Supporting Information

Catalytic recycling of PET waste bottles into a value-added amide monomer using a heterogeneous niobium pentoxide nanocatalyst

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1. Materials characterization studies

The bis(2-hydroxyethyl) terephthalamide (BHETA) obtained from PET aminolysis was qualitatively confirmed by ^{1}H, ^{13}C, and DEPT 135° NMR analyses (Bruker Avance III 400 MHz/54mm FT-NMR spectrometer). To elucidate the crystal structure of Nb_2O_5 materials, the powder X-ray diffraction (XRD) analysis was carried out on the Malvern PANalytical non-ambient XRD Empyrean-DY2584 (45 KW & 40 mA) instrument. The XRD data was collected in the 2θ range of 5–90° using Ni-filtered Cu Kα radiation as the X-ray source. The qualitative analysis of BHETA crystallites was also analyzed by the same powder XRD technique. A Bruker Alpha instrument (DTGS detector) was used for the FT-IR analysis (600 to 4000 cm^{-1}) of the BHETA monomer.

The thermogravimetry analysis (SDT Q600 TA instrument) was carried out to estimate the stability of the BHETA monomer from 50 to 800 ^{o}C (10 ^{o}C/min) under the N_2 atmosphere. The differential scanning calorimetry (DSC) on the TA Q200 instrument was carried out to estimate the melting point of the BHETA product. The NH_3-temperature programmed desorption (TPD) analysis to estimate the strength and the concentration of acid sites in the Nb_2O_5 catalysts was carried out on the Quantachrome autosorb-IQ instrument (TCD detector). The data was collected in the temperature range of 100-800 ^{o}C (10 $^{\circ}$C min^{-1}) after treating the Nb_2O_5 catalysts under He flow for 1 h at 200 ^{o}C temperature and then NH_3 adsorption with 5 vol% of NH_3/He (50 mL min^{-1}) for another 1 h.

To estimate the morphology/particle size of the Nb_2O_5 catalysts, the transmission electron microscopy (TEM) analysis was conducted using the JEOL JEM F200 instrument (200 kV accelerating voltage). A carbon-coated copper grid (200 mesh size) was used to prepare TEM samples. The N_2 adsorption-desorption analysis was conducted at -196 $^{\circ}$C (liquid N_2 temperature) using an Autosorb iQ Station 1 instrument. To determine the oxidation states of Nb and O in Nb_2O_5 catalysts, X-ray photoelectron spectroscopy (XPS) analysis was conducted using an AXIS Supra instrument (Al Kα radiation). Raman analysis was performed for Nb_2O_5 materials on a Horiba JY LabRAMHR800 instrument in the range of 100$-$1200 cm^{-1} using a He$-$Ne laser (632.8 nm, 20 mW).

2. Molecular weight determination of PET aminolysis oligomers by viscometry studies

The Ubbelohde viscometer (size 1C) is used to estimate the molecular weight and intrinsic viscosity of PET and its aminolysis oligomers. Standard solutions were prepared with a 60:40 ratio of phenol to tetrachloroethane, containing various concentrations of the PET aminolysis reaction mixture, in a 10 ml solution of phenol and tetrachloroethane. These solutions are then passed through the viscometer to measure the liquid flow time, allowing for the calculation of relative viscosity, using η_o = 1.24 as a reference.

The relative viscosity (η_{rel}) of the respective solution can be determined via $\eta_{rel} = \eta/\eta_o \sim t/t_o$ and the specific viscosity (η_{sp}) is also estimated by using $\eta_{sp} = \eta_{rel} -1$. This specific viscosity helps to find the intrinsic viscosity [η] of the reaction mixture as follows.

$[\eta] = ((1+4 \times \eta_{sp})^{1/2}-1)/K^1$, where K^1 is the constant having value of 0.35 and Mark−Kuhn−Houwink (MKH) equation, $[\eta] = KM^\alpha$ where K is 2.1×10^{-4} and α is 0.82 as reported in the literature[1–3].

The above procedure and equations are used to determine the intrinsic viscosity and molecular weight of PET and its oligomers. Various reaction mixtures, including pure PET flakes, a blank reaction (without a catalyst), and a reaction mixture with 1 wt% Nb_2O_5 catalysts (calcined at different temperatures), were tested to determine the molecular weight.

The molecular weight of the PET sample from the bottle used in the reaction was found to be ~75000 with an intrinsic viscosity [η] of 15.68 dL/g. The blank reaction indicated the cleavage of PET into oligomers with a molecular weight of ~21000 having a 4.47 dL/g intrinsic viscosity. The molecular weights and intrinsic viscosity [η] of the oligomers obtained after the reaction in the presence of 1 wt% Nb_2O_5-400, Nb_2O_5-450, and Nb_2O_5-500 were ~3700, 1000, and 5000 with 0.78, 0.21, and 1.06 dL/g, respectively. This data clearly indicates the lower molecular weight of the oligomers when the reaction is conducted over an Nb_2O_5-450 catalyst. Thus, a higher yield of BHETA monomer (92%) with 8% of oligomer yield was obtained over the Nb_2O_5-450 catalyst (entry 3, Table 1).

3. MALDI-TOF analysis for PET aminolysis reaction mixture

The molecular weight of PET aminolysis oligomers is determined using MALDI TOF analysis.[4,5] For this, a MALDI-reTOF/TOF UltrafleXtreme instrument (Bruker Daltonics, Bremen, Germany) fitted with pulsed ion extraction, LIFT devices, and reflector lens was used.

The analysis confirms the mass of the oligomers by identifying the repeating PET unit, the BHETA monomer, and byproducts, such as ethanolamine, ethylene glycol, and water (Fig. S2). The fragmentation of the PET polymer using ethanolamine into the BHETA monomer was performed over the Nb_2O_5-450 catalyst. The fractions of BHETA oligomers were found to be 215 and 240 g/mol, and the BHETA monomer ($C_{12}H_{16}O_4N_2$) molecular weights were confirmed to be around 240 and 259 g/mol, with water as a byproduct. Other oligomer molecular weights were also identified with higher m/z values at 270 and 346 g/mol, along with a few byproducts and minor fractions of other oligomers, indicated by low-intensity peaks. Thus, the MALDI-TOF analysis confirms that the PET polymer is converted into its respective monomers and oligomers via the aminolysis reaction in the presence of a Nb_2O_5-450 catalyst.
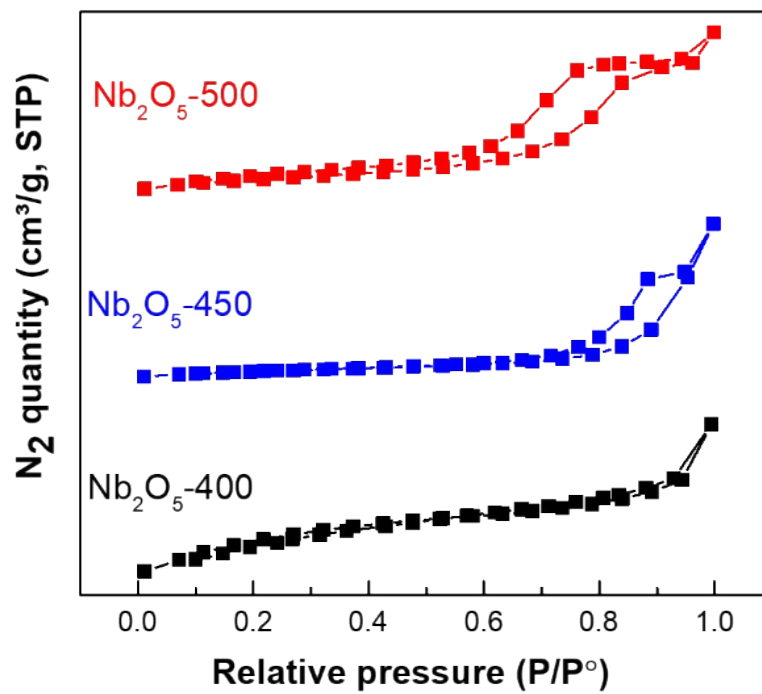
Fig. S1. N_2 adsorption-desorption isotherms of Nb_2O_5 catalysts.

Table S1: BET surface area (BET SA), average pore size, and average pore volume of Nb_2O_5 catalysts.

Catalyst	BET SA (m^2/g)	Average pore size (nm)	Average pore volume (cm^3/g)
Nb_2O_5-400	7	0.5	0.009
Nb_2O_5-450	28	2.1	0.154
Nb_2O_5-500	44	3.8	0.171

Table S2. Amount of acid sites estimated by NH_3-TPD analysis of Nb_2O_5 catalysts.

S. No.	Catalyst	Weak acid sites		Strong acid sites		Total acidity
		Temp (°C)	Amount (mmol/g)	Temp (°C)	Amount (mmol/g)	(mmol/g)
1	Nb_2O_5-400	-	-	637 (799)	0.109 (0.118)	0.227
2	Nb_2O_5-450	-	-	607	0.615	0.615
3	Nb_2O_5-500	232	0.070	648	0.015	0.085
4	Reused Nb_2O_5-450	-	-	608	0.468	0.468
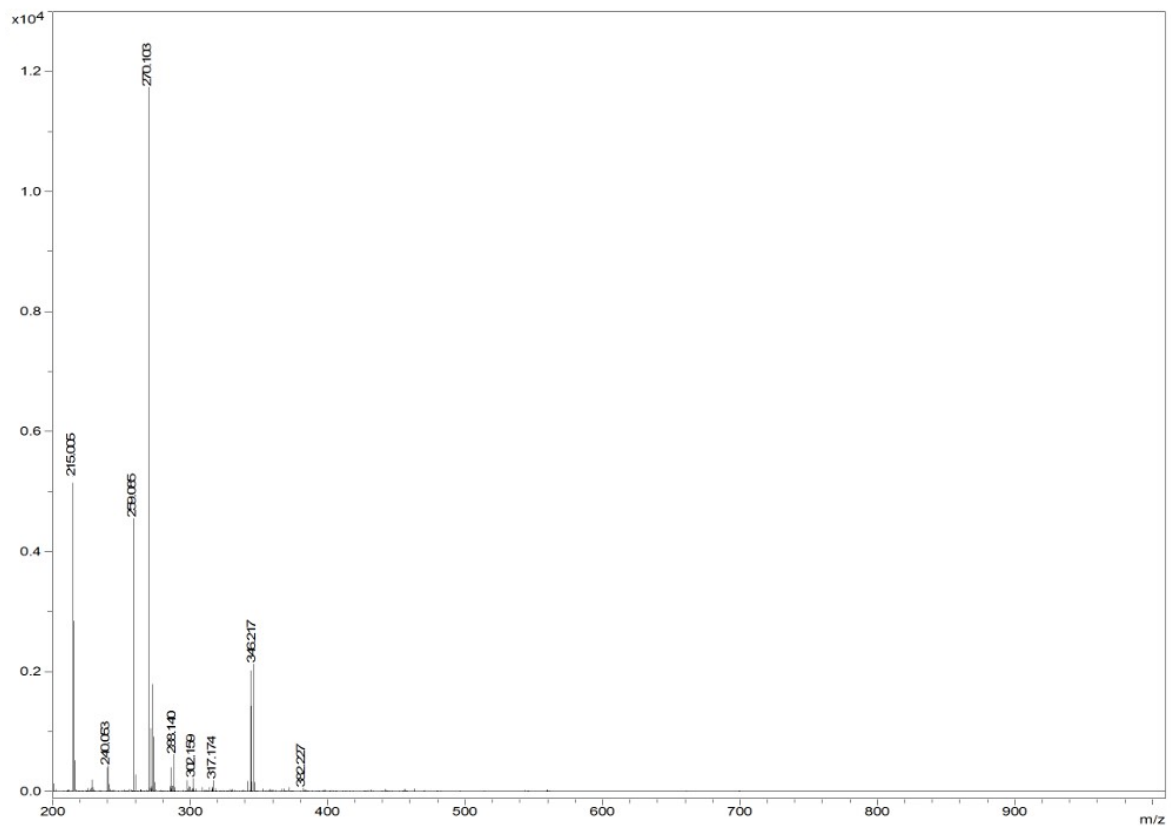
Fig. S2. MALDI-TOF spectra of PET aminolysis reaction mixture.
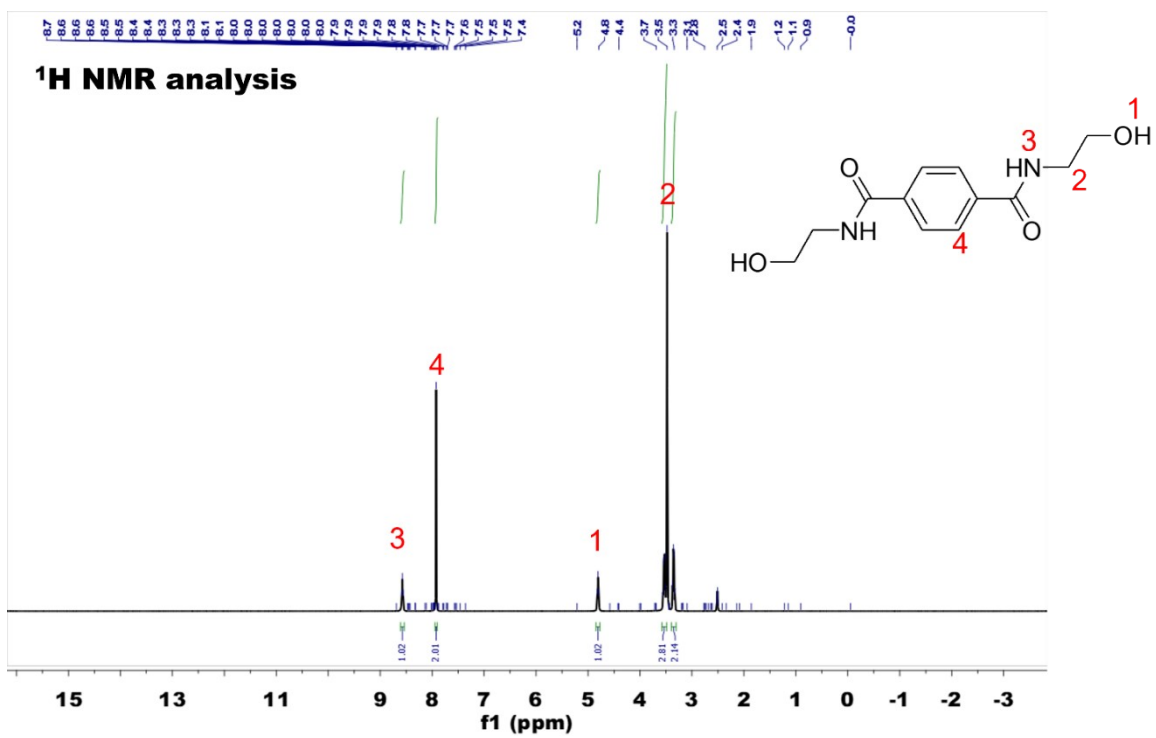
Fig. S3. ^{1}H NMR of BHETA monomer.
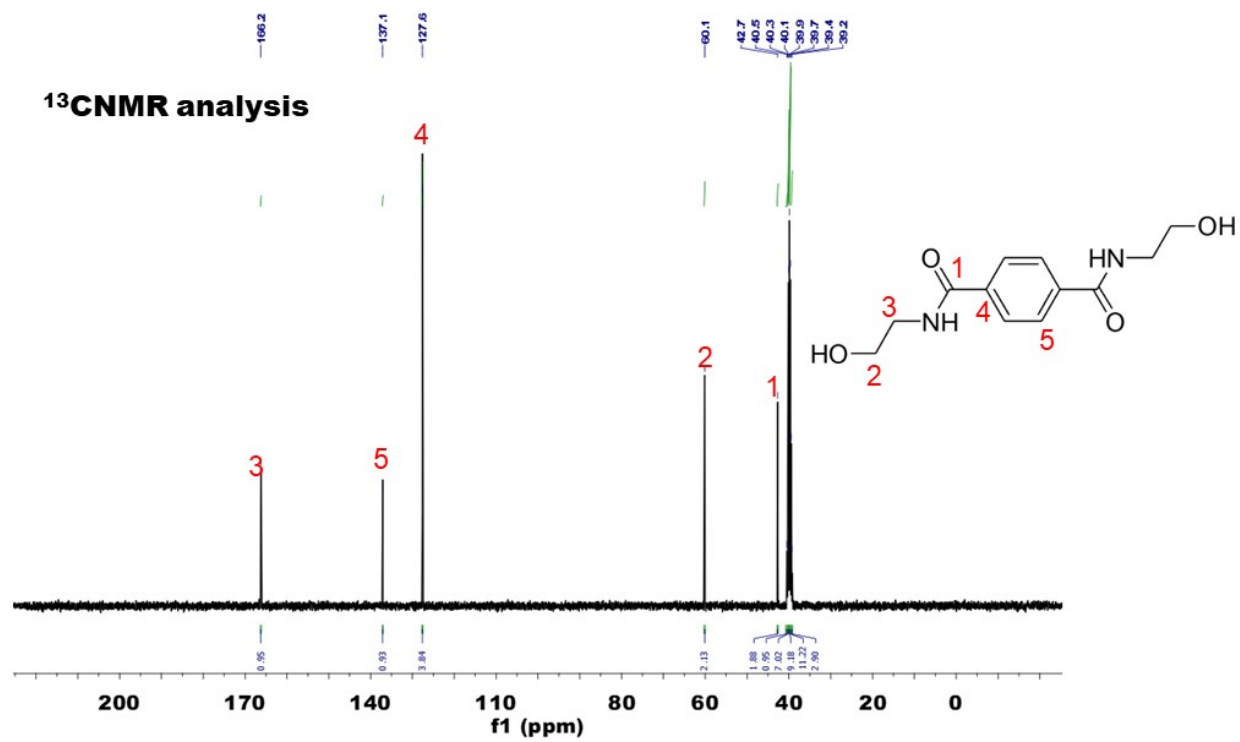
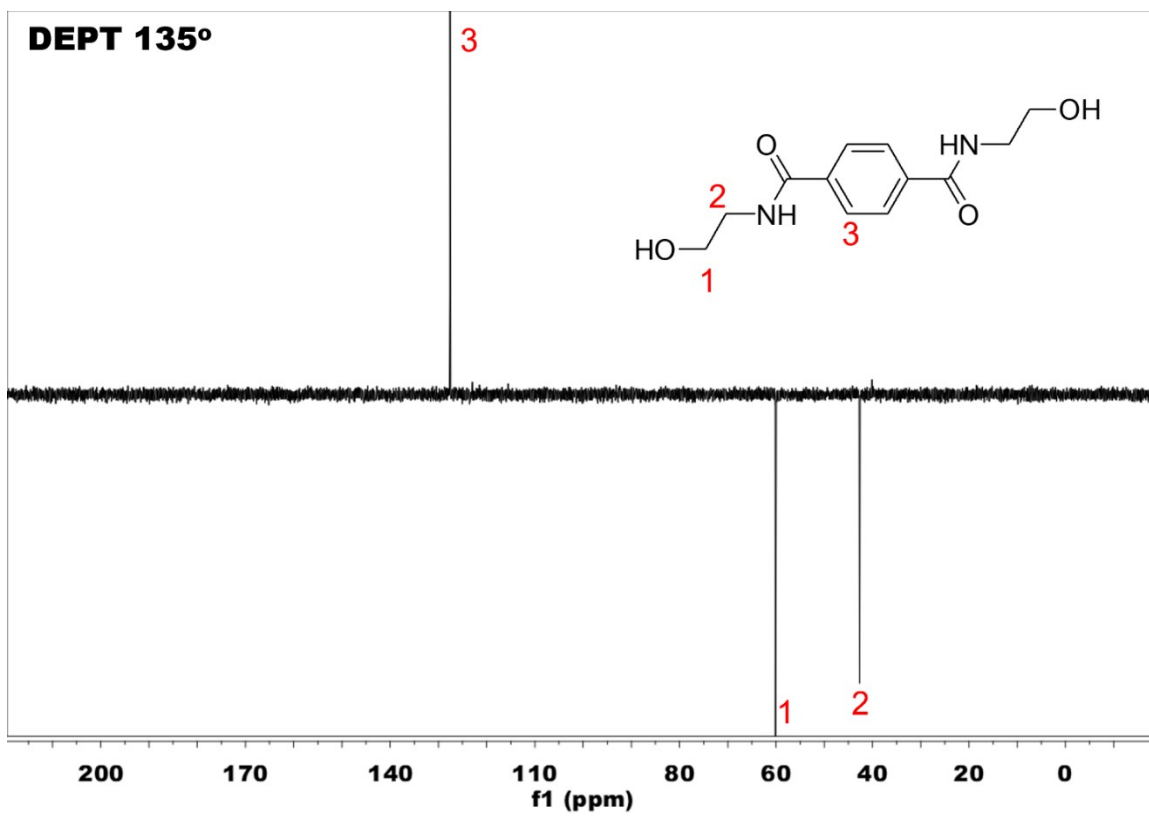Fig. S4. ^{13}C NMR of BHETA monomer.
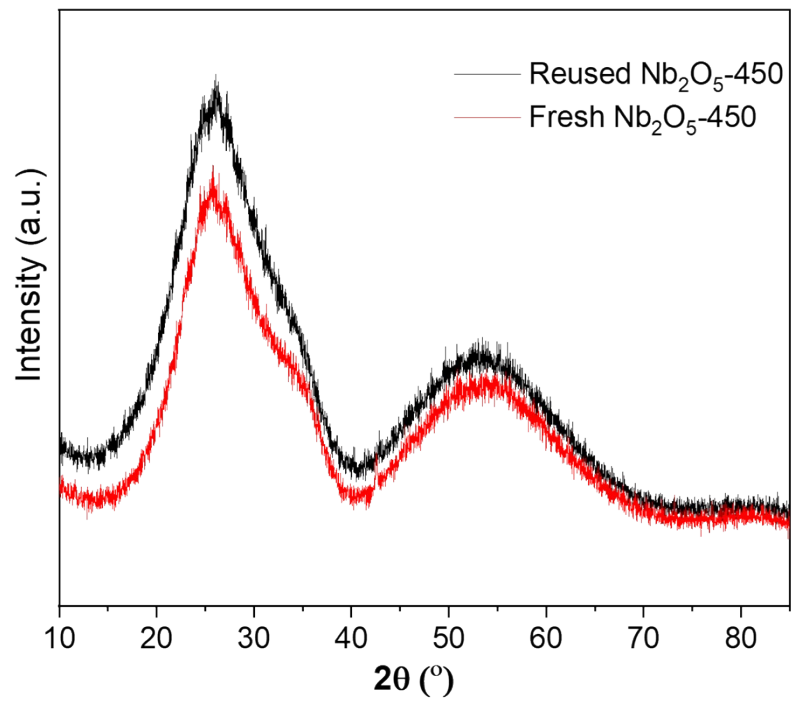
Fig. S5. DEPT analysis of BHETA monomer.

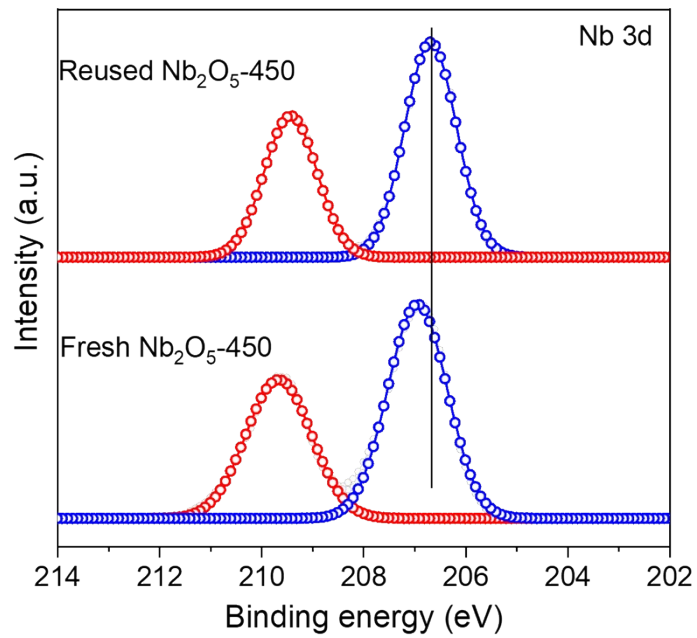Fig. S6. Powder XRD analysis of fresh and reused Nb_2O_5-450 catalysts.

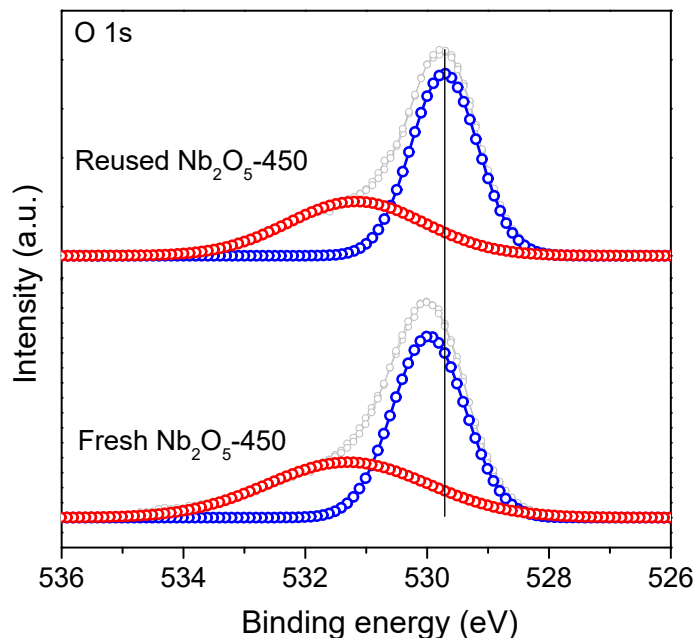Fig. S7: Nb 3d XPS spectra of fresh and reused Nb_2O_5-450 catalysts.

Fig. S8: O 1s XPS spectra of fresh and reused Nb_2O_5-450 catalysts.

References

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