

Supplementary Information

Carbonaceous deposits on cobalt particles reverse the catalytic patterns in butadiene hydrogenation

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Experimental section

Catalyst preparation

The Co-containing polymer precursor was prepared by a one-pot polymerization method. Dicyandiamide (15 g, 178.41 mmol, 99.0 wt.%, Aladdin) was added into 75 cm³ deionized water in a 250 cm³ beaker, which was then transferred to a water bath (343 K) with magnetic stirring for 15 min until completely dissolved. Co(NO₃)₂·6H₂O (7.4 g, 25.43 mmol, AR, 99.0 wt.%, Aladdin) was added into the above solution, mixed evenly and stirred for another 5 min. Formaldehyde (13.2 cm³, 178.41 mmol, 37 wt.%, Sinopharm) was added to the above solution with continuous stirring for 15 min. The mixture was transferred to an oil bath (373 K) to initiate the polymerization. During this process, magnetic stirring was continued for 11 h until the liquid was completely evaporated. The resulting purple solids were naturally cooled to room temperature, which were denoted as Co@NC-p. For the synthesis of Co@NC-T, Co@NC-p was placed in a quartz boat which was transferred into a tubular oven. The samples were then heated to 673, 873, and 1073 K (10 K min⁻¹, 2 h) in flowing N₂. The derived solids were denoted as Co@NC-T (*T* indicated the carbonization temperature in K). Activated carbon-supported Co (Co/AC) used for the temperature-programmed reduction was prepared by an incipient impregnation method. First, activated carbon was pre-dried in an oven at 373 K for 12 h. Second, Co(NO₃)₂·6H₂O (8.0813 g, 99.0 wt.%, Aladdin) was dissolved in deionized water of a certain mass ratio ($w_{AC} : w_{H_2O} = 1:1.2$) and stirred with a glass rod until completely dissolved. Afterward, the solution was dropped successively into the activated carbon (2g, 20-40 meshes), stirred swiftly with a glass rod, and dried in an oven at 373 K for 12 h. Lastly, the resulting light-purple solids were calcined in a

tubular oven at 773 K (10 K min⁻¹, 5 h) in flowing N₂.

Catalyst characterization

The specific surface area and pore volume of the Co catalysts were measured by N₂ sorption at 77 K on a Quantachrome Autosorb-1 instrument. Before the measurements, the solids were outgassed at 573 K for 3 h. Powder X-ray diffraction (PXRD) patterns were conducted on an X'Pert 3, PANalytical X-ray diffractometer using Cu K_α radiation in a scanning angle (2θ) range of 10-90° at a speed of 2° min⁻¹, with the tube voltage and the current were 40 kV and 40 mA, respectively. Raman spectra of the samples were collected on a confocal laser micro-Raman spectrometer (HORIBA, Lab RAM HR Evolution) under the following conditions: a wavelength of 532 nm, 60 s transits per sample, and a spectral resolution of 1 cm⁻¹. Temperature-programmed reduction with hydrogen (H₂-TPR) was studied on a Micromeritics Autochem II 2920 chemisorber. The catalyst (0.10 g) was loaded into a U-shaped quartz micro-reactor, pretreated in helium (30 cm³ min⁻¹) at 373 K for 2 h, and cooled to 323 K. 10 vol.% H₂/Ar was introduced and the reduction was initiated by increasing the temperature to 1073 K using a ramp of 10 K min⁻¹. The H₂ consumption was monitored by a thermal conductivity detector and a mass spectrometer. TEM images were acquired on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. The sample powders were dispersed in ethanol by ultrasonication and then the specimen was obtained by dropping a droplet suspension on a carbon film supported on a copper grid for analysis. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurement was carried out on a JEOL-ARM200F electron microscope. X-ray photoelectron spectroscopy (XPS) of the Co catalysts were carried out on a Thermo ESCALAB

250Xi spectrometer using a 15 kV Al K_{α} X-ray source as the radiation source. The binding energy was calibrated using the C 1s peak (284.3 eV) as the reference. The Co 2p and N 1s envelopes were fitted by mixed Gaussian-Lorentzian component profiles after Shirley background subtraction. The elemental concentrations were quantified based on the measured photoelectron peak areas (Co 2p, C 1s, N 1s and O 1s) after Shirley background subtraction, using PHI-MultiPak software and the built-in relative sensitivity factors, which were corrected for the system transmission function. Depth profile analyses of Co@NC were performed by first applying Ar ions sputtering of the sample under different conditions before the spectra acquisition.

Catalytic testing

The selective hydrogenation of 1,3-butadiene (BD) was studied in a continuous-flow fixed-bed micro-reactor at atmospheric pressure. The catalyst pellets (20-40 meshes) were packed between glass wools in the middle of a quartz reactor (length of 400 mm, internal diameter of 6 mm) that was placed vertically in an electronic oven coupled with a temperature controller. The catalysts were heated to 573 K (unless otherwise stated, 10 K min⁻¹) in N₂ (50 cm³ min⁻¹) and stayed for 1 h. Then the catalysts were reduced *in situ* by switching the gas to pure H₂ (50 cm³ min⁻¹, 1 h). Then, the reactor was cooled to the desired temperature and the reaction was started by admitting the reactive gases comprising 4.03 vol.% BD/N₂, pure H₂ or 10 vol.%H₂/Ar, and the balancing N₂. The gaseous reaction products from the reactor outlet were periodically analyzed online by using an Agilent 7890B chromatograph equipped with a CEC-Alumina column (30 m × 0.53 mm × 10 μm) and a flame ionization detector (FID). The calibrations of BD and the products were conducted by using standard gases with known concentrations. In a typical test, 25-50 mg

catalysts were loaded, and the mixed gases containing a fixed BD concentration of 0.63 vol.% and H₂:BD = 5-125 (mol:mol) balanced by N₂ with a total flow (F_T) of 75 cm³ min⁻¹ were applied, corresponding to gas hourly space velocity (GHSV) of 112500-180000 cm³ g_{cat}⁻¹ h⁻¹. In the temperature-ramping tests, a ramp-up mode was adopted and the data were collected after stabilization at each temperature for 40 min.

For calculation of the conversion (X) and product selectivity (S), **Eqs. 1,2**, were applied as follows,

$$X (\%) = (F_{\text{BD,in}} - F_{\text{BD,out}}) / F_{\text{BD,in}} \times 100 \quad (1)$$

$$S_i (\%) = F_{i,\text{out}} / \sum_j F_{j,\text{out}} \times 100 \quad (2)$$

$F_{\text{BD,in}}$ and $F_{\text{BD,out}}$ were the inlet and outlet BD flow rates (mol min⁻¹), respectively, and $F_{i,\text{out}}$ and $F_{j,\text{out}}$ were the outlet flow rates (mol min⁻¹) of different products. i (j) = 1-butene, *trans*-2-butene, *cis*-2-butene, or butane. Good carbon balances (typically within 100 ± 2, %) were obtained under all the tested conditions.

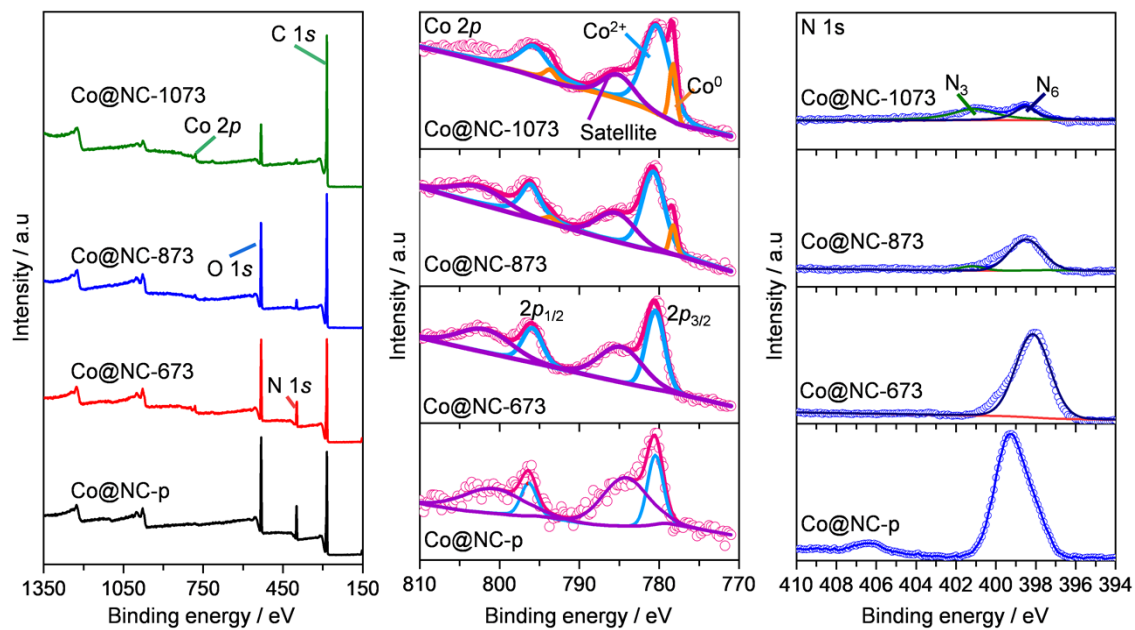


Fig. S1. The full (left), Co 2*p* (middle), and N 1*s* (right) XPS spectra of the Co precursor (Co@NC-p) and the carbonized analogues Co@NC-*T*. N3 and N6 in the N 1*s* spectra represented the quaternary and pyridinic N species, respectively.

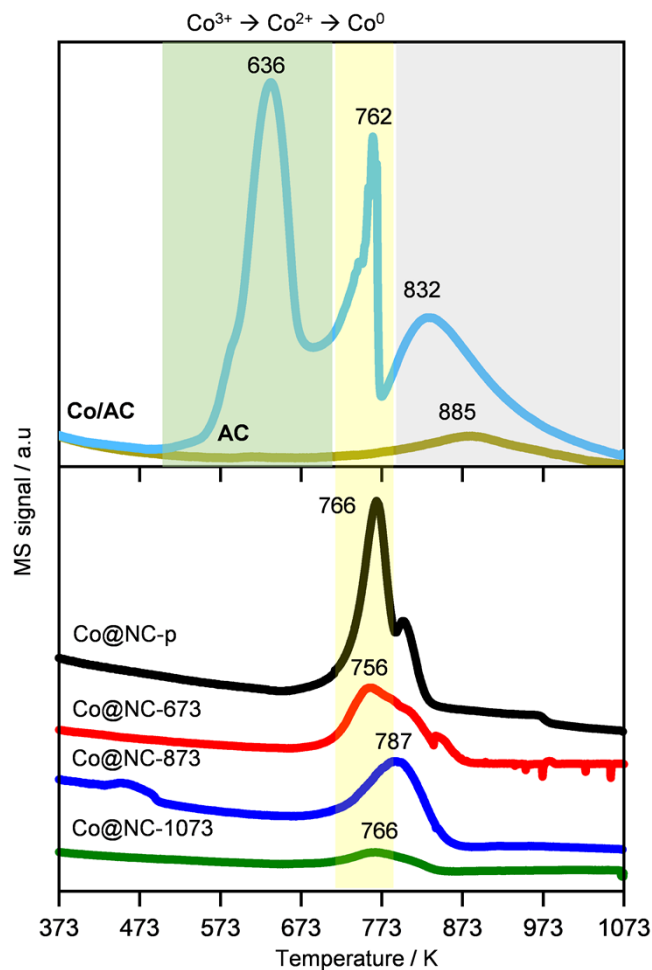


Fig. S2. The H_2 consumption profiles of Co@NC-p and Co@NC-T , and the reference Co/AC and AC in the temperature-programmed reduction. For Co/AC , three reduction peaks were found, each centered at 636, 762, and 832 K, respectively. The high-temperature reduction could be assigned to the reduction of the O-containing functionalities on the carrier, and the two low-temperature reductions were attributed to the consecutive reduction of $\text{Co}^{3+} \rightarrow \text{Co}^{2+} \rightarrow \text{Co}^0$. The absence of the low-temperature peak centered around 636 K for Co@NC suggested the absence of Co^{3+} species which agreed well with the XPS results.

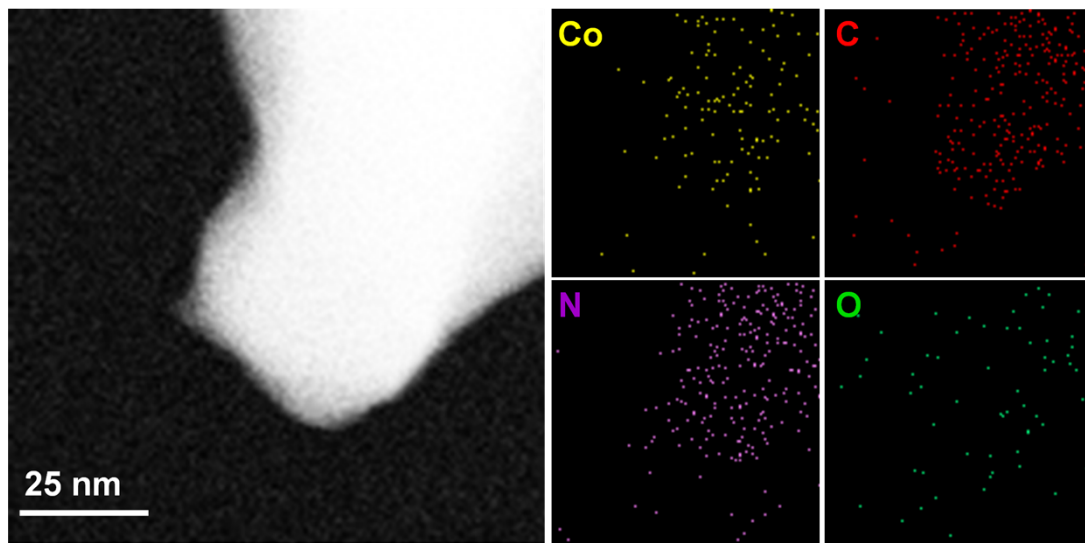


Fig. S3. The HAADF-STEM images of Co@NC-673 with elemental color mapping, showing the absence of any Co particles and the even distribution of the Co species on the sample.

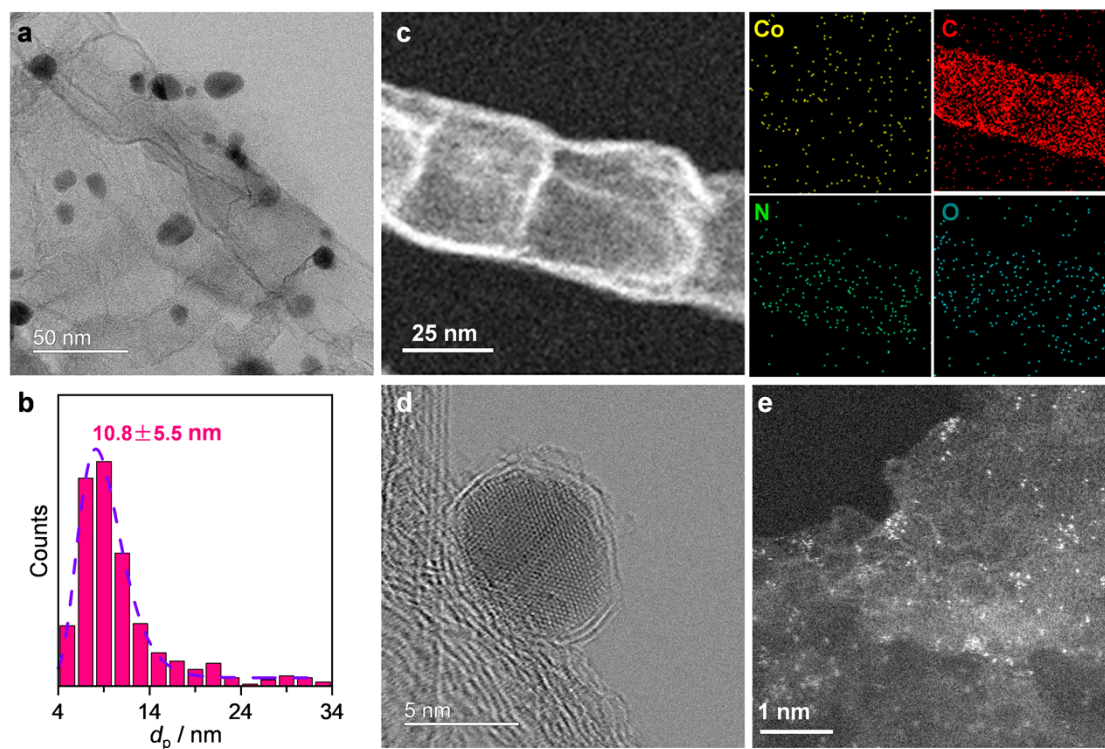


Fig. S4. (a) TEM image of Co@NC-873, and (b) the corresponding particle size distribution. (c) HAADF-STEM images with elemental color mapping demonstrating the formation of tube-like morphology of the NC carrier and the composition. (d) Zoom in TEM image showing a single Co particle. (e) Additional HAADF-STEM image evidencing the presence of single Co atoms.

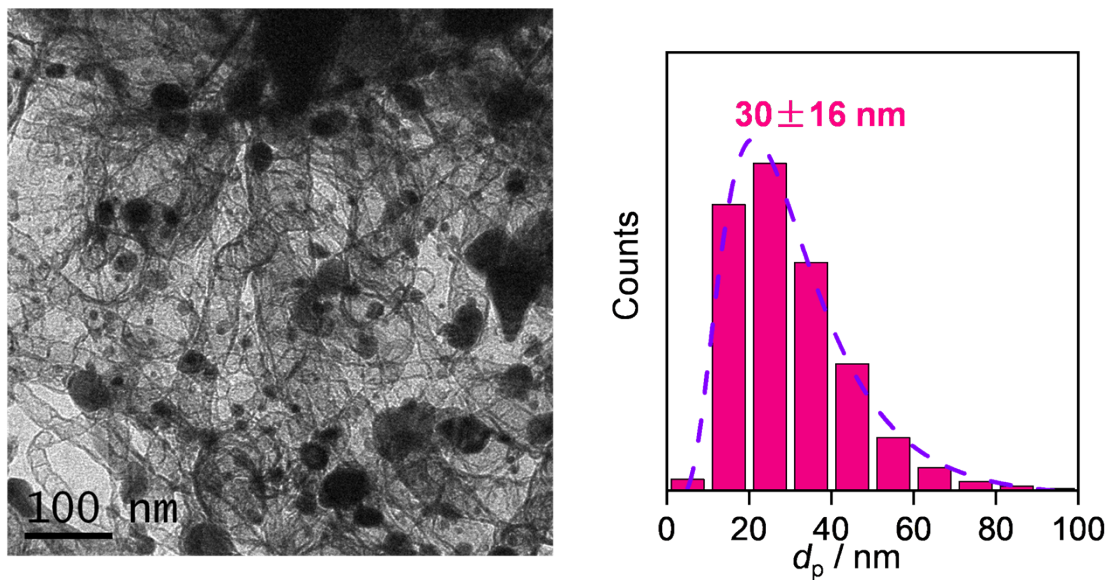


Fig. S5. Additional TEM image of Co@NC-1073 accompanied with the particle size distribution.

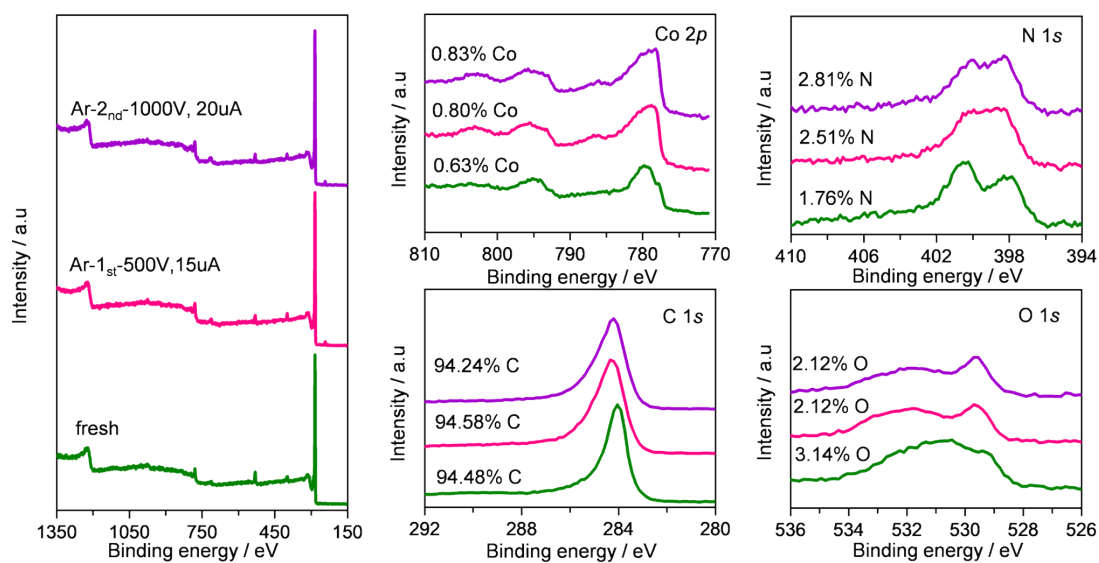


Fig. S6. XPS depth profile analyses of Co@NC-1073 after the sputtering treatments under different conditions. The increased shares of the surface Co after sputtering might be due to the coverage of graphene layers as observed by HAADF-STEM.

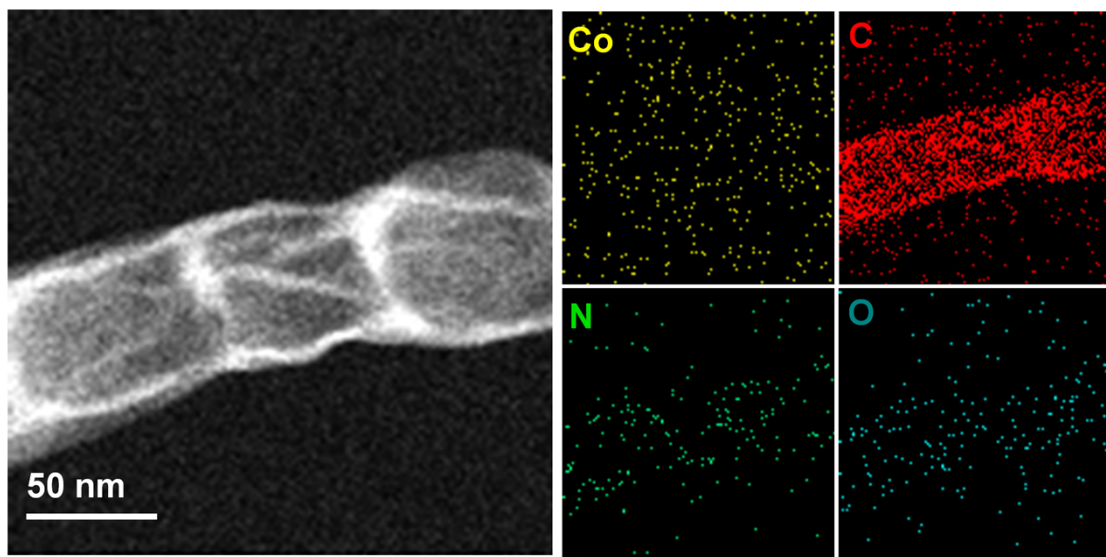


Fig. S7. The HAADF-STEM images of Co@NC-1073 with elemental color mapping.

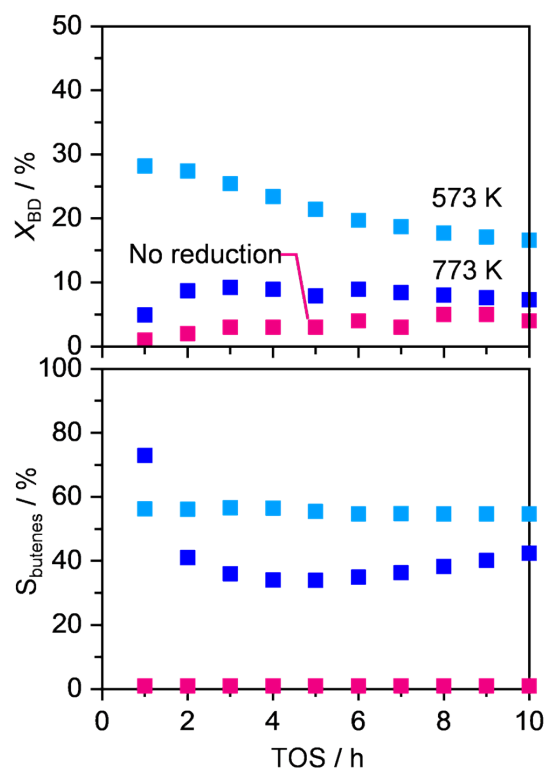


Fig. S8. Effects of reduction temperatures on the catalytic performance of Co@NC-1073 in BD hydrogenation. Reaction conditions: $T = 303$ K, $H_2:BD = 50:1$, $W_{cat} = 25$ mg, $GHSV = 180000$ $cm^3 g_{cat}^{-1} h^{-1}$.

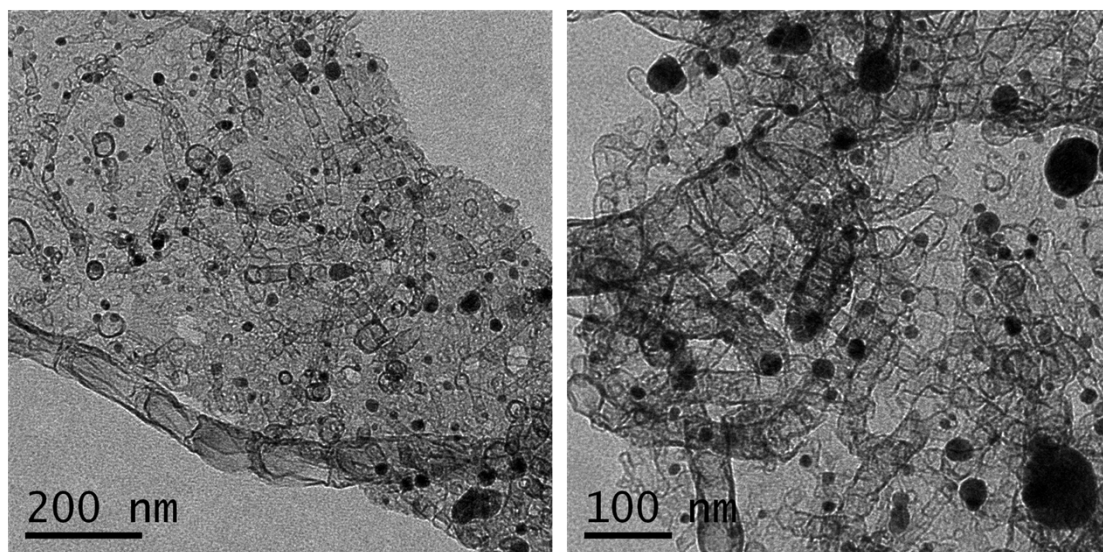


Fig. S9. TEM images of Co@NC-1073 after the HCl leaching treatment.

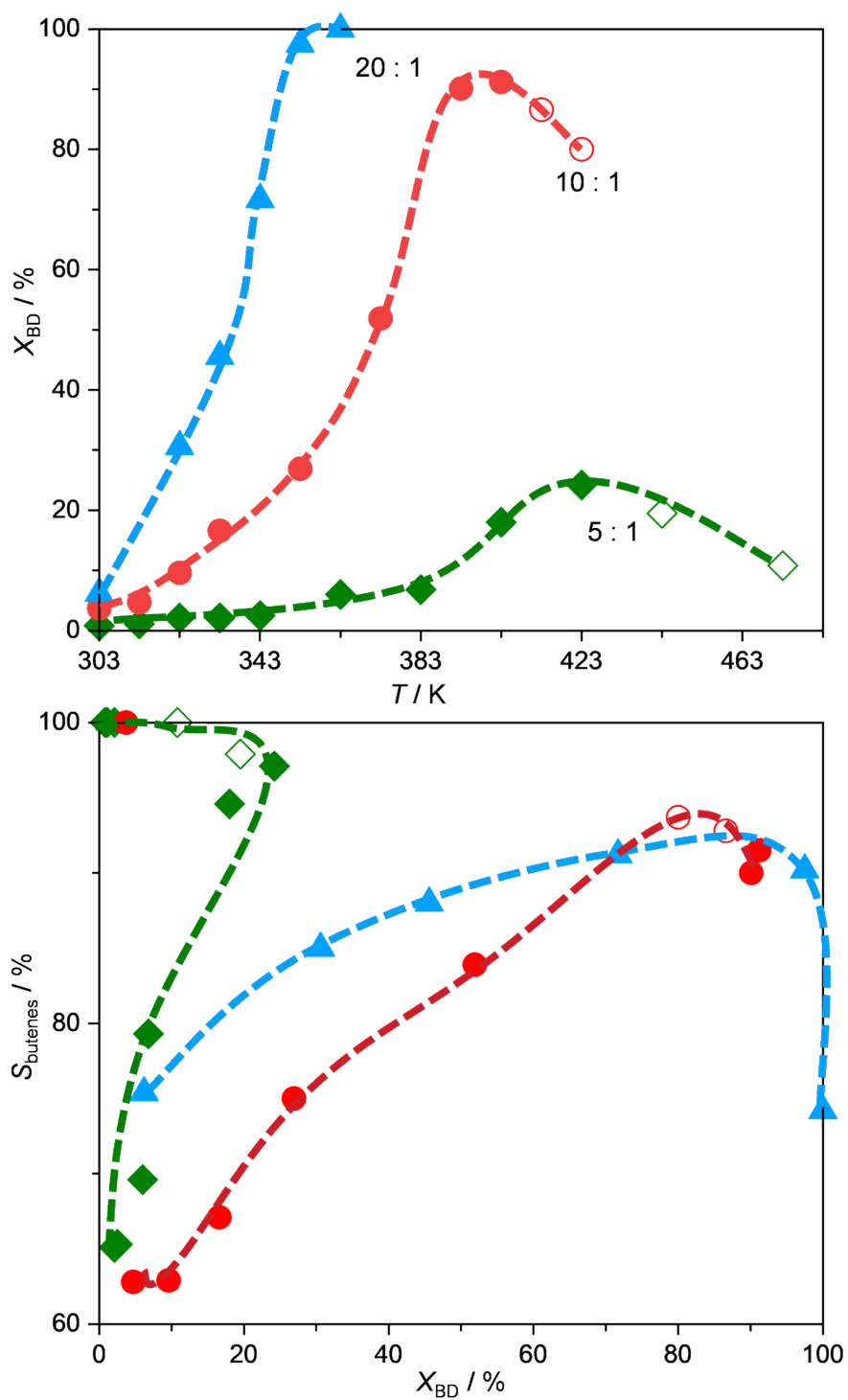


Fig. S10. Light-up curves and the conversion-selectivity patterns of Co@NC-1073 in BD hydrogenation at different H_2 :BD ratios. The open symbols indicated catalysts deactivation at higher temperatures. Reaction conditions: $W_{cat} = 50$ mg, $GHSV = 90000$ cm^3 g_{cat}^{-1} h^{-1} .

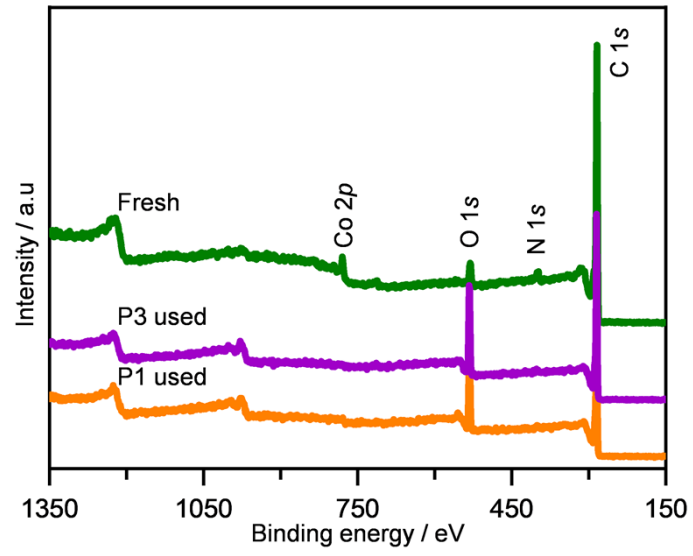


Fig. S11. The full XPS spectra of fresh Co@NC-1073, and P1 and P3 catalysts after the catalytic uses.