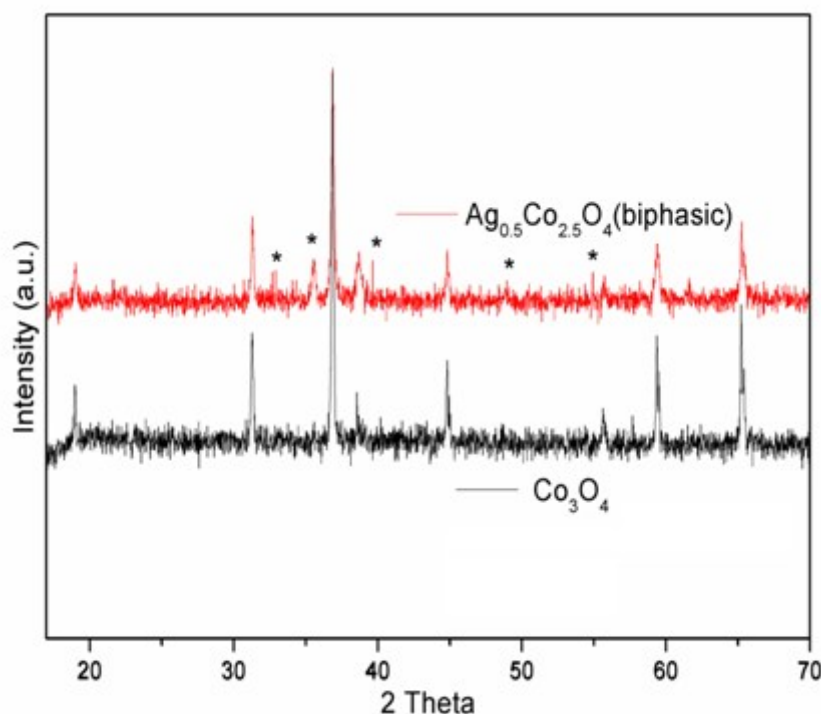


## Supplementary file

### Preparation of CO and NO

The CO was prepared by disproportionation of formic acid with conc.  $\text{H}_2\text{SO}_4$  and NO by reaction of sodium nitrite with conc.  $\text{H}_2\text{SO}_4$  and  $\text{FeSO}_4$  in a special glass apparatus. Gases generated are passed through saturated solution of KOH separately as by products like  $\text{CO}_2$  and  $\text{NO}_2$  generated, gets absorbed in the alkali solution and dried over molecular sieves as well as calcium chloride to remove moisture. Purity of CO and NO were checked on gas chromatograph and found to be pure. The Ar and  $\text{O}_2$  gases used were from pure commercial cylinders.

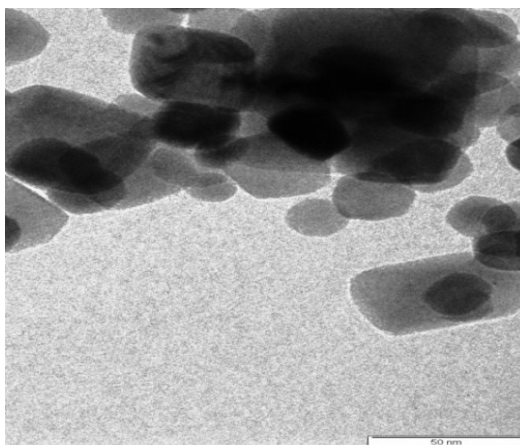
### XRD



**Supplementary figure 1.** XRD pattern of pristine  $\text{Co}_3\text{O}_4$  and higher dopant ( $\text{Ag}_{0.5}\text{Co}_{2.5}\text{O}_4$  biphasic).

XRD indicates monophasic nature and no extra reflection of Co or CoO is seen in pristine  $\text{Co}_3\text{O}_4$ , whereas higher dopant  $\text{Ag}_{0.5}\text{Co}_{2.5}\text{O}_4$  resulted in biphasic composition. The XRD pattern showed 111 ( $\sim 18.9^\circ$ ), 220 ( $\sim 31.3^\circ$ ), 311 ( $\sim 36.8^\circ$ ), 222 ( $\sim 38.56^\circ$ ), 400 ( $\sim 4.8^\circ$ ), 511 ( $\sim 59.3^\circ$ ), 440 ( $\sim 65.2^\circ$ ) and 533 ( $\sim 78.5^\circ$ ) which indicate cubic phase of cobalt oxide spinel. Two theta values are matching well with JCPDS card no. 42-1467. Broadening indicates poor crystalline nature of the prepared catalysts.

## TEM



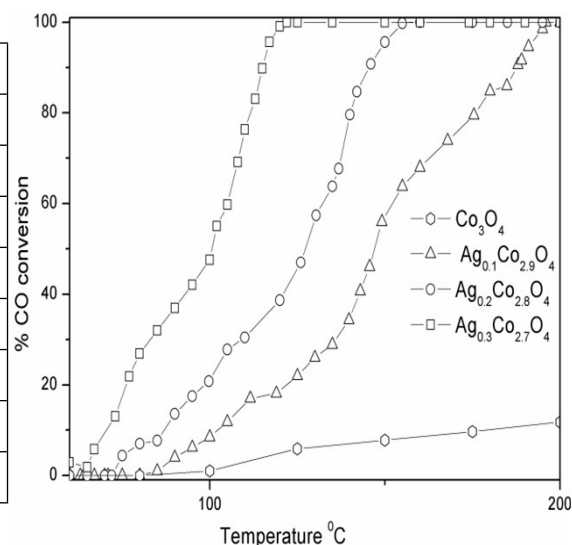
**Supplementary figure 2.** TEM image of  $\text{Ag}_{0.2}\text{Co}_{2.8}\text{O}_4$  also shows particles are of 10-25 nm size.

## NO-CO conversion

Nitric oxide gets reduced over catalyst surface to form  $\text{N}_2$  and  $\text{N}_2\text{O}$  by CO. Whereas CO gets oxidized over the surface to form  $\text{CO}_2$ . Efficiency of catalyst for this reaction depends on less percentage formation of  $\text{N}_2\text{O}$ . Conversion of  $\text{N}_2\text{O}$  was monitored on porapak Q column. For substituted catalyst low level of  $\text{N}_2\text{O}$  formation is observed which is represented in **Table 1**. It was observed that CO conversion was in line with NO conversion and no decrease in activity was observed (**Supplementary figure 3**).

**Supplementary table 1. Percentage NO conversion, percentage  $\text{N}_2\text{O}$  and  $\text{N}_2$  selectivity.**

Temperature in $^{\circ}\text{C}$	$\text{Ag}_{0.3}\text{Co}_{2.9}\text{O}_4$			$\text{Ag}_{0.2}\text{Co}_{2.8}\text{O}_4$			$\text{Ag}_{0.1}\text{Co}_{2.9}\text{O}_4$		
	%NO	% $\text{N}_2\text{O}$	% $\text{N}_2$	%NO	% $\text{N}_2\text{O}$	% $\text{N}_2$	%NO	% $\text{N}_2\text{O}$	% $\text{N}_2$
75	12.88	Very low	-100	--	--	--	--	--	--
100	47.48	Very low	-100	21.31	22.56	77.44	7.1	--	--
120	99	0	100	11.87	11.87	88.13	17.9	--	--
125	100	0	100	5.56	4.99	95.01	22	27.3	72.7
150	100	0	100	4.7	0	100	56.54	12.6	87.4
175	100	0	100	100	0	100	80.98	4.92	95.08
200	100	0	100	100	0	100	100	0	100



**Table 1.** Percentage NO conversion, percentage  $\text{N}_2\text{O}$  and  $\text{N}_2$  selectivity for NO-CO redox reaction.

**Supplementary figure 3.** CO conversion

## Analysis of NO

N<sub>2</sub> and N<sub>2</sub>O

Percentage conversion of NO was observed on molecular sieve 13x column. This GC column cannot detect the formation of N<sub>2</sub>O, so Porapak Q was used to determine the N<sub>2</sub>O formation. Peak area for N<sub>2</sub>O was calibrated with calibrated mixture using 0.5 ml injector volume for calibrated mixture of 1:1 N<sub>2</sub>O and CO<sub>2</sub>.

Total % of NO conversion = % of N<sub>2</sub>O formation + % of N<sub>2</sub> formation

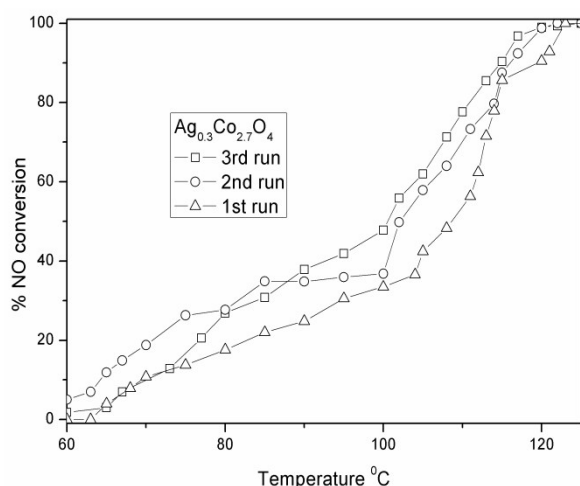
Percentage conversion of NO was analysed on molecular sieve 13x column and percentage formation of N<sub>2</sub>O on porapak Q column.

% N<sub>2</sub> selectivity was found out as follows.

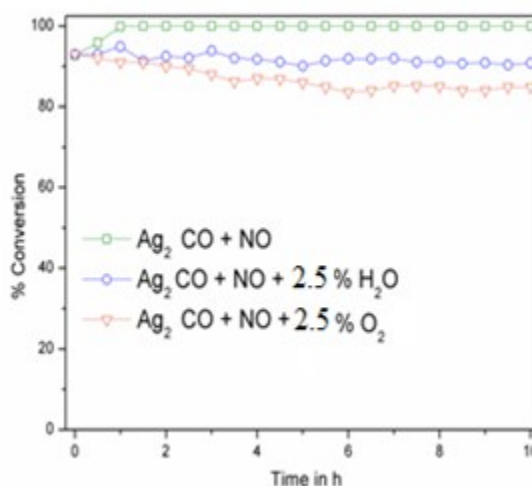
% N<sub>2</sub> selectivity = 100 – % N<sub>2</sub>O formation.

## Stability test.

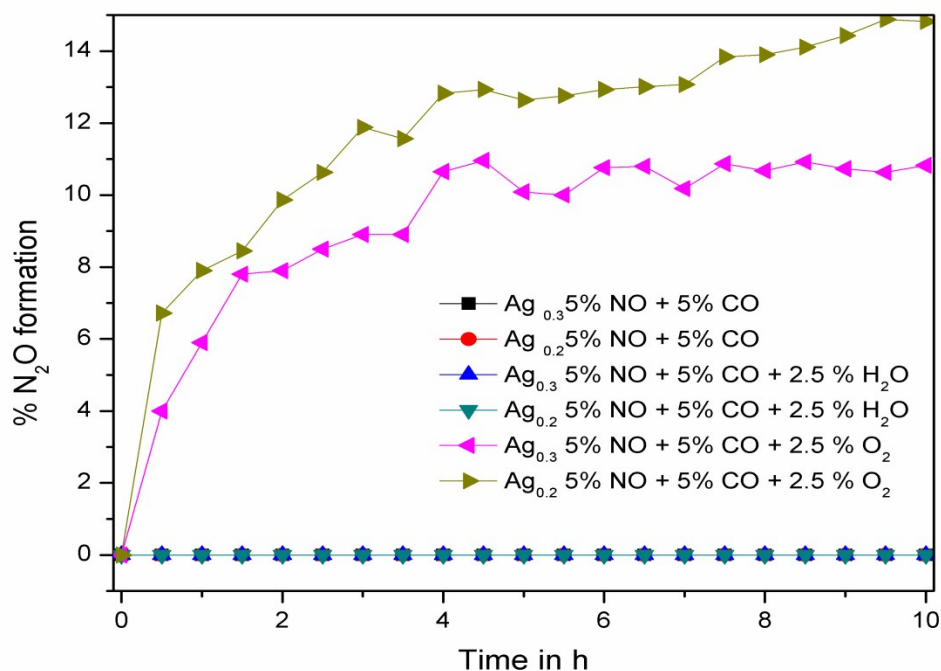
Catalyst reproducibility was checked thrice without employing any activation or regeneration procedure after the first run. Test showed NO conversion was reproducible over the used catalyst (**supplementary figure 4**). Catalyst stability at 150 °C with different reaction condition is studied. Same feed gas composition of 5% NO and 5% CO in Ar at 5000 ml h<sup>-1</sup> was employed in determining catalyst stability in moisture and O<sub>2</sub> (**supplementary figure 5**). It was observed for NO-CO redox reaction over Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub> that there was increase in activity. Moisture tolerance study indicates there was marginal decrease in initial activity at low levels (2.5%) moisture. Introductions of 2.5% O<sub>2</sub> has visible decrease in activity which is reflective of competitive oxidation of catalyst surface by O<sub>2</sub> rather than NO.



**Supplementary figure 4.** Catalyst reproducibility test for Ag<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub>.



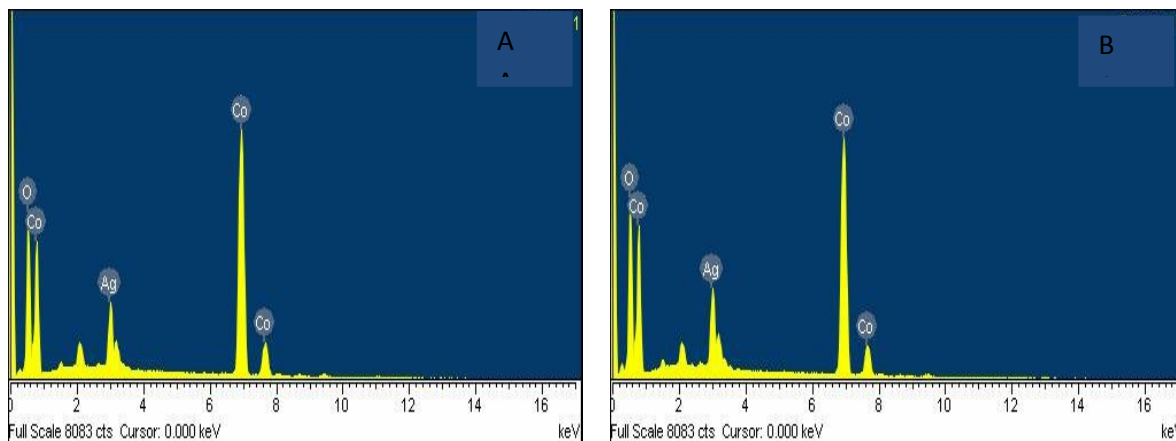
**Supplementary figure 5.** Catalyst activity in different reaction condition for Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub>.



**Supplementary figure 6.** N<sub>2</sub>O selectivity for the catalyst stability test under various test conditions.

N<sub>2</sub>O selectivity for stability tests under various reaction conditions is shown in **Supplementary figure 6**. Oxygen has increased the formation of N<sub>2</sub>O as oxygen competes for re-oxidation of catalyst surface with NO. It lowers the dissociative adsorption of NO over the catalyst surface to form N<sub>2</sub>. Moisture however has no effect on N<sub>2</sub>O formation possibly water molecules only block the active catalyst sites rather than actively participation in NO-CO redox reaction. There was no N<sub>2</sub>O observed during 10 h of reaction stability test in absence of oxygen.

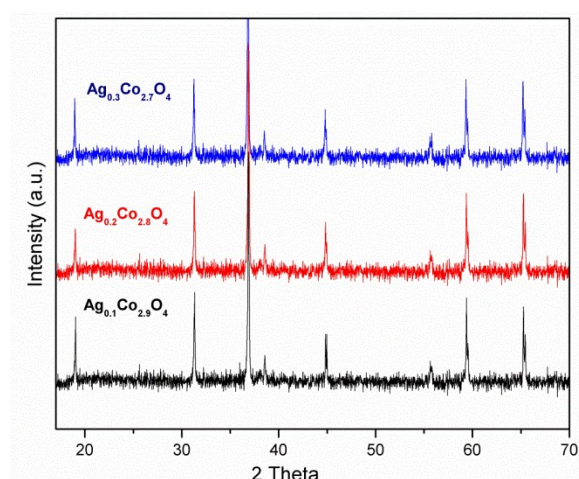
#### EDS analysis of Ag<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub> and Ag<sub>0.5</sub>Co<sub>2.5</sub>O<sub>4</sub>



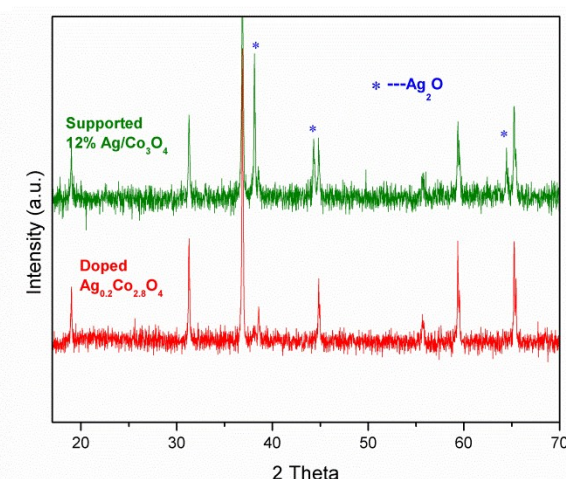
**Supplementary figure 7.** EDS of A) Ag<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub> and B) Ag<sub>0.5</sub>Co<sub>2.5</sub>O<sub>4</sub> biphasic.

EDS shows the presence of silver in the substituted catalysts for monophasic catalyst  $\text{Ag}_{0.3}\text{Co}_{2.7}\text{O}_4$  and for biphasic catalyst  $\text{Ag}_{0.5}\text{Co}_{2.5}\text{O}_4$  in **Supplementary figure 7 A&B**. Thus, XRD and EDS studies indicates that silver is incorporated in lower concentration cobalt oxide spinels but higher concentration of Ag results in biphasic catalyst confirmed by XRD.

### Repeat XRD analysis of the catalysts.



**Supplementary figure 8.** XRD of doped catalysts (repeated).



**Supplementary figure 9.** XRD pattern showing the difference between 12% doped and supported Ag for  $\text{Co}_3\text{O}_4$ .

XRD pattern for three silver substituted catalysts was repeated again which shows better signal to noise ratio. Repeat analysis of diffraction pattern did not show any extra reflections (**Supplementary figure 8**). Also there is increase in the lattice parameter with increase in silver substitution and shown in Table s below. In addition, XRD pattern of supported catalyst for 12% Ag on  $\text{Co}_3\text{O}_4$  is recorded which shows reflections of  $\text{Ag}_2\text{O}$  (**Supplementary Figure 9**). Thus it can be concluded that in doped catalysts Ag is present in the lattice but its position in lattice needs detail investigation.

### Supplementary table 2. Lattice parameters

Catalyst	Lattice parameter (Å)
$\text{Ag}_{0.1}\text{Co}_{2.9}\text{O}_4$	8.0768
$\text{Ag}_{0.2}\text{Co}_{2.8}\text{O}_4$	8.0811
$\text{Ag}_{0.3}\text{Co}_{2.7}\text{O}_4$	8.0895