# **Supplementary Information**

# Catalytic imidazolysis of PET plastic waste using self-assembled NbO<sub>x</sub> nanorods

Bhattu Swapna<sup>a,#</sup>, CK Fiba<sup>a,b,#</sup>, Madam Bobby Barnabas<sup>a</sup>, Regulagadda Suryanarayana<sup>c</sup>, Putla Sudarsanam<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi 502284, Telangana, India <sup>b</sup>School of Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam 686560, Kerala, India <sup>c</sup>Extrovis Pvt Ltd, Kukatpally 500072, Hyderabad, Telangana, India

Corresponding author email: <a href="mailto:sudarsanam.putla@chy.iith.ac.in">sudarsanam.putla@chy.iith.ac.in</a>

# These authors contributed equally

#### 1. Materials and chemicals

PET waste bottle (Kinley), imidazole (SRL, 99% purity,  $C_3H_4N_2$ ), methanol (SRL, 99.8% purity, CH<sub>3</sub>OH), commercial niobium pentoxide (SRL, 99.9% purity, Nb<sub>2</sub>O<sub>5</sub>), ammonium niobate oxalate hydrate (Sigma Aldrich, 99.5% purity, C<sub>4</sub>H<sub>4</sub>NNbO<sub>9</sub>·xH<sub>2</sub>O), and sodium carbonate (SRL, 99.5% purity, Na<sub>2</sub>CO<sub>3</sub>).

### 2. Catalyst synthesis

The  $Nb_2O_5$  nanospheres and self-assembled nanorod-like morphology of  $NbO_x$  are prepared using modified hydrothermal methods.

**2.1** Nb<sub>2</sub>O<sub>5</sub> nanospheres (Nb<sub>2</sub>O<sub>5</sub>-NSp): Firstly, the required amount of Nb precursor was dissolved in 35 mL of deionized water<sup>1</sup>. Then, about 35 mL of ethanol was added and stirred for 30 min at room temperature. This solution was transferred to the Teflon-lined autoclave for hydrothermal treatment at 180 °C for 24 h. Then, the solid sample was washed with deionized water multiple times by centrifugation till the pH reached 7. The sample was ovendried overnight at 100 °C and then subjected to thermal treatment at 300 °C for 2 h to get the Nb<sub>2</sub>O<sub>5</sub>-NSp catalyst.

**2.2 Self-assembled nanorod-like morphology of NbO**<sub>x</sub> (NbO<sub>x</sub>-NR): The required amount of Nb precursor was dissolved in 120 mL of deionized water (Scheme S1)<sup>2</sup>. Then, 1 g of sodium carbonate was added and magnetically stirred for 30 min at room temperature. This solution was transferred into the PPL-lined autoclave for hydrothermal treatment at 200 °C for 12 h. Then, the obtained solid sample was centrifuged with deionized water and ethanol until pH reached 7 and oven-dried for 12 h (80 °C), which was further calcined at 300 °C for 2 h to get the self-assembled NbO<sub>x</sub>-NR catalyst.



Scheme S1. Hydrothermal synthesis procedure of self-assembled nanorod-like NbO<sub>x</sub> catalyst.

## 3. Reaction procedure of PET imidazolysis

The reaction of PET imidazolysis was carried out using imidazole (IMD) at 160 °C for 4 h in methanol solvent **(Scheme S2)**. The used Kinley PET bottles (collected from the household) were washed with soap water/acetone, and then oven-dried at 70 °C. After cutting into small pieces, the PET chips were ground with the help of a mixer grinder. Then, the required amount of PET and IMD was taken in a 25 mL pressure tube. The reactions were conducted using a 5 wt% catalyst with respect to the PET amount. After the reaction, centrifugation was carried out to separate the solid fraction from the reaction mixture. The solid fraction contains both the catalyst and the unreacted plastic. But, in the case of the complete

conversion of PET, the solid fraction is nothing but the catalyst. The liquid fraction contains TBI monomer, PET oligomers, unreacted imidazole, and ethylene glycol byproduct. The removal of the imidazole, ethylene glycol, and PET oligomers from the liquid fraction was carried out by adding the required amount of acetonitrile, in which TBI monomer is not soluble<sup>3</sup>. The sample was taken in a beaker, and methanol was evaporated in an oven to collect the pure TBI powder. Then, the yield of isolated TBI monomer was estimated according to the equation given below. A gas chromatograph (GC-2030, Shimadzu) equipped with an HP-5 column and a flame ionization detector was used for the qualitative analysis of ethylene glycol and TBI monomer.



Scheme S2. PET imidazolysis procedure to get the isolated TBI monomer.

The conversion of PET and the yield of TBI were estimated using the following equations<sup>4–6</sup>.

$$PET \ conversion \ (\%) = \frac{Wi \ of \ PET - Wf \ of \ PET}{Wi \ of \ PET} \times 100$$

Wherein W<sub>i</sub> and W<sub>f</sub> are PET's initial and final weights, respectively.

$$TBI \ yield \ (\%) = \frac{Experimental \ yield \ of \ TBI}{Theoretical \ yield \ of \ TBI} \times 100$$

Oligomers conversion (%) = PET conversion (%) - TBI yield (%)

#### 4. Catalyst characterization

The NMR spectra (<sup>1</sup>H, <sup>13</sup>C, and DEPT 135 NMR) were obtained using a Bruker Avance III 400 MHz/54 mm FT-NMR spectrophotometer to confirm the formation of TBI monomer from PET imidazolysis. Powder XRD analysis was conducted to determine crystal planes and phases of NbO<sub>x</sub> materials (Malvern PANalytical non-ambient XRD Empyrean-DY2584 with Ni-filtered Cu K $\alpha$  radiation at 45 kW & 40 mA). The FT-IR analysis of the TBI monomer and PET polymer was performed using a Bruker Alpha instrument (600-4000 cm<sup>-1</sup>) with a DTGS detector. The molecular weight of the TBI monomer was analyzed by HR-MS analysis (Agilent 6538 UHD Q-TOF with electron spray ionization mode) with sodium and potassium metal ionization.

The NH<sub>3</sub>-TPD measurements (ChemBET Pulsar automatic chemisorption analyzer, Quantachrome Instruments) were conducted to estimate the acidity of the catalysts. The samples were pretreated at 200 °C for 1 h under He flow and cooled to 100 °C. Then, NH<sub>3</sub> adsorption was facilitated by flowing NH<sub>3</sub>/He (5 vol%) at 100 °C. The sample temperature gradually increased to 800 °C at a constant heating rate of 10 °C/min under a He flow of 30 mL/min, and the resulting chemisorbed NH<sub>3</sub> provided the strength and concentration of the acid sites. The morphology of NbO<sub>x</sub>-based catalysts was studied by SEM analysis (SEM CARL ZEISS EVO18 instrument) in a scanning range from 50 nm to 1 mm using an electron beam range of 200 V–30 kV. The samples were prepared in an ethanol solution, subsequently spincoated onto a silicon surface, and then sputtered with gold.

The specific surface area, pore size, and pore volume of the catalysts were evaluated using N<sub>2</sub> adsorption-desorption analysis (Autosorb iQ Station 1 instrument) at -196 °C (liquid N<sub>2</sub> temperature). Before analysis, all samples underwent vacuum drying at 200 °C for 2 h to remove physisorbed species. XPS analysis was conducted under ultra-high vacuum conditions on an AXIS Supra with Al K $\alpha$  radiation to determine the oxidation states of Nb on the catalyst's surface. The binding energy of the adventitious carbon at 284.6 eV was used for charge correction. Raman spectroscopy analysis was carried out using a Horiba JY LabRAMHR800 instrument. The spectra were collected (100–1300 cm<sup>-1</sup> range) using a He–Ne (632.8 nm, 20 mW) laser.









**Fig. S1.** (a) <sup>1</sup>H NMR, (b) <sup>13</sup>C NMR, (c) DEPT 135 NMR analyses of TBI monomer, and (d) FT-IR analysis of PET polymer and TBI monomer.



Fig. S2. HR-MS spectra of TBI monomer detected by the Na<sup>+</sup> and K<sup>+</sup> ions.

**Table S1:** Literature comparison of the PET imidazolysis reaction.

S. No.	Reaction conditions	TBI yield (%)	References
1	Microwave synthesis reactor, PET:IMD = 1:8 molar ratio (2 g PET), 180 °C, 80 min	82	3
2	Pressure tube, PET:IMD = 1:16 molar ratio (0.5 g PET), 160 °C, 4 h, methanol	91	Present work

**Table S2:** Effect of various solvents on PET imidazolysis using the NbO<sub>x</sub>-NR catalyst.

S. No.	Solvent	PET conversion (%)	TBI yield (%)
1	Methanol	99	91
2	Acetone	62	23
3	Ethanol	51	14
4	Isopropyl alcohol	43	9
5	1,4-dioxane	56	16

**Table S3:** BET surface area, average pore volume, and average pore size of the catalysts.

S. No.	Catalyst	BET surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)
1	Nb <sub>2</sub> O <sub>5</sub> -Com	1.8	0.004	109.6
2	Nb <sub>2</sub> O <sub>5</sub> -NSp	134.0	0.205	78.9
3	NbO <sub>x</sub> -NR	18.9	0.039	125.4





**Fig. S4.** (a) SEM images of fresh and (b) reused NbO<sub>x</sub>-NR catalyst. (c) Powder XRD and (d) Raman spectra of fresh and reused NbO<sub>x</sub>-NR catalyst.

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