

SUPPLEMENTARY DATA

Low temperature simultaneous detoxification of NO and CO over precious metal-free nanocomposite metal oxides

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Experimental Section

A glycine-assisted combustion method was employed to prepare the manganese composed cobalt- copper composite oxides series. The amount of metal as a weight percent has been used for formulating the prepared oxide material. Metal nitrate such as $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich), and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as the sources of metals. By dissolving the respective metal nitrate salts in double distilled water, a weighed amount of glycine was added to the mixture containing metal ions with constant stirring and heating. After that, the mixture was kept at 80 °C in an electric oven for slow evaporation of water and further, the obtained gel was combusted at 200 °C for 2 h. Furthermore, final heat treatment of around 500 °C for 4 h was given to obtain the requisite oxides. For simplicity, the prepared oxides such as $\text{CoO}_x\text{-CuO}_x$, $\text{CoO}_x\text{-CuO}_x - 10\% \text{ Mn}$, $\text{CoO}_x\text{-CuO}_x - 20\% \text{ Mn}$ and $\text{CoO}_x\text{-CuO}_x - 30\% \text{ Mn}$ are abbreviated as Co-Cu, Co-Cu-10Mn, Co-Cu-20Mn and Co-Cu-30Mn, respectively.

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Characterization

X-ray diffraction studies of powdered samples were carried out on RIGAKU ULTIMA IV diffractometer using Cu K α source at a wavelength of 1.5418. Jeol/JEM 2100 instrument operating at 200 kV was employed for HRTEM analysis. Further, IMAGEJ software was used for determining the particle size distribution. As surface area in heterogeneous catalysis is essential, it has been studied at liquid nitrogen temperature on QUANTACHORME AUTOSORB iQ-MP-C instrument. Prior to N₂ sorption analysis, the sample was treated at 200 °C for 2 h. The chemical states of the element were evaluated with the XPS tool over the PHI 5000 versa probe II spectrophotometer. Reaction patterns of the catalysts were H₂ TPR studies on QUANTACHORME AUTOSORB iQ-MP-C instruments equipped with a TCD detector. For TPR analysis quartz tube was used where a 100 mg sample was sandwiched between quartz wool plugs. The percentage of Mn present is determined over Agilent 4210 Microwave plasma-Atomic Emission Spectrometer.

Catalytic Study

The redox conversion reaction of NO and CO was carried out by loading the catalyst in a continuous flow glass reactor. The 0.9 g catalyst was loaded in between glass wool plugs so as the catalyst will be sandwiched between the glass wool. The gases such as NO and CO were prepared via standard preparative route whereas gases such as H₂ (99%), N₂ (99.9%), and Ar (99.995%), were used from pure commercial sources. Further the reactant i.e. 5% CO and 5% NO in 90% Ar were passed over the catalyst placed in an electric oven at flow rate of 5000 ml h⁻¹. As the reaction proceeded, the progress of the reaction was monitored on an on-line gas

chromatogram. During the reaction, for separations of the gases Porapak Q and Molecular sieve 13x column were used which later identified on thermal conductivity detector (TCD).

Standard preparative route for Carbon monoxide (CO) and Nitric Oxide (NO)



Obtained gases later passed over various traps for purification and the final gases thus analyzed for purity on GC.

Calculation for % conversion of CO

$$\% \text{ CO conversion} = \left(\frac{\text{CO}(in) - \text{CO}(out)}{\text{CO}(in)} \times 100 \right)$$

Calculation for % conversion of NO

$$\% \text{ NO conversion} = \left(\frac{\text{NO}(in) - \text{NO}(out)}{\text{NO}(in)} \times 100 \right)$$

Table S1: AES studies on the prepared Co-Cu-Mn based catalyst.

Catalyst composition	% Mn Concentration
Co-Cu	0
Co-Cu-10Mn	9.51
Co-Cu-20Mn	21.12
Co-Cu-30Mn	29.36

1. BET surface area.

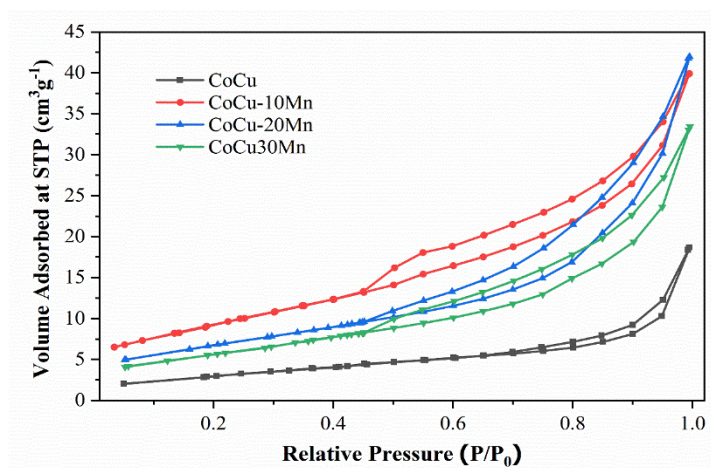


Figure S1: N₂ adsorption-desorption isotherm of Mn containing Co-Cu composite oxide series.

2. XPS of Mn 2p.

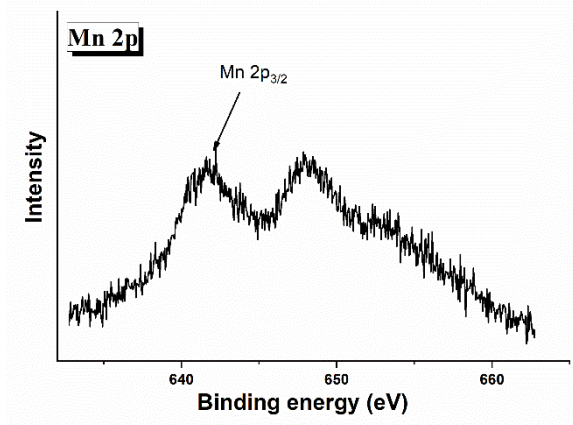


Figure S2: XPS spectra of Mn2p from Co-Cu-10Mn catalyst.

3. Recyclability study

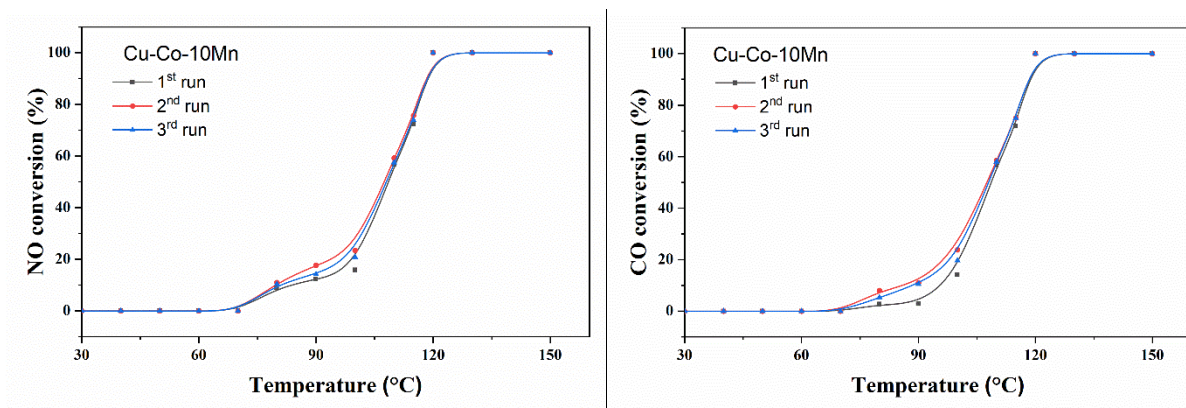


Figure S3: NO-CO reaction for 3 cycles over Co-Cu-10Mn catalyst

4. N₂O formation

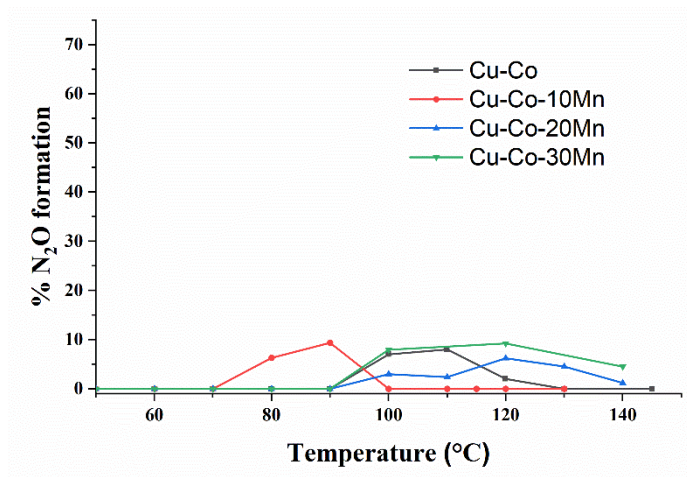
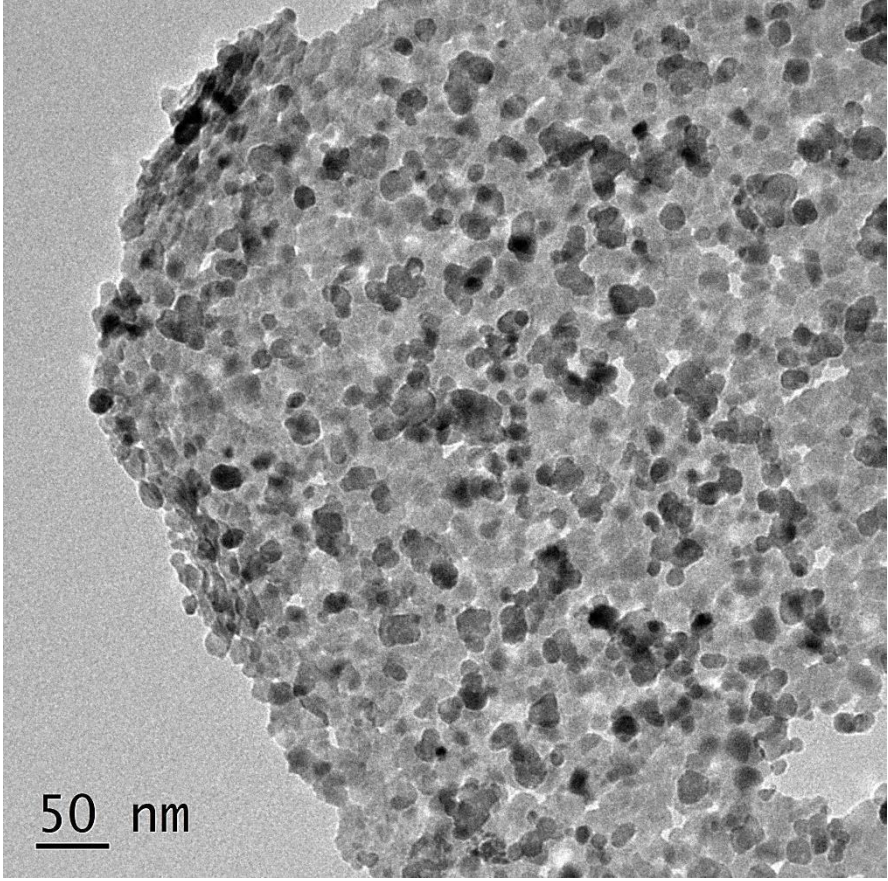
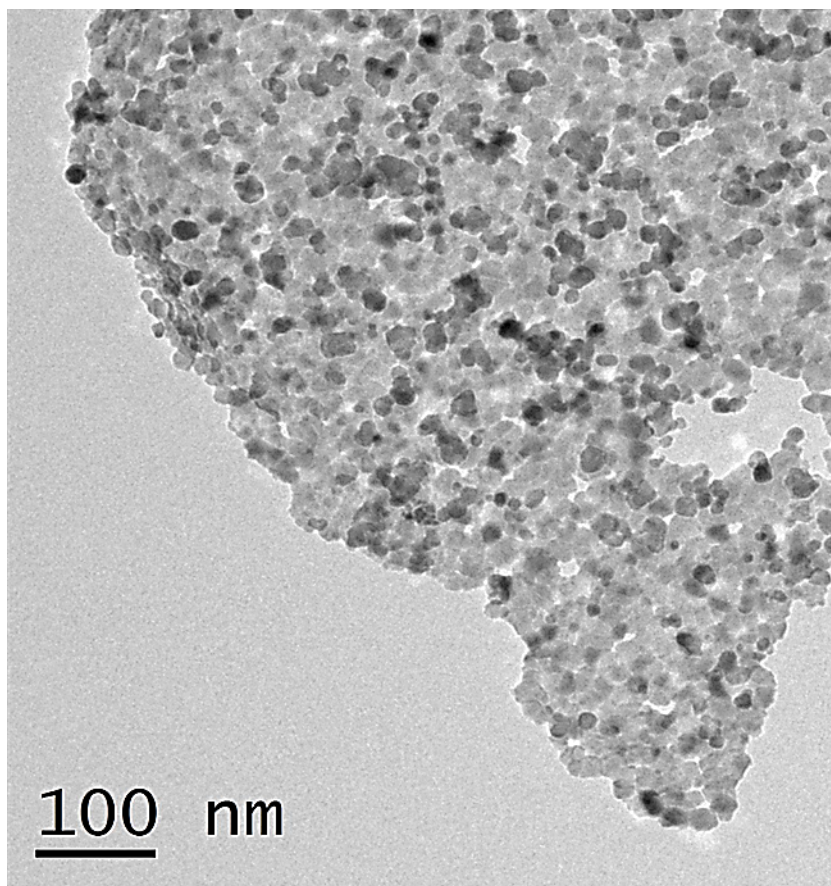


Figure S4: N₂O formation over studied catalyst.

5. TEM of Co-Cu-10Mn





6. CO oxidation with NO

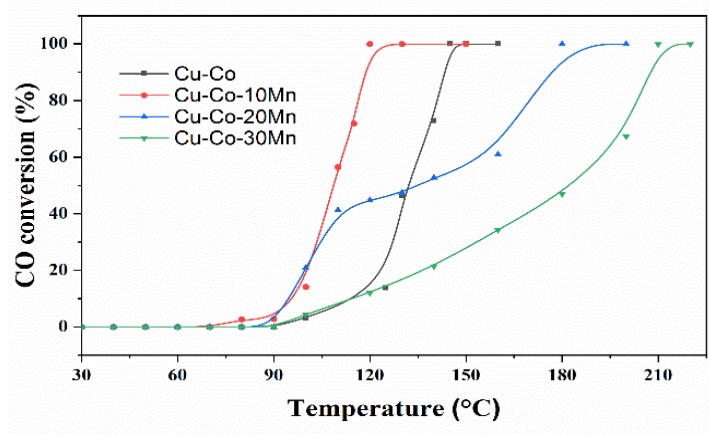


Figure S5: CO oxidation with NO over Co-Cu, Co-Cu-10Mn, Co-Cu-20Mn and Co-Cu-30Mn (5% NO and 5% CO in Ar at flow rate of 5000 mL h⁻¹).

7. CO TPD studies

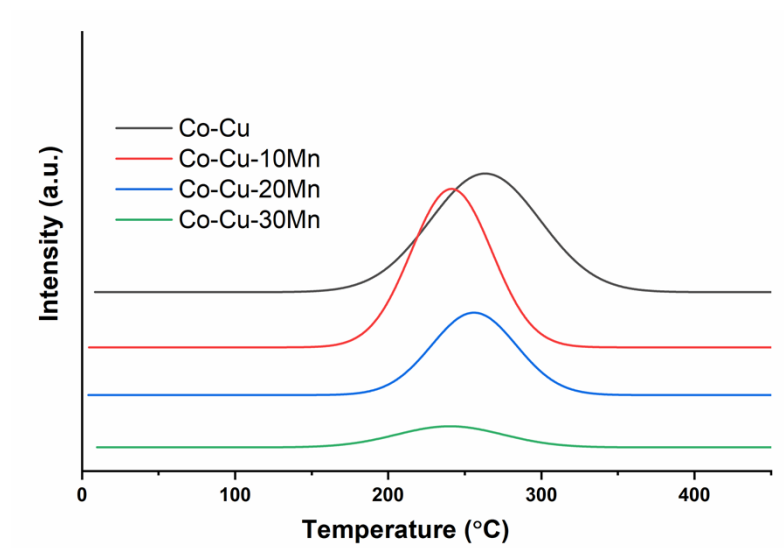


Figure S6: CO-TPD over Mn modified Co-Cu catalyst