# SUPPORTING INFORMATION

## *Efficient selective hydrogenation of benzonitrile over $TiO_2$-supported nickel catalysts*

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## Materials

All of the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemicals were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All of the solvents and the chemicals were used directly without purification.

**Preparation of catalysts**

The solution was prepared by adding 0.16 g of $Ni(NO_3)_2{\cdot}6H_2O$ and 0.06 g of ammonium persulfate to 10 mL of deionized water, and 0.3 g of $TiO_2$ was added and stirred, followed by ultrasonication in an ultrasonic machine for 30 min, and dropwise addition of $NH_4HCO_3$ (1 M, 20 mL) with stirring at room temperature. The solution was hydrothermalized in an oven at 150 °C for 6 h. After hydrothermalization, the solution was washed three times with deionized water and ethanol, respectively, and dried at 70 °C overnight. The obtained solid was then calcined under nitrogen flow (500 °C, 5 °C/min) for 2 h, following the reduction in $H_2$ flow at 350 °C, 450 °C, 550 °C (2 °C/min) for 4 h. Ni/$TiO_2$-450, Ni/$TiO_2$-350, Ni/$TiO_2$-550 were obtained.

**Catalyst characterization**

Transmission electron microscopy (TEM) images were acquired on a Talos F200X electron microscope at an acceleration voltage of 200 kV. The sample was firstly dispersed in ethanol and dropped onto copper grids for observation. SEM images and were taken on an FEI Nova FEG-SEM instrument. EDS mapping was taken with a FEI Tecnai G2 F20 S-TWIN TEM. HAADF-STEM images were recorded on a double-corrected FEI Titan3 FEG-TEM instrument with electron acceleration energy of 300 keV. Powder X-ray diffraction (XRD) studies were conducted on a Rigaku RINT-2200 X-ray diffractometer with a Cu Kα source at 40 kV and 20 mA. The morphology and sizes of the samples were studied by high-resolution transmission electron microscopy (HRTEM, JEM-2100 from JEOL). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCALAB 250Xi system equipped with a hemispherical analyzer, and a monochromatic Al Kα was used as radiation source. The Ni content in the as-prepared catalysts was determined by inductively coupled plasma-atomic emission spectrometry (ICP-OES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

**Hydrogenation of benzonitrile**

The hydrogenation reaction of benzonitrile was conducted in a stainless steel autoclave featuring a mechanical stirrer, pressure gauge, and automatic temperature control. In a typical experiment, benzonitrile (0.5 mmol), Ni/$TiO_2$-T (20 mg), and solvent (10 mL) were added to the autoclave. The atmosphere inside the reactor was then completely replaced with $H_2$ and pressurized to 15 bar $H_2$. Subsequently, the reaction was conducted at the desired temperature with magnetic stirring at 1000 rpm. After the reaction, the reactor was allowed to cool down in ice water, and the products were identified using gas chromatography-mass

spectroscopy (thermo scientitic,GC-MS-TRACE1300|ISQ7000) and then quantified with gas chromatography (Shimadzu, GC-2010 Plus), utilizing ethylbenzene as an internal standard.

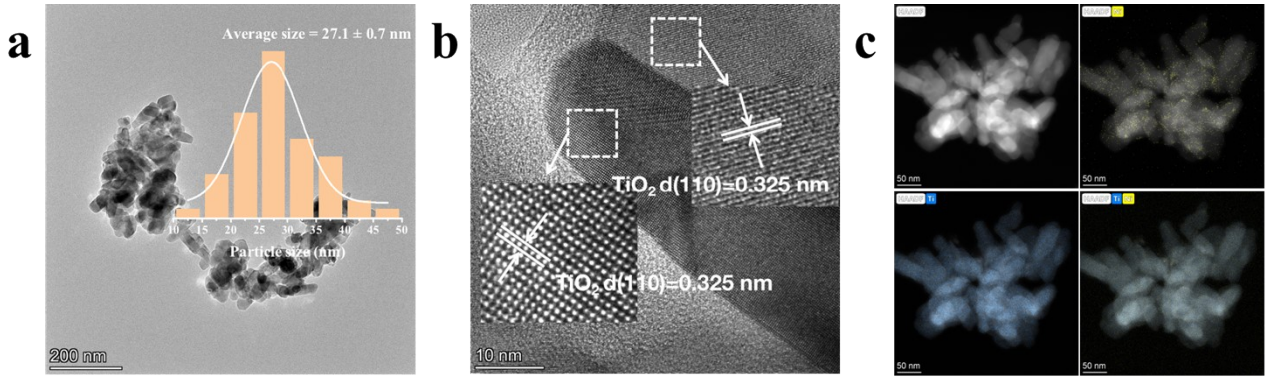



**Figure S1.** Characterizations for Ni/$TiO_2$-350 catalyst: a) TEM image, inset: particle distribution; b)HR-TEM image; c) HAADF-STEM image and corresponding EDX elemental mapping images.

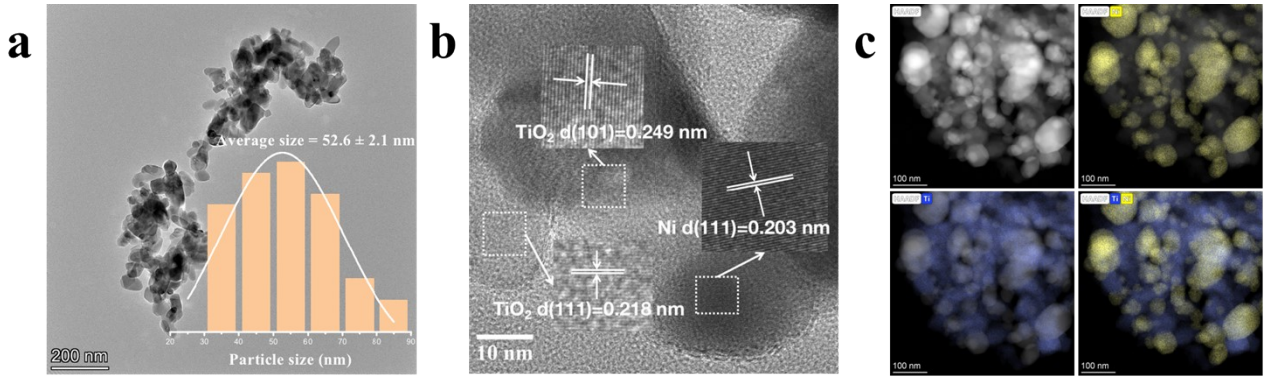



**Figure S2.** Characterizations for Ni/$TiO_2$-550 catalyst: a) TEM image, inset: particle distribution; b)HR-TEM image; c) HAADF-STEM image and corresponding EDX elemental mapping images.

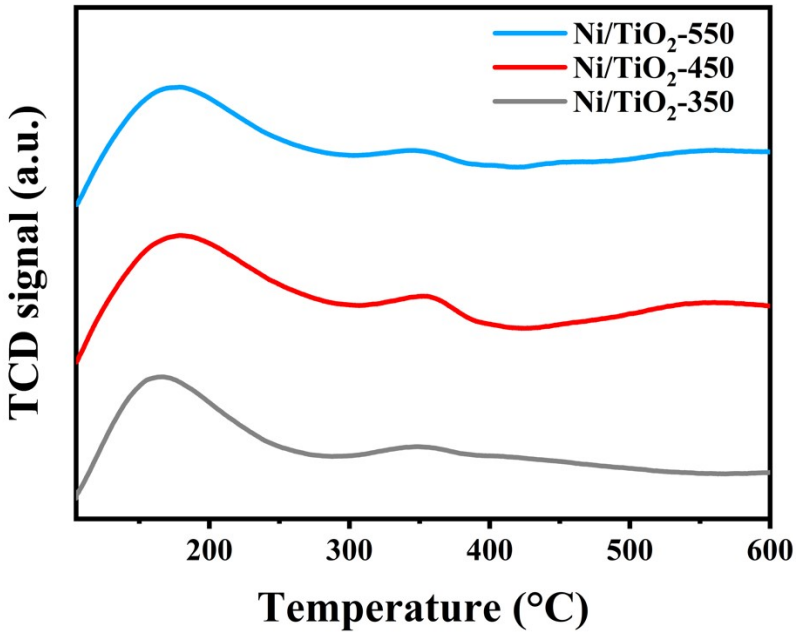



**Figure S3**. $H_2$-TPD profiles of the *as*-prepared Ni/$TiO_2$-T catalysts.

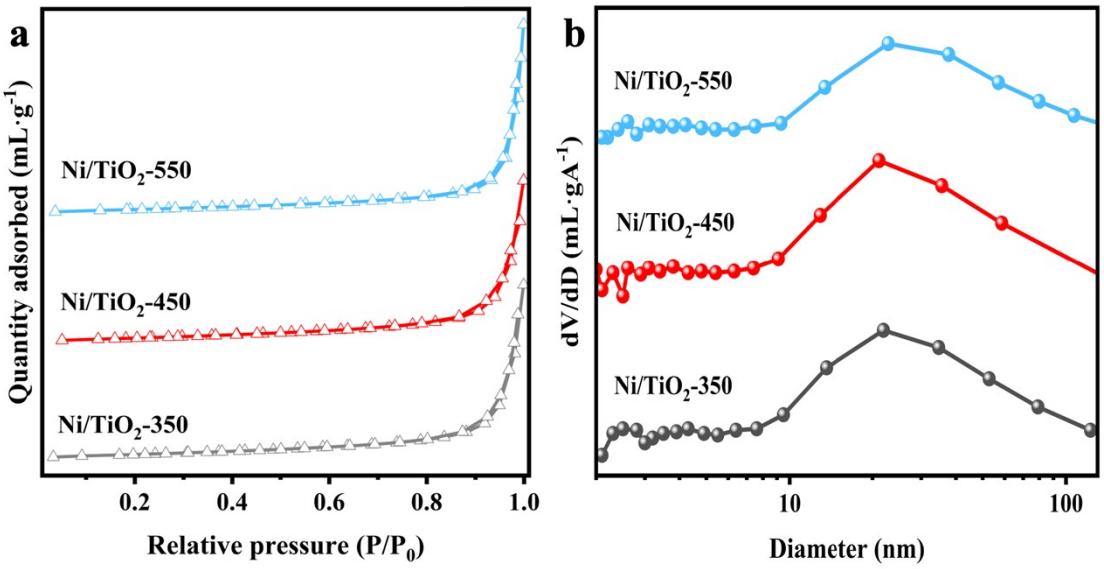



**Figure S4.** a) $N_2$ adsorption-desorption isotherms *as*-prepared Ni/$TiO_2$-T catalysts., **b)** Pore distribution of samples *as*-prepared Ni/$TiO_2$-T catalysts.

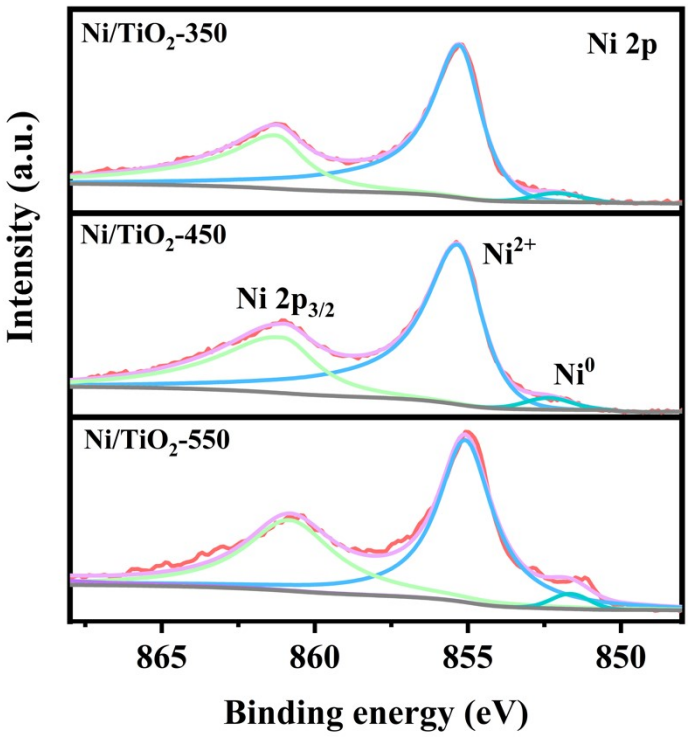



**Figure S5.** High-resolution XPS spectra for Ni 2p orbitals of Ni/$TiO_2$-T catalysts.

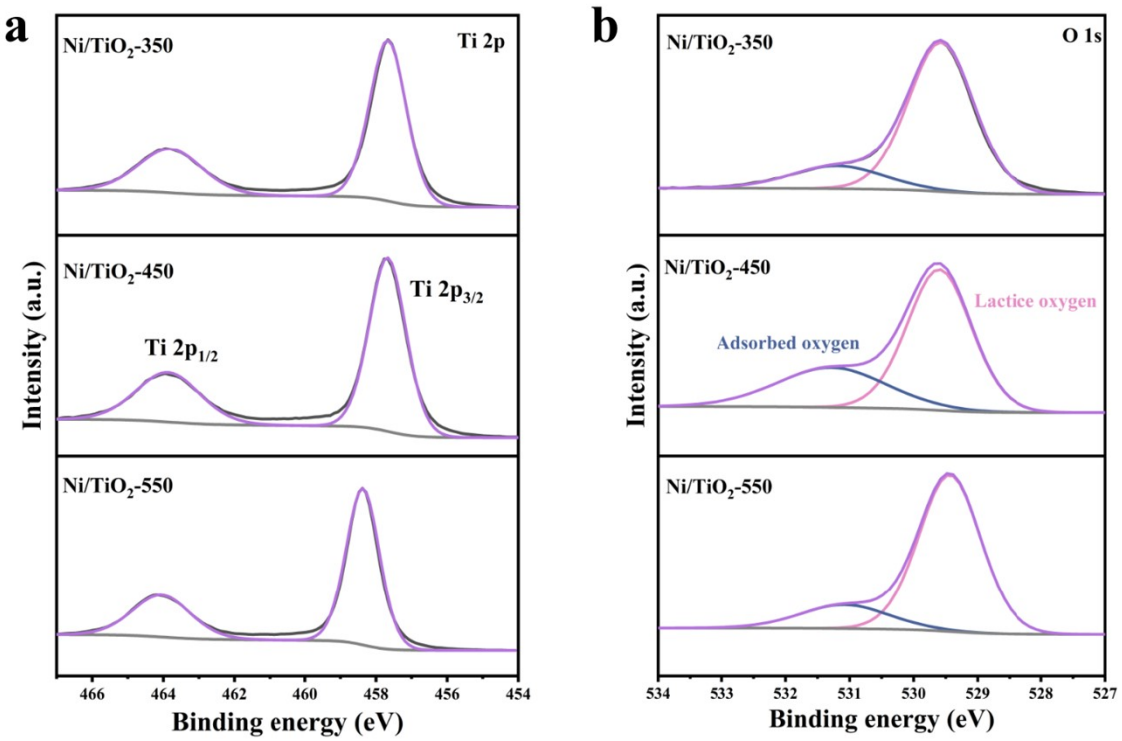



**Figure S6.** XPS spectra of Ni/$TiO_2$-T catalysts: a) Ti 2p orbitals; b) O 1s orbital.

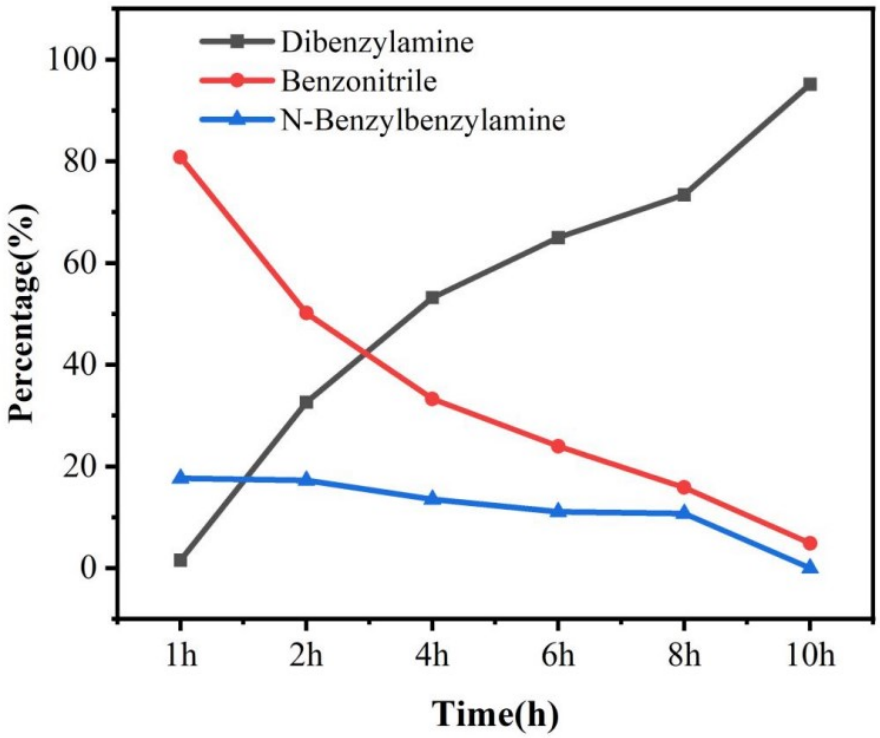



**Figure S7.** Time course experiment on catalytic hydrogenation of benzonitrile. Reaction conditions: benzonitrile (0.5 mmol), ethanol (10 ml), hydrogen (20 bar), catalyst (20 mg) and 80 °C

**Table S1.** Summary of content of Ni in $Ni/TiO_2$-T catalysts determined with ICP-OES

| Entry | Catalyst | Ni content (wt.%) |
|---|---|---|
| 1 | $Ni/TiO_2$-350 | 3.9 % |
| 2 | $Ni/TiO_2$-450 | 3.2 % |
| 3 | $Ni/TiO_2$-550 | 4.3 % |
| 4 | $Ni/TiO_2$-450-imp | 0.2 % |

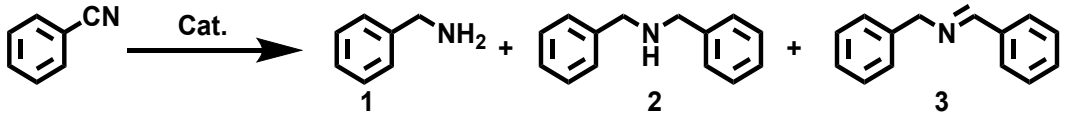
**Table S2.** The texture properties of the as-prepared $Ni/TiO_2$-T catalysts.

| Entry | Catalayst | surface area ($m^2/g$) | Pore size (nm) | Pore volume ($cm^3/g$) |
|---|---|---|---|---|
| 1 | $Ni/TiO_2$-350 | 23.19 | 18.3 | 0.22 |
| 2 | $Ni/TiO_2$-450 | 22.46 | 17.6 | 0.20 |
| 3 | $Ni/TiO_2$-550 | 20.68 | 22.1 | 0.23 |

**Table S3.** The atomic percentage of the Ni species in the $Ni/TiO_2$-T catalysts determined by Ni 2p XPS.

| Entry | Catalyst | $Ni^0$ (852.3 eV) (%) | $Ni^{2+}$ (855.3 eV) (%) |
|---|---|---|---|
| 1 | $Ni/TiO_2$-350 | 6.3 | 93.7 |
| 2 | $Ni/TiO_2$-450 | 4.2 | 95.8 |
| 3 | $Ni/TiO_2$-550 | 3.3 | 96.7 |

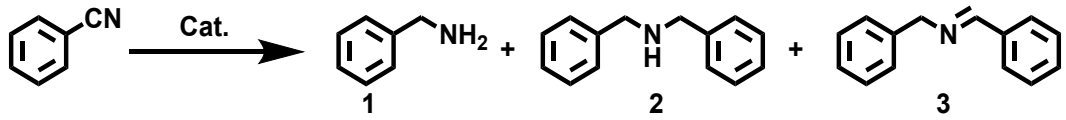
**Table S4.** Results of catalytic hydrogenation of benzonitrile in different solvents.




| Entry | Solvent | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|---|
| | | | 1 | 2 | 3 |
| 1 | n-Hexane | 62 | 3 | 14 | 45 |
| 2 | Toluene | 50 | 7 | 13 | 30 |
| 3 | Cyclohexane | 39 | 4 | 8 | 27 |
| 4 | 1,4-Dioxane | - | - | - | - |
| 5 | Tetrahydrofuran | 16 | 6 | 2 | 8 |
| 6 | Methanol | 73 | - | 15 | 58 |
| 7 | Ethanol | 67 | - | 53 | 14 |
| 8 | Dimethylacetamide | 15 | - | - | 15 |

**Reaction conditions:** Benzonitrile (0.5 mmol), $H_2$ (20 bar), catalyst (20 mg), 80 °C and 4 h.

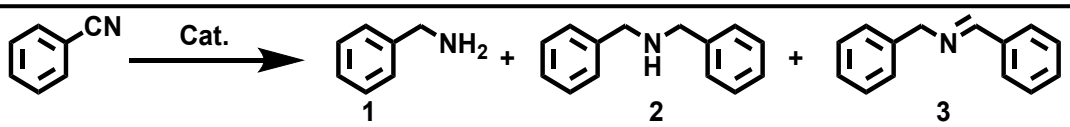
**Table S5.** Results of catalytic hydrogenation of benzonitrile at different temperatures




| Entry | Temperature (°C) | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|---|
| | | | 1 | 2 | 3 |
| 1 | 60 | 35 | - | 4 | 31 |
| 2 | 70 | 55 | - | 10 | 45 |
| 3 | 80 | 67 | - | 53 | 14 |
| 4 | 90 | 86 | - | 68 | 18 |
| 5 | 100 | 92 | - | 92 | - |

**Reaction conditions:** Benzonitrile (0.5 mmol), ethanol (10 mL), catalyst (20 mg), $H_2$ (20 bar), and 4 h.

**Table S6.** Hydrogenation results of benzonitrile at different hydrogen pressures




| Entry | $H_2$ (bar) | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|---|
| | | | 1 | 2 | 3 |
| 1 | 1 | 24 | - | - | 25 |
| 2 | 5 | 37 | - | - | 37 |
| 3 | 10 | 64 | - | 11 | 53 |
| 4 | 20 | 67 | - | 53 | 14 |

**Reaction conditions:** Benzonitrile (0.5 mmol), ethanol (10 mL), catalyst (20 mg), 80 °C, and 4 h.

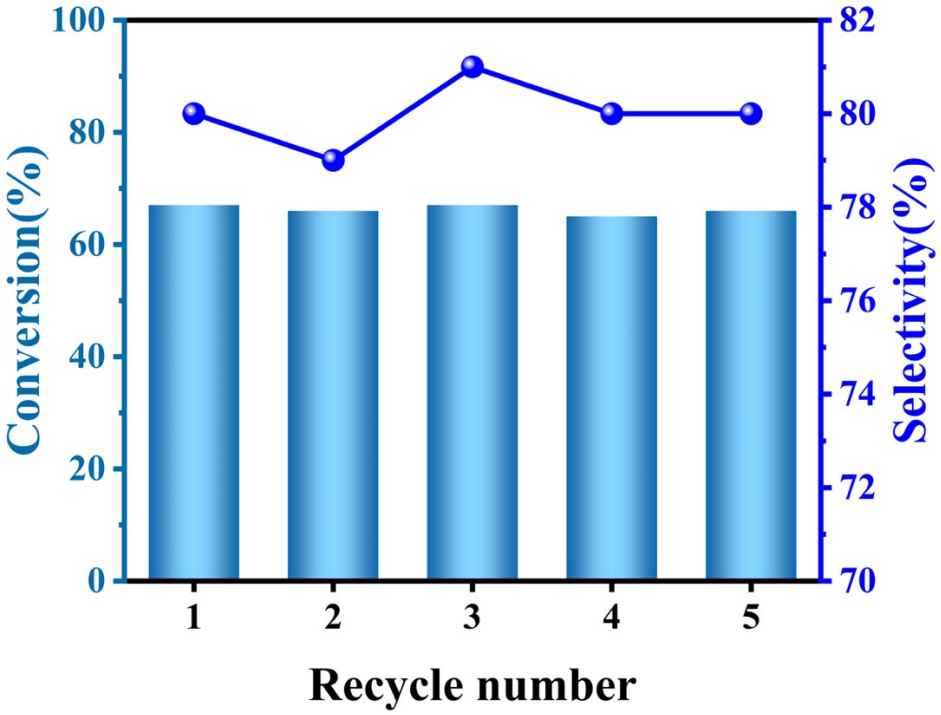



**Figure S8.** Recycling test of the Ni/TiO2-450 catalyst.