerobic oxidation of Alcohols:

Oxidation of Primary and Secondary Benzylic Alcohols (Method A): A mixture of alcohol (10 mmol), *t*-BuONO (0.041 g, 4 mol%) and catalyst **2** (0.45 g, ~1 mol%) in AcOH (3 mL) was prepared in a two-necked flask at 40 °C. The flask was then filled with pure oxygen (balloon filled). The resulting mixture was stirred at 40 °C under an oxygen atmosphere (for the indicated time in the Table 2. The progress of the reaction was monitored by GLC using internal standard addition method. After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed three times with Et_2O ($3 \times 25 \text{ mL}$) the excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds (Table 2). In most cases, the selectivity of products was analyzed by GC to be more than 99% without any chromatographic purification.

Oxidation of Secondary Aliphatic Alcohols (Method B): A mixture of alcohol (10 mmol), *t*-BuONO (0.041 g, 4 mol%), NaBr (0.15 g, 15 mol%) and catalyst **2** (0.90 g, ~2 mol%) in AcOH (3 mL) was

prepared in a two-necked flask at 80 °C. The flask was then filled with pure oxygen or air (balloon filled). The resulting mixture was stirred at 80 °C under an oxygen atmosphere for the indicated time in the Table 2. The progress of the reaction was monitored by GLC using internal standard addition method. After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed three times with Et₂O (3 × 25 mL) the excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds (Table 2). In most cases, the purity and selectivity of products was analyzed by GC to be more than 99% without any chromatographic purification.

Oxidation of Allylic Alcohols (Method c): A mixture of alcohol (10 mmol), *t*-BuONO (0.041 g, 4 mol%) and catalyst **2** (1.35 g, ~3 mol%) in AcOH (3 mL) was prepared in a two-necked flask at 60 °C. The flask was then filled with pure oxygen (balloon filled). The resulting mixture was stirred at 60 °C under an oxygen atmosphere for the indicated time in the Table 2. The progress of the reaction was monitored by GLC using internal standard addition method. After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed three times with Et₂O (3 × 25 mL) the excess of solvent was removed under reduced pressure to give the corresponding carbonyl compounds (Table 2). In most cases, the purity of products was analyzed by GC to be more than 99% without any chromatographic purification.

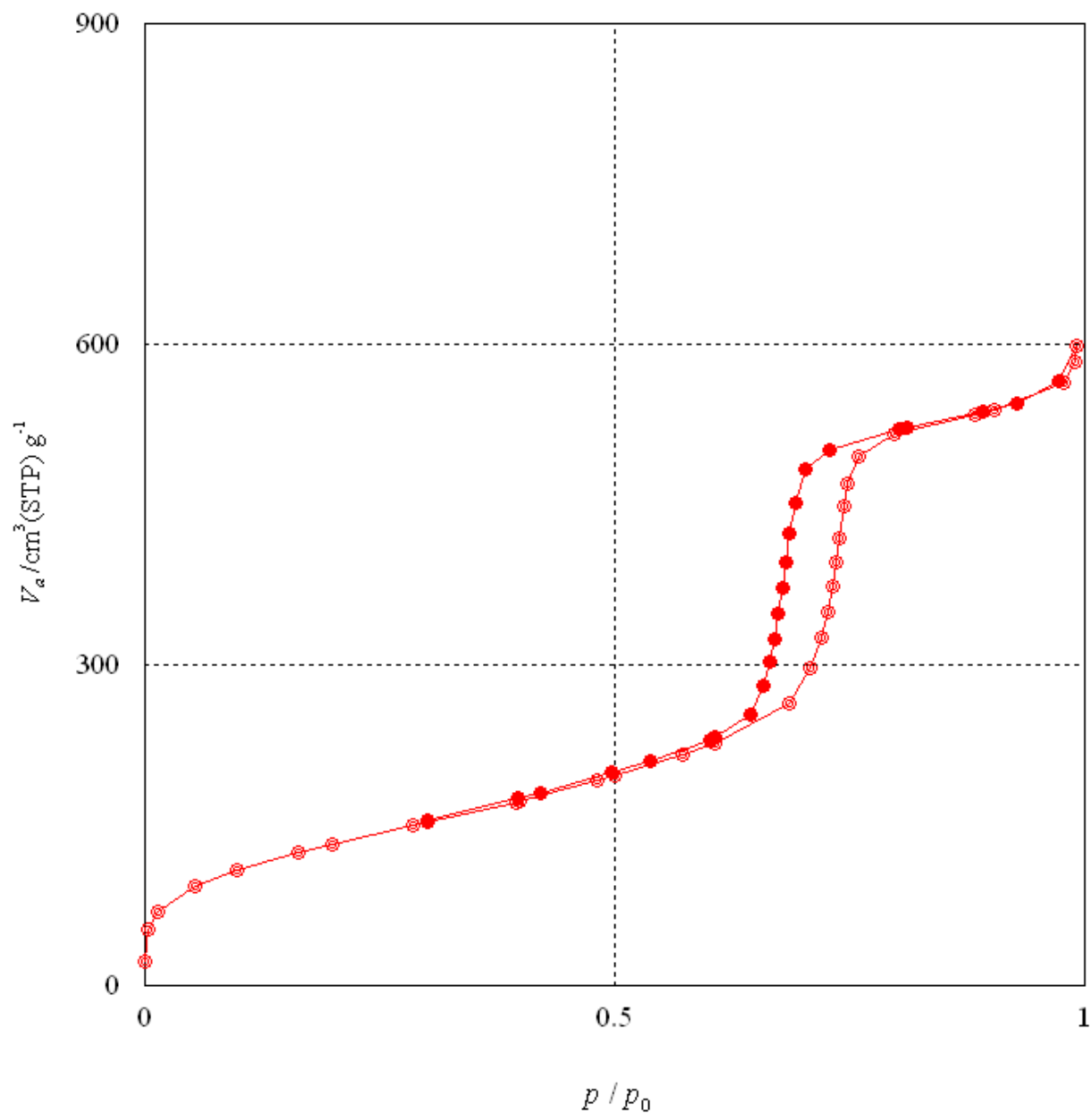


Fig 1S. N_2 adsorption-desorption isotherm of SBA-15-TEMPO catalyst **1** prior to ionic liquid loading

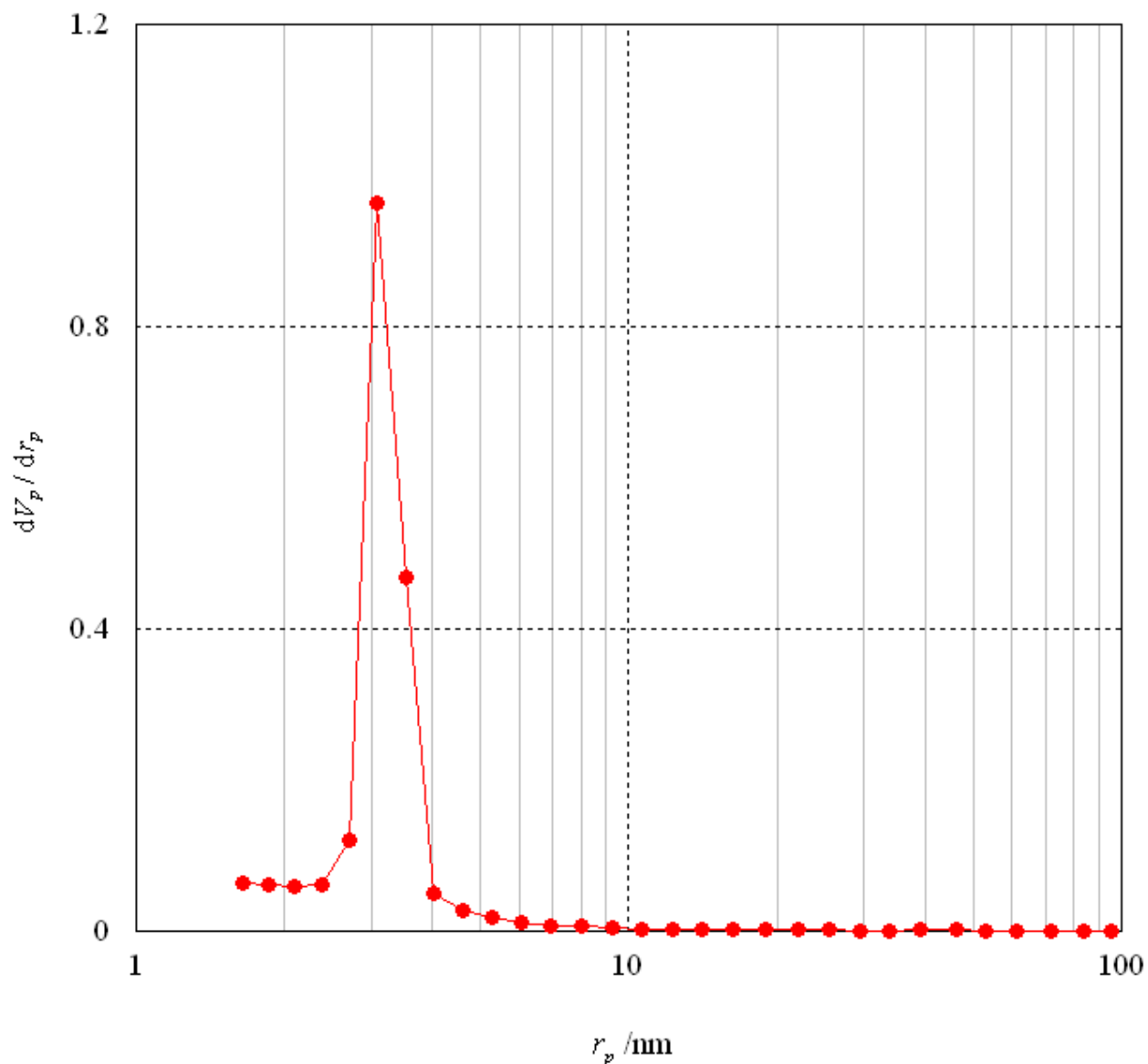


Fig 2S. BJH average pore size of SBA-15-TEMPO catalyst **1** prior to ionic liquid loading

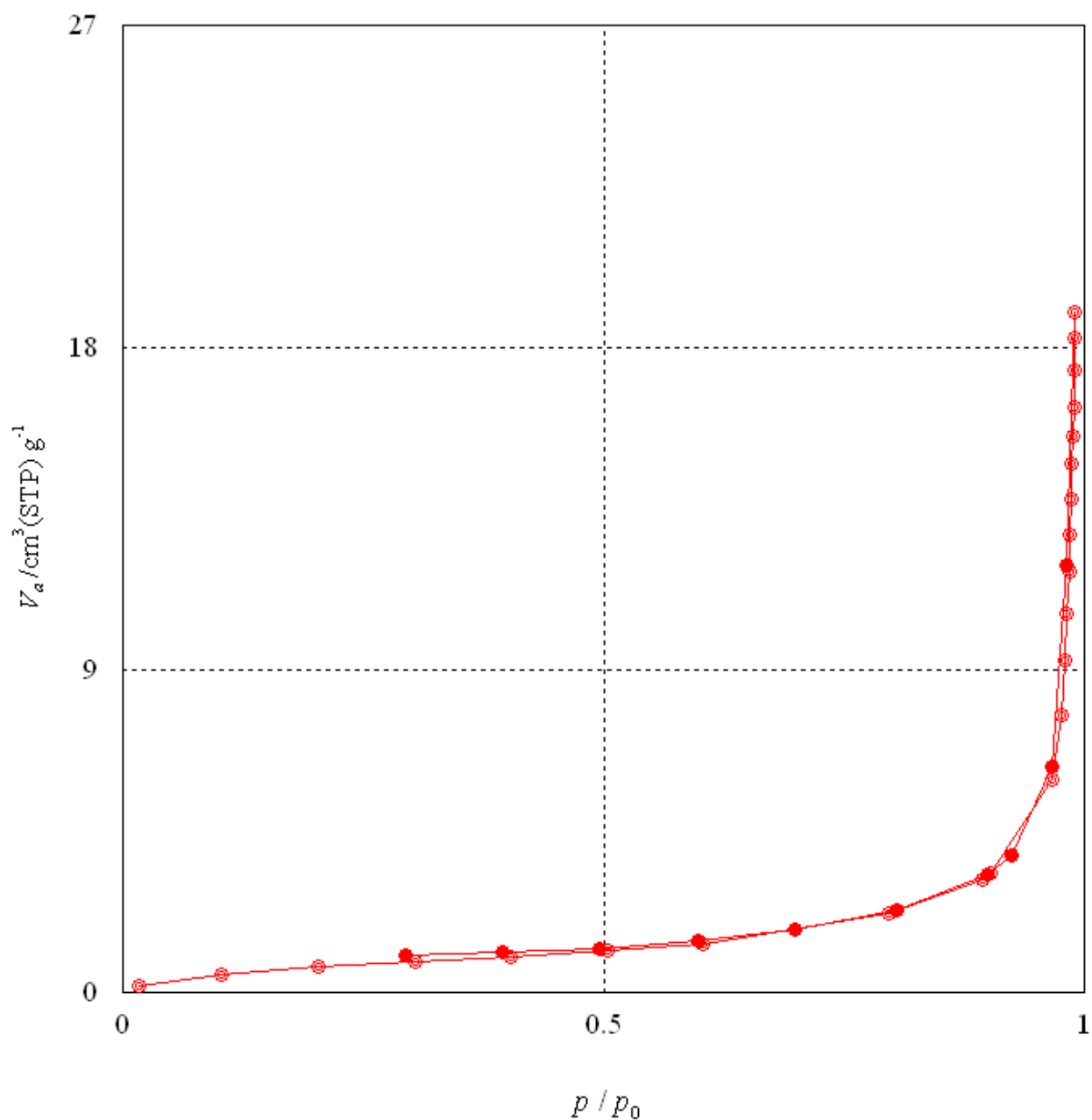


Fig 3S N_2 Adsorption-desorption isotherm for SBA-15-functionalized-TEMPO confined ionic liquid **2**

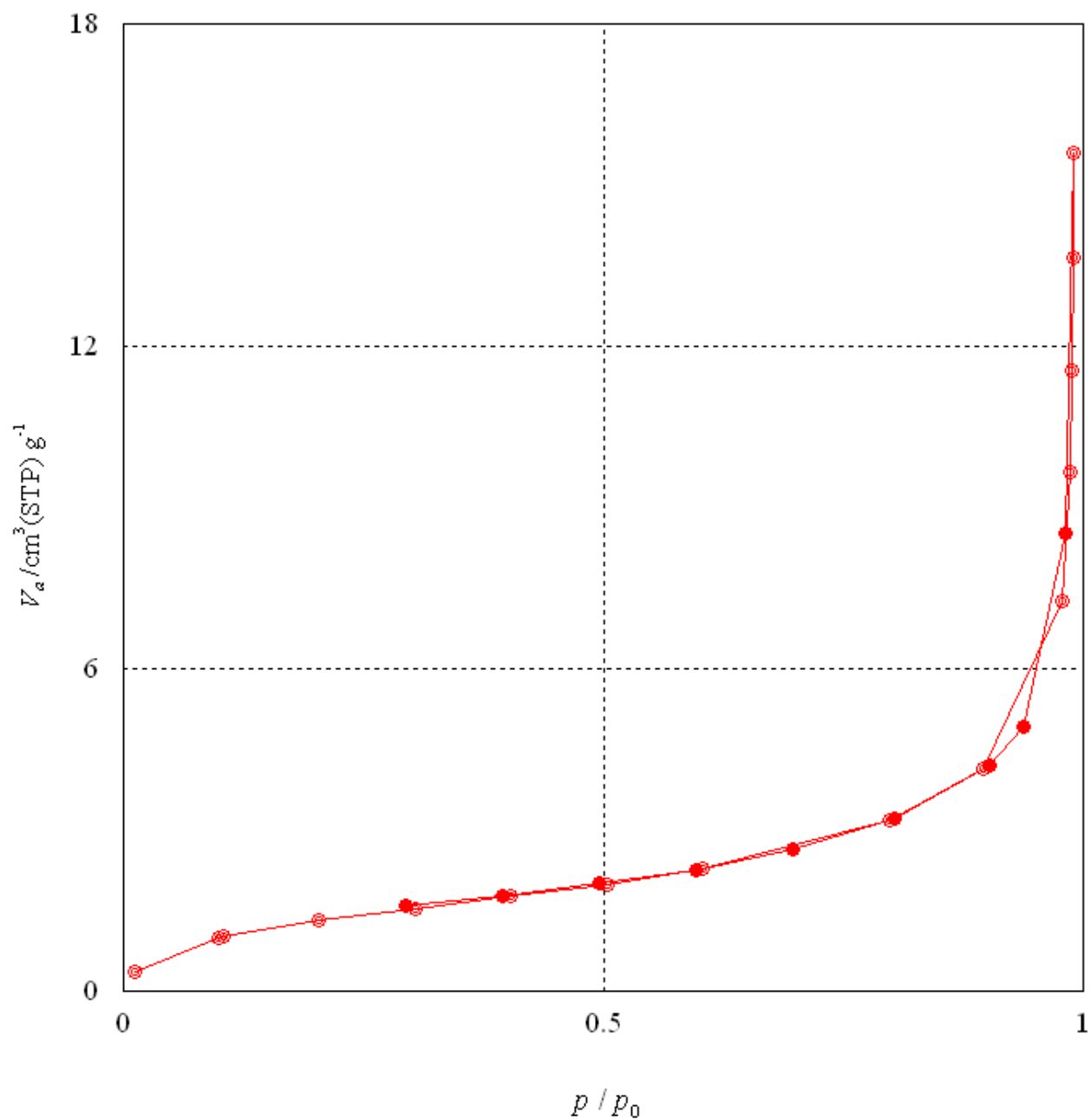


Fig 4S. N_2 Adsorption-desorption isotherm of recovered SBA-15-functionalized-TEMPO confined ionic liquid **2** from aerobic oxidation of benzyl alcohol

Table 1S. Yields obtained in the aerobic oxidation of benzyl alcohol to afford benzaldehyde in the presence of **2**.

Reaction Run	1	2	3	4	5	6	7	8	9	10	11	12
Reaction Time (h)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
GC Conversion (%)	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99	>91

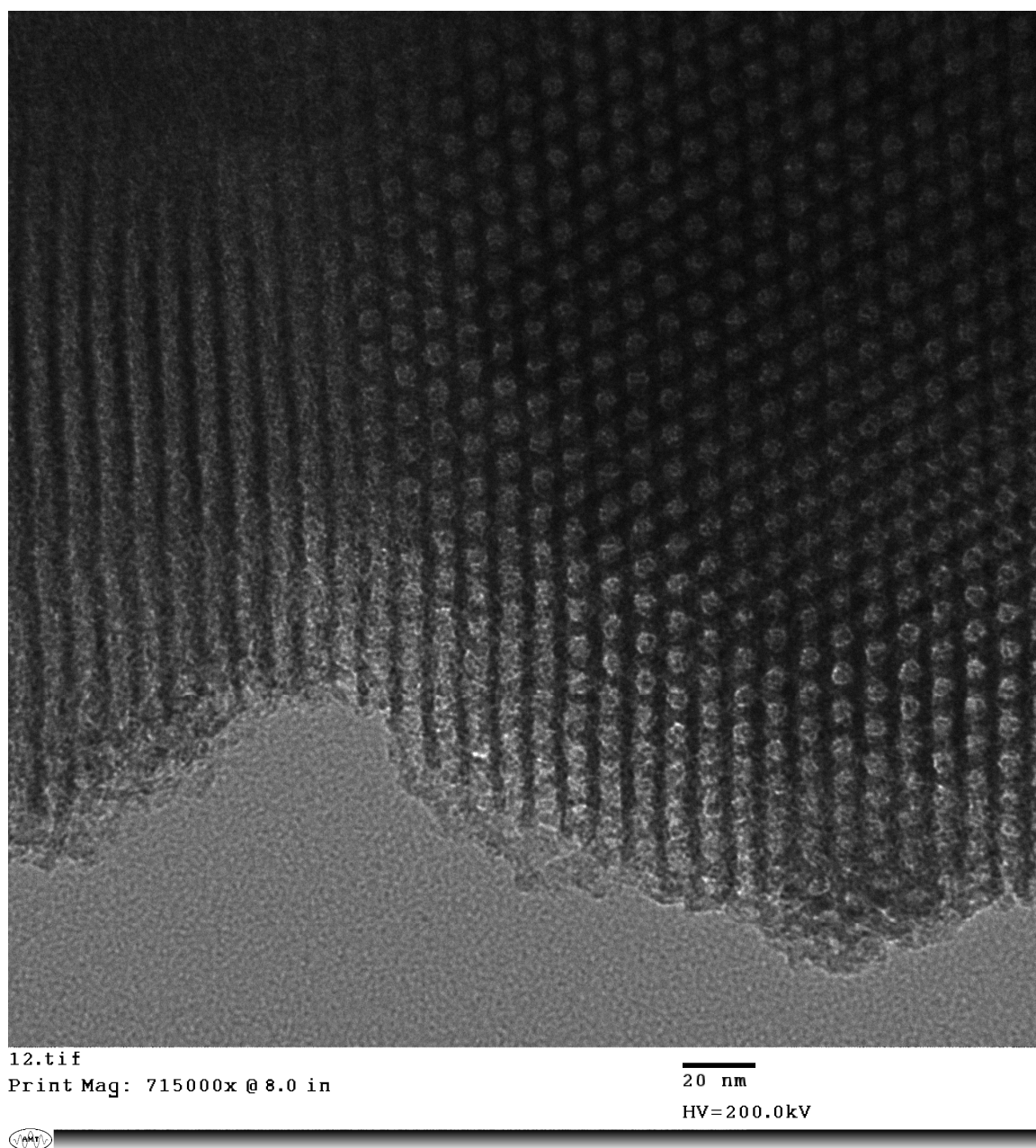


Fig 5S. TEM image of recovered SBA-15-functionalized-TEMPO confined ionic liquid **2** from aerobic oxidation of benzyl alcohol