Support Information

Rich surface Co(III) ions enhanced Co nanocatalyst benzene /toluene oxidation performance derived from $Co^{II}Co^{III}$ layered double hydroxide

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Experimental

Synthesis of CoAl*x* LDHs (ammonia-releasing reagents route). The synthesis LDHs samples are based on the co-precipitation method. In a typical procedure，Firstly, three solutions of $Co(NO_3)_2·6H_2O$ (Co^{2+}, 15 mmol) and $Al(NO_3)_3·9H_2O$（Al^{3+}, 5 mmol）dissolved in 75 mL of methyl alcohol. Secondly，NH_4OH (water solution 30%) was added slowly to a meter ions mixed nitrate salt solution with constant agitation, keeping at constant PH 9.0; Hexamethylenetetramine (HMT, 25mmol) and urea ($(NH_2)_2CO$, 50mmol) were dissolved in other meter ions mixed nitrate salt solution, respectively. The solutions were transferred to a Teflon autoclave, and then the sealed containers were placed in an oven at 150 °C for 6h.

Reaction solvents route. In a typical synthesis, urea ($(NH_2)_2CO$, 50mmol), $Co(NO_3)_2·6H_2O$ (Co^{2+}, 15mmol), and $Al(NO_3)_3·9H_2O$（Al^{3+}, 5 mmol）with a Co^{2+}/Al^{3+} molar ratio of 3.0 and a molar ratio of urea to Al cations of 10 were dissolved in 75 mL of deionized water and ethanol (70ml ethanol + 5ml deionized water), respectively. Then the solutions were transferred to a Teflon autoclave, and then the sealed containers were placed in an oven at 150 °C for 6h.

Subsequently, the products were centrifuged, washed with deionized water and ethanol, and then dried at 80 °C for overnight, denoted as sample CoAl*x* LDH (*x* represents NH_4, HMT, urea, H_2O and ET)

Catalyst characterization

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The powder X-ray diffraction (XRD) data of the samples were collected at room temperature using a Panalytical X'Pert PRO system within the range of scattering angle 2θ of 5–90°. The BET specific surface area and pore size distributions of all catalysts were obtained with N_2 adsorption/desorption method according to the Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) methods, respectively. The N_2 adsorption-desorption isotherms of samples were measured via N_2 adsorption at −196 °C on an automatic surface analyzer (AS-1-C TCD, Quantachrome Corp, USA). Before measurement, every sample was outgassed at 150 °C for 6 h. The morphologies and element distribution of samples were characterized by field-emission scanning electron microscopy (SEM) via an electron microscope (SEM, JEOL JSM-6700F, Japan, 15kv, 10mM), equipped with an energy dispersive X-ray detector. The microstructures of samples were recorded on transmission electron microscopy (TEM, JEOL JEM-2010F) with an accelerating voltage of 200 kV. The Raman spectra were conducted on a Renishaw RM2000 Raman Spectrometer using laser wavelength = 532 nm from 100 to 1000 cm^{-1}, recorded at a resolution of 1 cm^{-1}. The temperature-programmed reduction of hydrogen (H_2-TPR) with 30mg catalyst (40-60 mesh) was carried out in a U-shaped quartz reactor under a gas flow (10% H_2/Ar, 25 mL min^{-1}) with Automated Catalyst Characterization System (Autochem 2920, MICROMERITICS). In each procedure, the temperature was raised to 800 °C from room temperature at a constant rate of 10 °C min^{-1}. Surface species of all catalysts were determined by X-ray photoelectron spectroscopy (XPS) using an XLESCALAB 250Xi electron spectrometer from VG Scientific with monochromatic Al Ka radiation, the binding energies of all of the elements were referenced to the C 1s line at 284.8 eV from carbon impurities. The acidity of the oxide catalysts was determined by temperature-programmed desorption of ammonia (NH_3-TPD) experiments by using a Micromeritics Instrument Corporation -- AutoChem II 2920 equipped with a thermal conductivity detector (TCD) and a mass quadrupole spectrometer. 50 mg catalyst was pre-treated in was performed by flowing 5% NH_3/He stream from room temperature to 400 °C and held for 1h (50 mL min^{-1}) and then cooling to room temperature. The samples were heated from room temperature to 500 °C in pure He (50 mL min^{-1}). The temperature programmed desorption of O_2 (O_2-TPD) with 50 mg catalysts was pre-heated in 5% O_2/He flow from room temperature to 400 °C and held for 1h (50 mL min^{-1}), and then cooling to room temperature. the catalysts were heated from room temperature to 800 °C at 10 °C min^{-1} in pure He (50 mL min^{-1}).

Catalytic activity evaluation

The evaluation of the catalytic activity was conducted in a fixed-bed quartz tubular micro-reactor (φ= 6 mm) at a space velocity (SV) of 60,000 mL g^{-1} h^{-1}, and 100 mg (40–60 mesh) catalyst mixed with 200 mg of quartz sands (40–60 mesh) was placed in the quartz reactor with quartz wool packed at both ends of the catalyst bed. The reactant gas composed of 100 ppm gaseous benzene or 191ppm gaseous toluene balanced with air (20% O_2 + balance N_2) was purged into the reactor at a continuous flow 100 mL min^{-1}. The concentrations of reactant gas were analyzed by a gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and the concentrations of CO_2 in the outlet gas was monitored by another FID with a conversion furnace for converting CO_2 to CH_4. The range of catalytic activity testing temperatures was 120 to 260 °C. The complete conversion of benzene (η_{benzene}) was calculated according to the following equation:

$$\eta_{\text{benzene}} = \frac{C_{benzene,in} - C_{benzene,out}}{C_{benzene,in}} \times 100$$

$$\eta_{CO_2} = \frac{C_{CO_2,out}}{6 \times C_{benzene,in}} \times 100$$

Where $C_{\text{CO2,out}}$ (ppm), $C_{\text{benzene,in}}$ (ppm) and $C_{\text{benzene,out}}$ (ppm) are the concentrations of CO_2 in the outlet gas, benzene in the inlet and outlet gas, respectively.

For consideration of the water vapor’s effect on the catalytic activity, the on-stream benzene oxidation experiments were carried out in the presence and absence of 3.6 vol% water vapor. Typically, an air flow (50 mL min^{-1}) was used for bubbling water in a 500ml conical flask at 40 °C, then mixed with another air flow (50 mL min^{-1}) containing gaseous benzene (159 ppm) in another 500mL conical flask. The mixed gas that composed a relative water vapor (3.6 vol%) and benzene (80 ppm) was used for catalytic test in 230 °C.

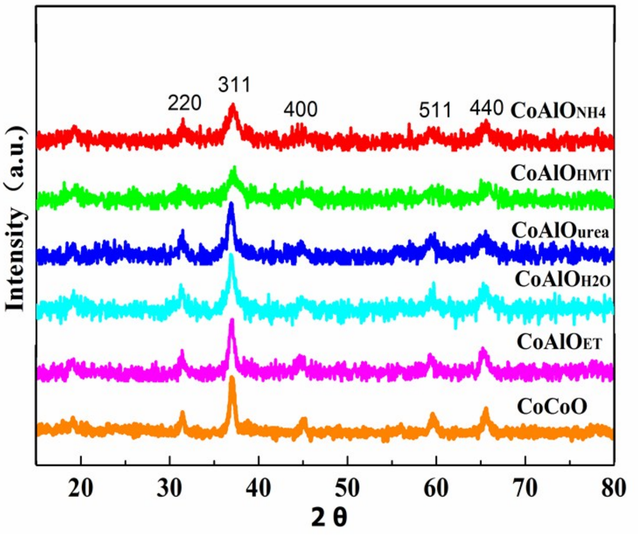


Fig. S1. XRD patterns of all metal oxides

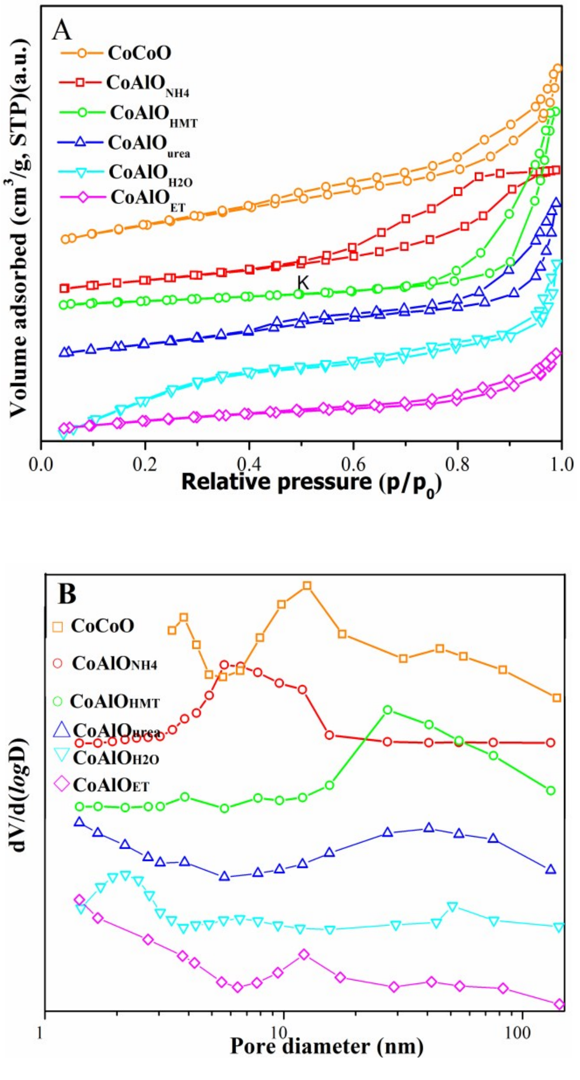


Fig. S2. N_2 adsorption/desorption isotherms and pore/size distribution for all metal oxides.

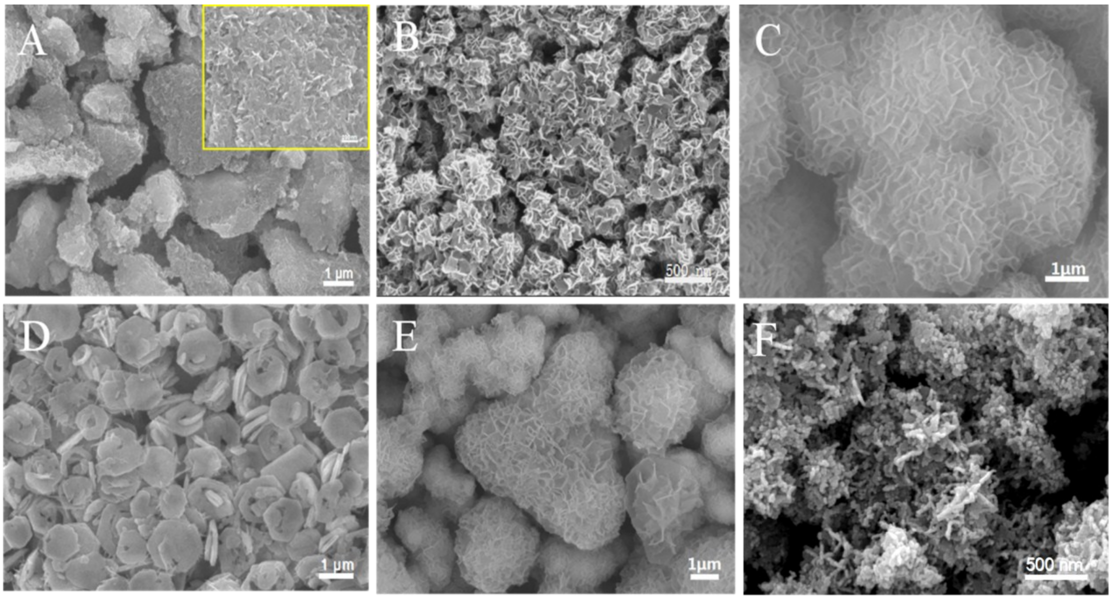
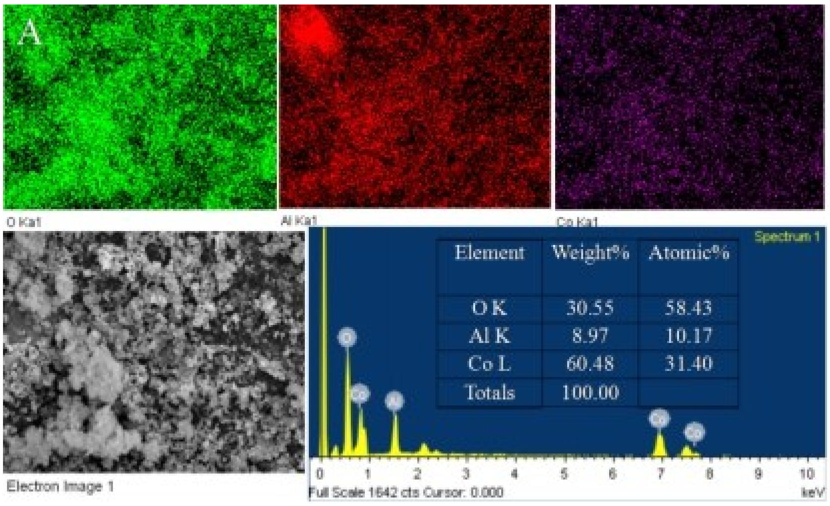


Fig. S3. (A-E) SEM images of the $CoAlO_{NH4}$, $CoAlO_{HMT}$, $CoAlO_{urea}$, $CoAlO_{H2O}$, $CoAlO_{ET}$ and CoCoO.



Element	Weight%	Atomic%
O K	30.55	58.43
Al K	8.97	10.17
Co L	60.48	31.40
Totals	100.00	

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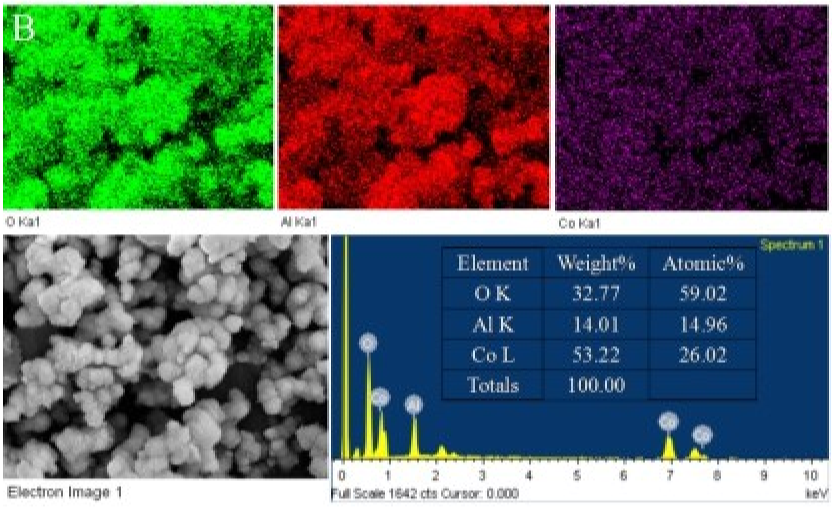
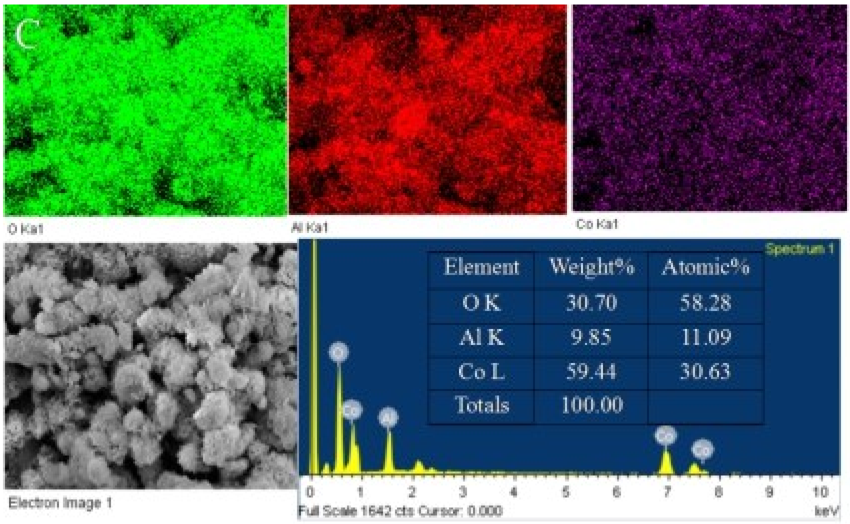


Element	Weight%	Atomic%
O K	32.77	59.02
Al K	14.01	14.96
Co L	53.22	26.02
Totals	100.00	



Element	Weight%	Atomic%
O K	30.70	58.28
Al K	9.85	11.09
Co L	59.44	30.63
Totals	100.00	

Fig. S4. SEM images, element distributions and EDX datum of the $CoAlO_{HMT}$, $CoAlO_{urea}$ and $CoAlO_{ET}$.

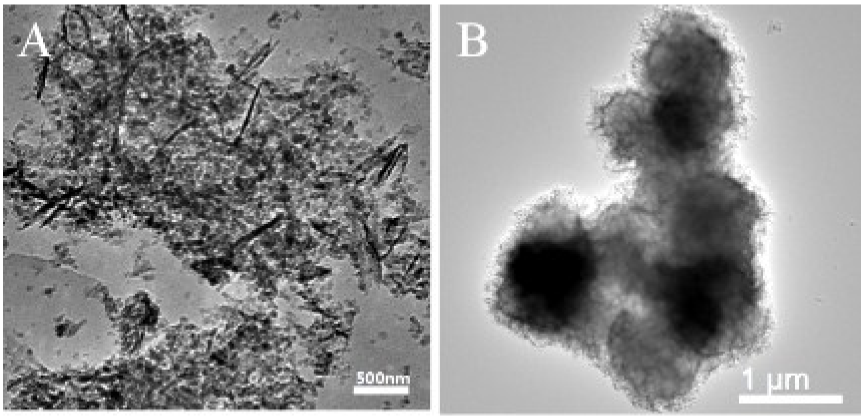


Fig. S5. TEM images of the $CoAlO_{NH4}$ (A) and $CoAlO_{urea}$ (B) catalysts.

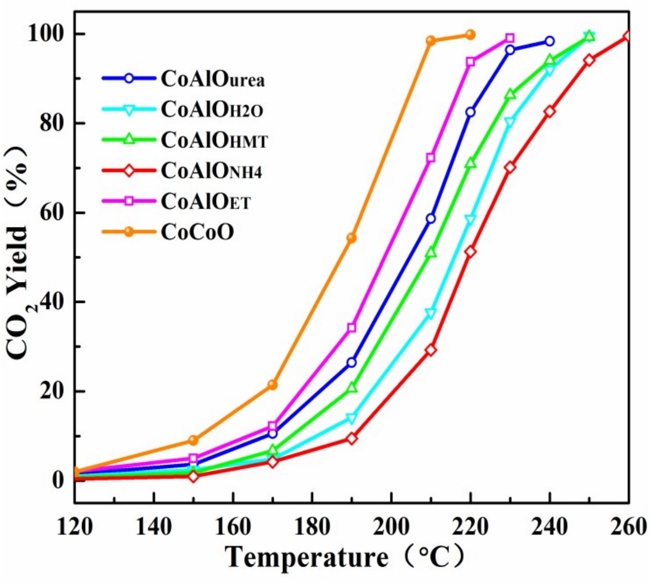


Fig. S6. Produced CO_2 yield as a function of reaction temperature over all catalysts