

Supporting Information

Morphology dependence of Nb₂O₅ Supported Cobalt oxide on Catalytic Toluene Oxidation

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Catalyst Characterisation

X-ray diffraction (XRD) patterns were obtained through Bruker AXS-D8 Advance between 5° and 80° at a step length of 5° min^{-1} with a Cu $K\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$).

Elemental analysis was performed using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique on Agilent720ES.

The N_2 adsorption–desorption isotherm, BET surface area, t-plot area, pore size, and pore volume of the catalysts were measured at -196°C with a Micromeritics ASAP2010 instrument by using the Barrett-Joyner-Halenda method. Before the test, each sample was pretreated at 573 K for 2 h under $7\text{-}10 \text{ mmHg}$.

Transmission electron microscopy (TEM) and high-resolution TEM images were collected on a JEM-F200 instrument at a voltage of 200 kV . The as-prepared samples were first treated to ultrasonic dispersion in ethanol and subsequently dried on a carbon film supported with a copper grid.

X-ray photoelectron spectroscopy (XPS) patterns were measured on a Thermo Scientific ESCALAB 250Xi spectrometer electronic energy spectrum at 300 W by using Al $K\alpha$ X-rays as the excitation source. The data were processed using XPS-PEAK software, and surface element contents were calculated through XPS peak areas. The binding energies were calibrated using C $1s$ at 284.8 eV .

H_2 -temperature programmed reduction (H_2 -TPR) was performed on a Micromeritics AutoChem II 2920 apparatus. Briefly, 100 mg of samples with $40\text{-}60$ mesh was pretreated at 300°C for 70 min in the helium atmosphere in the U-shape quartz reactor. For H_2 -TPR, the samples were first cooled down to 30°C and then were reacted with hydrogen from 50 to 750°C with a heating rate of $10^\circ \text{C min}^{-1}$ under the atmosphere of $10\% \text{ H}_2/\text{He}$ ($50 \text{ mL}\cdot\text{min}^{-1}$).

NH₃-temperature programmed desorption (NH₃-TPD) was performed on a Micromeritics AutoChem II 2920 apparatus. Briefly, 100 mg of samples with 40-60 mesh was pretreated at 500 °C for 60 min in the Ar flow in the U-shape quartz reactor. Then the samples were first cooled down to 50 °C and the gas mixture (30ml/min) of 10% NH₃/Ar was introduced to absorb for 1h. Pure Ar was purged to remove the excess NH₃. Then the desorption was conducted by heating the temperature to 800°C (10°C/min).

Density functional theory Calculations

All calculations were performed using the density functional theory (DFT) technique using the Vienna ab initio simulation package (VASP). Spin-polarized calculations were performed using the generalized gradient approximation (GGA) combined with the Perdew–Burke–Ernzerhof (PBE) method to determine the exchange and correlation energies. The projector-augmented wave (PAW) method was used to represent the core–valence electron interactions. The typical plane-wave cutoff energy was 400 eV for basis-set expansion. For geometry optimization calculations, forces were converged below 0.03 eV/Å. The SCF convergence energy was 1×10⁻⁴ Ha. A 1×1×1 k-point mesh was used to perform all the calculations.

Two-layer slab model surfaces of Nb₂O₅ (001) and (180) substitution was built to calculate the adsorption energies and Gibbs free energies. Two p (3×3) unit cell expansions were used to model the surface of Nb₂O₅ (001) and (180). A vacuum of 15 Å was used to simulate the surface under periodic boundary conditions.

The adsorption energy (E_{ads}) of the C₇H₈, and the other molecule on the surface was calculated as follows (eq 1):

$$E_{ads} = E_{adsorbate + surface} - E_{surface} - E_{gas} \quad (1)$$

where E_{surface} is the clean surface relaxation energy of the surface slab, E_{gas} is the energy of a free gas molecule under conditions of vacuum, and $E_{\text{adsorbate+surface}}$ is the energy of the composite system. As the calculations are performed at 0 K at a fixed cell volume, the differences in the Gibbs free energy should equal the differences in the total energy. By this definition, a negative value of E_{ads} corresponds to exothermic and spontaneous adsorption processes.

The barrier energy, ΔE , for a difference between transition state energy difference and standard product formation enthalpy is defined as follows. The energy barrier calculation of O_2 to O-O on $\text{CoO}_x/\text{Nb}_2\text{O}_5(001)$ as an example (eq 2):

$$\Delta E = (E_{\text{O-O-CN001}} - E_{\text{stab-CN001}}) - (E_{\text{O}_2-\text{CN001}} - E_{\text{stab-CN001}}) \quad (2)$$

where $E_{\text{O-O-CN001}}$ and $E_{\text{O}_2-\text{CN001}}$ are the energies of the O-O and O_2 adsorbed on $\text{CoO}_x/\text{Nb}_2\text{O}_5(001)$, $E_{\text{stab-CN001}}$ is the energy of the $\text{CoO}_x/\text{Nb}_2\text{O}_5(001)$ surface slab. As the calculations are performed at $t=0$ K at a fixed cell volume, the differences in the Gibbs free energy should equal the differences in the total energy. By this definition, the lower the ΔE is, the easier it is to react.

Figures

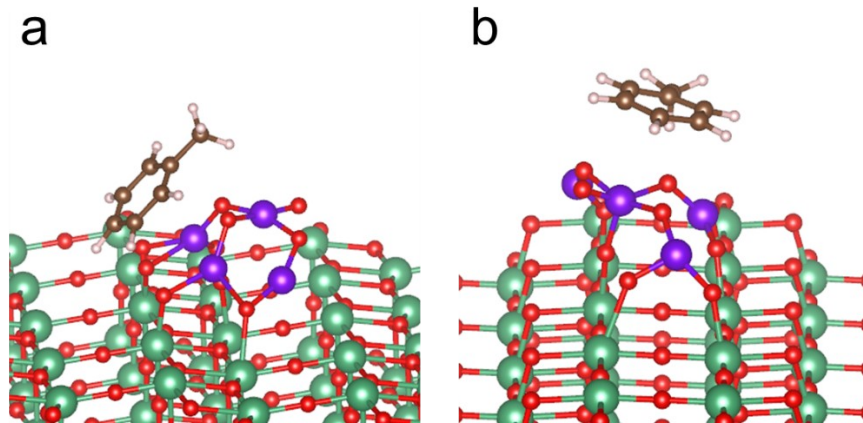


Figure S1 Models of toluene adsorption energies on (a) $\text{CoO}_x/\text{Nb}_2\text{O}_5(001)$, (b) $\text{CoO}_x/\text{Nb}_2\text{O}_5(180)$.

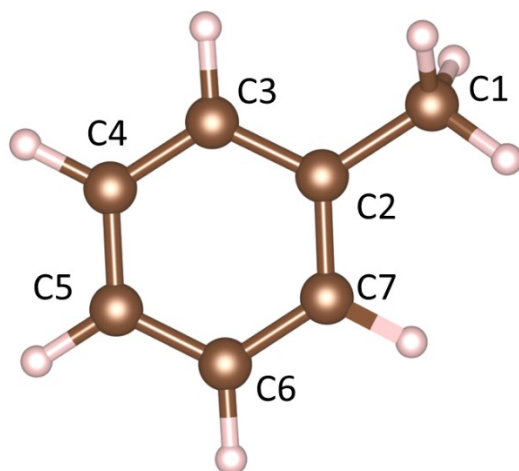


Figure S2 Carbon atom number of toluene model.

Table

Table S1 The bader charge and state value of CoO_x/Nb₂O₅(180), (b) CoO_x/Nb₂O₅(001).

Sample	Atom	Bader Charge	State Value
CoO _x /Nb ₂ O ₅ (180)	Co1	7.686	2.628
	Co2	7.743	2.515
	Co3	7.652	2.697
	Co4	8.210	1.581
	Average	7.823	2.355
CoO _x /Nb ₂ O ₅ (001)	Co1	7.515	2.971
	Co2	7.657	2.686
	Co3	7.704	2.592
	Co4	7.793	2.415
	Average	7.667	2.666

Table S2 Toluene adsorption value calculated by DFT calculation.

Sample	C1-C2	Δ C1-C2	C1-H	Δ C1-H	Co-C	C1-C2-C5	Δ C1-C2-C5
CoO _x /Nb ₂ O ₅ (180)	1.514	0.013	1.101	0.003	2.467	169.052	-10.845
			1.100	0.000			
			1.097	-0.006			
CoO _x /Nb ₂ O ₅ (001)	1.502	0.001	1.096	-0.002	2.677	169.809	-10.088
			1.103	0.003			
			1.098	-0.005			
C ₇ H ₈	1.501		1.098			179.896	
			1.100				
			1.103				