

ESI file for

Reactive adsorption of NO₂ over NaCoO₂-Co₃O₄ nanocomposite: Experimental study and first-principles calculations

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Section 1: Synthesis of (Na,Co)-BTC MOF

The MOF was prepared by sonicating (Sonics Vibra-cell 500 W, 20 kHz, 44% amplitude) freshly prepared cobalt hydroxide with H₃BTC solution (0.21 mol L⁻¹ in DMF). Cobalt hydroxide was prepared by adding 82.5 mL of methanolic NaOH solution (1.30 mol L⁻¹) in 75 mL of Co(NO₃)₂·6H₂O salt solution in DMF (0.55 mol L⁻¹).

Section 2: Analytical instruments

The surface morphology was probed by a Hitachi S-4300 field emission scanning electron microscope (FE-SEM, Japan). The dried samples were coated with Au-Pt alloy using an E-1048 Hitachi ion sputter to improve the signal-to-noise ratio. The 2D elemental mapping was performed on an X-Maxn 80 T energy-dispersive X-ray spectroscope (Oxford, United Kingdom). Fourier-transform infrared (FTIR) spectra were recorded on a Cary670 FTIR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded at 25 °C on an Ultima IV X-ray diffractometer (Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a Ni filter. Thermal gravimetric analysis (TGA) of MOF was performed on a TG 209 F3 Thermogravimetric Analyzer (NETZSCH, Germany). N₂ adsorption-desorption measurements were conducted on Quantachrome Instruments v10.0 (Florida, United States) after degassing samples at 120 °C for 6 h. The chemical states of constituent elements were analyzed using an X-ray photoelectron spectrometer (XPS, Nexsa spectrometer system, Thermo Scientific, United Kingdom) focused with Al K α monochromator (1486.6 eV). Spectra were charge corrected to the main line of the C 1s spectrum (aromatic carbon) set to 284.7 eV. Spectra were analyzed using CasaXPS software (version 2.3.14) with GL(p) = Gaussian/Lorentzian product formula, where the mixing is determined by $m = p/100$, GL(100) is a pure Lorentzian, and GL(0) is a pure Gaussian. We have used GL(30) in this study.

Section 3: DFT calculations

A spin-polarized density functional theory (DFT) ^{1,2} investigation was conducted to study the bare and NO₂ gas molecule adsorbed Co₃O₄ and NaCoO₂ surface by utilizing the Vienna ab initio simulation package (VASP) ³. VASP package incorporates the projector augmented wave (PAW) and generalized gradient approximation (GGA) methods to properly include the interactions between ions and electrons ^{4,5}. For all the structural and electronic properties calculations, cutoff energy of 500 eV, and the Brillouin-zone integration using a Monkhorst-Pack scheme ⁶ with a $5 \times 5 \times 1$ k-point grid was considered. We enforced the convergence criteria for the total energy and atomic forces as 10⁻⁴ eV and 0.02 eV/Å, respectively. To describe the adsorption of the NO₂ gas molecules on the Co₃O₄ and NaCoO₂ surface accurately, we considered the van der Waals

interaction using the DFT-D3 method ⁷. For the surface interaction study with NO₂ gas molecule on Co₃O₄ and NaCoO₂ surfaces and removing the interaction between the imaginary surfaces, we considered a 15 Å vacuum region in the Z direction. For the graphical representations, we considered the VESTA package ⁸. The adsorption energy (E_{ad}) of the NO₂ gas molecule on the Co₃O₄ and NaCoO₂ surface is obtained from the following equation (1):

$$E_{ad} = E_{Surface + NO_2} - E_{Surface} - E_{NO_2} \quad (1)$$

In the above equation, the initial three terms represent the ground state energy of the Co₃O₄ or NaCoO₂ surface, the ground state energy of the isolated gas molecules, and the ground state energy of the complex configuration for the NO₂ gas molecule, respectively. To obtain the donor and acceptor nature of the NO₂ gas molecule, we considered the Bader charge analysis ⁹. The formulation for the charge density difference ($\Delta\rho$) is reported as:

$$\Delta\rho = \rho_{Surface + NO_2} - \rho_{NO_2} - \rho_{Surface} \quad (2)$$

In the above equation, the first three terms on the right-hand side describe the charge density of the complex system, the charge density of the isolated gas molecules, and the charge density of the Co₃O₄ or NaCoO₂ surface, respectively.

References

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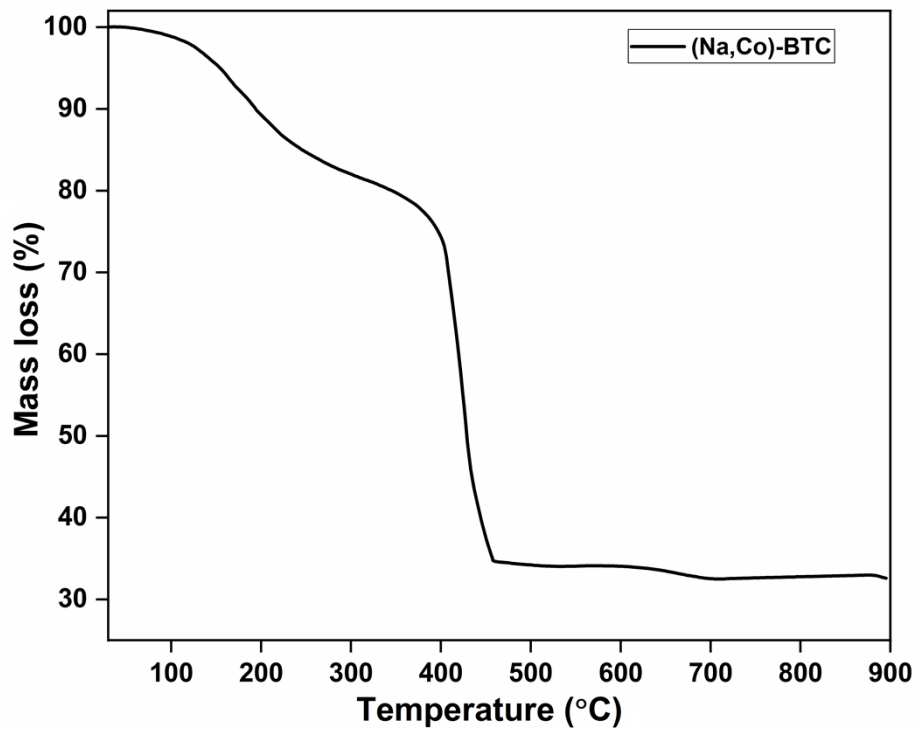


Figure S1. TGA profile of (Na,Co)-BTC.

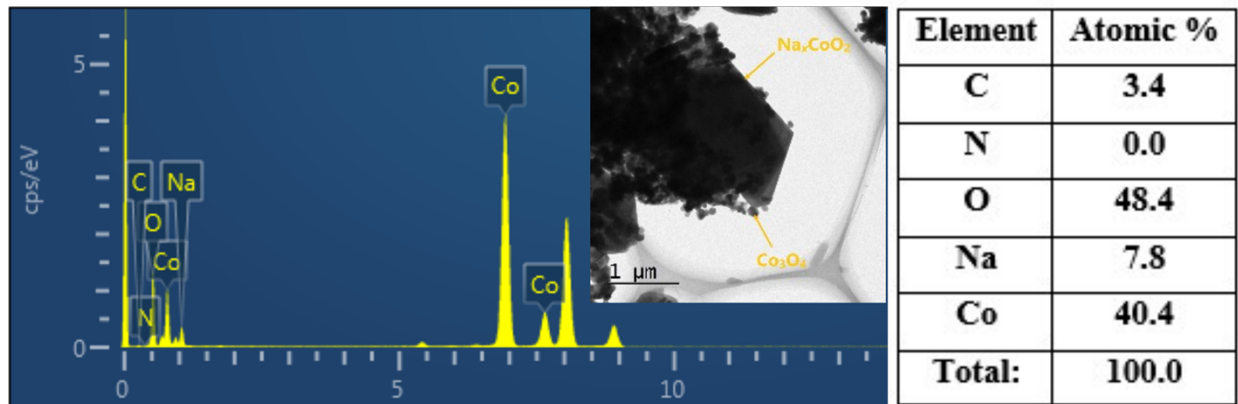


Figure S2. TEM-EDAX analysis of NaCoO.

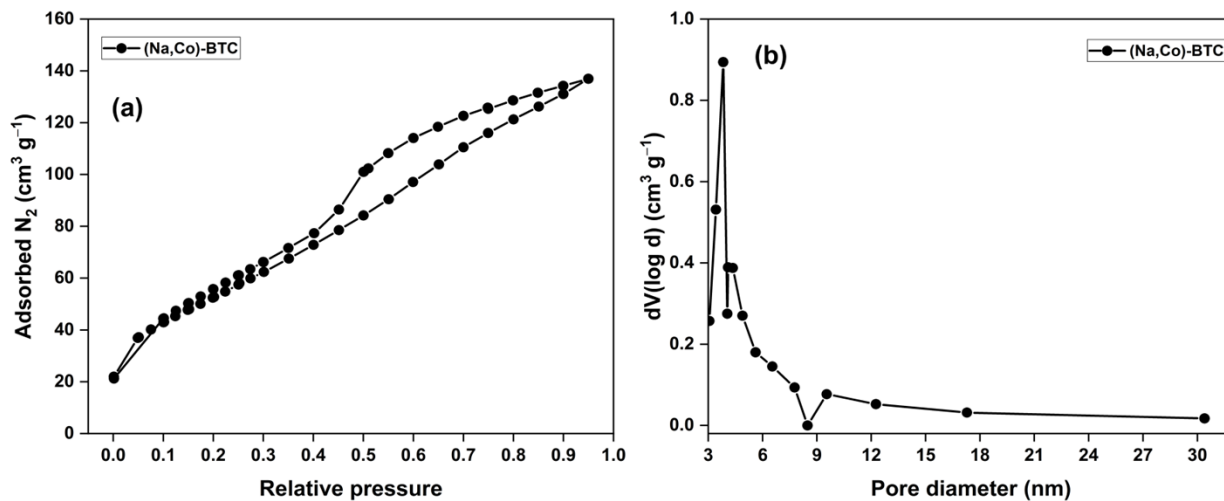


Figure S3. (a) N_2 adsorption-desorption isotherm; (b) Pore size distribution of (Na,Co)-BTC.

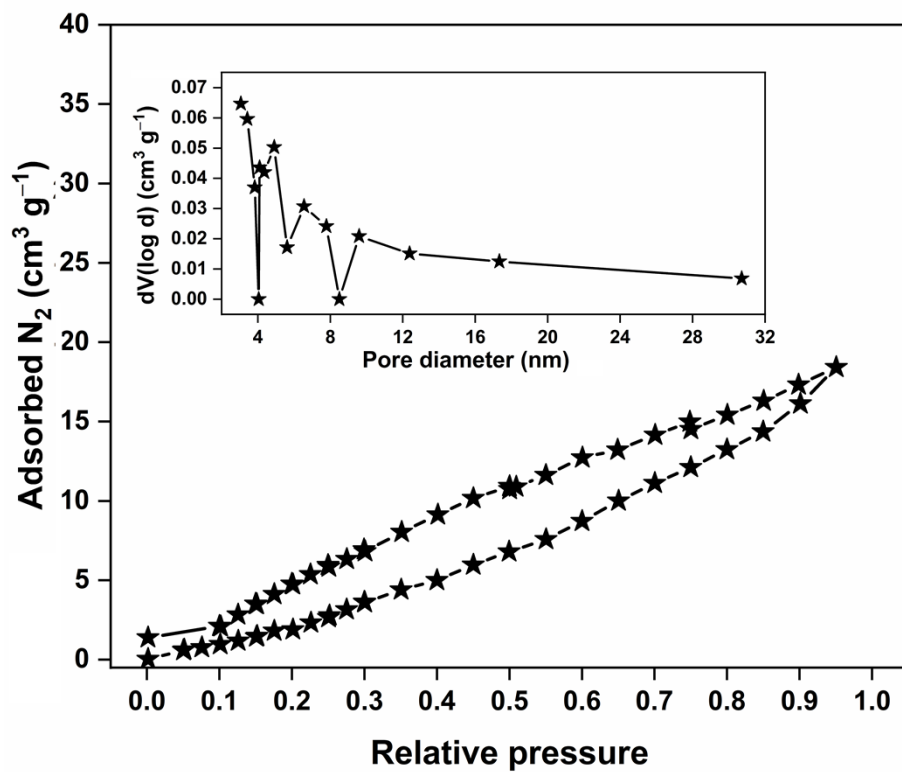


Figure S4. N_2 adsorption-desorption isotherm (pore size distribution in inset).

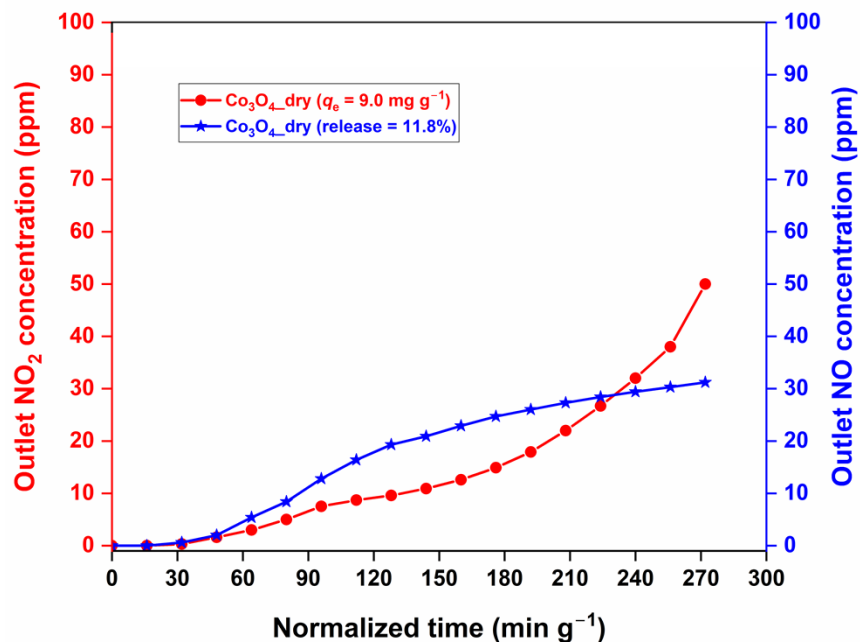


Figure S5. Outlet NO₂ and NO concentration as a function of normalized time for dry *Co₃O₄.
 Conditions: $T = 25\text{ }^{\circ}\text{C}$, mass = 0.25 g, flow rate = 0.2 L min⁻¹.

*Co₃O₄ was prepared by air calcination of commercially procured Co(OH)₂ at 500 °C for 2 h in a muffle furnace.

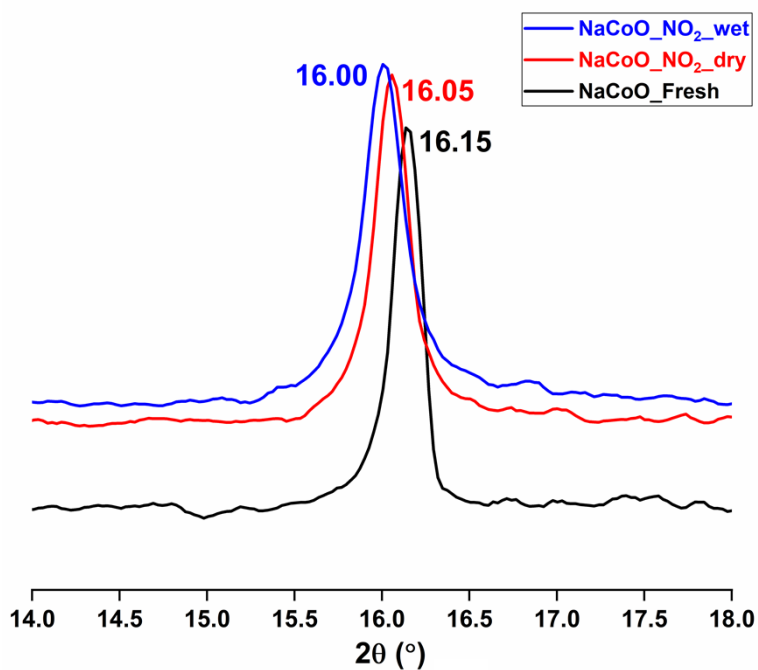


Figure S6. PXRD patterns ($2\theta = 14\text{-}18^{\circ}$) of NO₂-adsorbed NaCoO samples in dry and wet conditions.

Table S1. Atomic composition of fresh and NO₂-exposed NaCoO samples.

| Samples | Elements (At. %) | | | | |
|----------------------------|------------------|------|------|------|-----|
| | C | O | Na | Co | N |
| NaCoO_Fresh | 26.9 | 49.0 | 10.2 | 13.9 | 0.0 |
| NaCoO_NO ₂ _dry | 22.3 | 49.1 | 9.8 | 15.7 | 3.1 |
| NaCoO_NO ₂ _wet | 24.6 | 48.3 | 13.5 | 11.4 | 2.2 |

Table S2. The peak-fitting results of N 1s high-resolution signal of fresh and NO₂-exposed NaCoO samples.

| Sample | Assignment | E_B (eV) | FWHM (eV) | At. % |
|----------------------------|------------------------------|------------|-----------|-------|
| NaCoO_NO ₂ _dry | NO ₂ ⁻ | 403.8 | 2.4 | 33.7 |
| | NO ₃ ⁻ | 407.5 | 2.7 | 66.3 |
| NaCoO_NO ₂ _wet | NO ₂ ⁻ | 404.1 | 2.0 | 33.6 |
| | NO ₃ ⁻ | 406.5 | 2.3 | 66.4 |

Table S3. The peak-fitting results of Na 1s high-resolution signal of fresh and NO₂-exposed NaCoO samples.

| Sample | Assignment | E_B (eV) | FWHM (eV) | At. % |
|----------------------------|-------------------------------|------------|-----------|-------|
| NaCoO_Fresh | Na ^{+_{esc}} | 1070.4 | 1.4 | 20.9 |
| | Na ^{+_{fsc}} | 1071.6 | 1.9 | 79.1 |
| NaCoO_NO ₂ _dry | Na ^{+_{esc}} | 1071.0 | 1.9 | 49.2 |
| | Na ^{+_{fsc}} | 1072.2 | 2.3 | 50.8 |
| NaCoO_NO ₂ _wet | Na ^{+_{esc}} | 1071.2 | 1.9 | 26.8 |
| | Na ^{+_{fsc}} | 1072.7 | 2.1 | 38.6 |
| | Na ^{+_{-OH}} | 1074.3 | 2.1 | 34.6 |

Table S4. The peak-fitting results of Co 2p_{3/2} high-resolution signal of fresh and NO₂-exposed NaCoO samples.

| Sample | Assignment | E_B (eV) | FWHM (eV) | At. % |
|----------------------------|------------------|------------|-----------|-------|
| NaCoO_Fresh | Co ³⁺ | 779.6 | 1.4 | 53.2 |
| | Co ²⁺ | 780.8 | 2.5 | 46.8 |
| | Satellite | 782.4 | 3.2 | - |
| | Satellite | 788.0 | 2.5 | - |
| NaCoO_NO ₂ _dry | Co ³⁺ | 779.7 | 1.5 | 56.0 |

| | | | | |
|---------------------------------|------------------|-------|-----|------|
| | Co ²⁺ | 781.0 | 1.9 | 44.0 |
| | Satellite | 782.6 | 2.5 | - |
| | Satellite | 789.8 | 2.7 | - |
| NaCoO_NO₂_wet | Co ³⁺ | 779.7 | 2.0 | 37.5 |
| | Co ²⁺ | 781.7 | 2.3 | 62.5 |
| | Satellite | 783.5 | 2.6 | - |
| | Satellite | 790.3 | 2.5 | - |

Table S5. The peak-fitting results of O 1s high-resolution signal of fresh and NO₂-exposed NaCoO samples.

| Sample | Assignment | <i>E_B</i> (eV) | FWHM (eV) | At. % |
|---------------------------------|-------------------|----------------------------------|------------------|--------------|
| NaCoO_Fresh | O–Na | 529.8 | 1.1 | 16.8 |
| | O–Co | 530.7 | 1.4 | 28.4 |
| | O–H | 532.0 | 1.5 | 30.3 |
| | H ₂ O | 533.1 | 1.9 | 21.1 |
| | Na Auger | 534.8 | 2.0 | 3.4 |
| NaCoO_NO₂_dry | O–Na | 529.7 | 1.1 | 15.6 |
| | O–Co | 530.6 | 1.3 | 27.2 |
| | O–H/O–N* | 531.9 | 1.8 | 28.2 |
| | H ₂ O | 533.4 | 1.9 | 21.5 |
| | Na Auger | 535.1 | 1.9 | 7.5 |
| NaCoO_NO₂_wet | O–Na | 529.8 | 1.5 | 10.1 |
| | O–Co | 531.3 | 1.7 | 20.6 |
| | O–H/O–N | 532.6 | 1.8 | 30.2 |
| | H ₂ O | 534.1 | 1.9 | 26.2 |
| | Na Auger | 535.4 | 2.0 | 12.9 |