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# Communication

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Low temperature nitric oxide reduction over silver substituted spinel cobalt oxide.

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Catalytic reduction of NO by CO is performed over novel silver substituted cobalt oxide nano sized spinels, prepared via citric acid assisted sol-gel method. Catalysts are characterized by XRD, TEM, BET surface area measurements and CO chemisorption studies. Ag substitution in spinel cobalt oxide lattice enhances CO chemisorption, hence catalytic activity significantly. Prepared catalysts show excellent stability in the reaction conditions. Effect of moisture and oxygen dosage is studied for the reaction. The catalysts are found to be highly selective for N<sub>2</sub> over N<sub>2</sub>O.

# INTRODUCTION

Low temperature reduction of nitric oxide (NO) by carbon monoxide (CO) is one of the challenging reactions being studied by many research groups all over the world. Low temperature reduction of NO by NH<sub>3</sub> as reducing agent has been reported by many research groups.<sup>1, 2</sup> Unfortunately, NH<sub>3</sub> has to be added externally in such exhaust treatment systems, thus its practical application is limited. CO is a very convenient reducing agent which is present in the exhaust systems itself. Literature cites very few reports on low temperature NO-CO reaction which has been achieved using Cu and Au based catalyst.<sup>3-6</sup>

Cobalt spinel compounds are proven to be efficient in CO oxidation at low temperatures.<sup>7,8</sup> Co<sub>3</sub>O<sub>4</sub> has a promising role in low temperature CO oxidation due to its high surface oxygen mobility. It is proven that CO oxidation by lattice oxygen is an important step in nitric oxide reduction by CO.<sup>9</sup> Thus, materials like spinel cobalt oxide can be good candidates for low temperature nitric oxide reduction. As per L. Wang et. al., pristine Co<sub>3</sub>O<sub>4</sub> undergoes a phase change to CoO in the reaction condition due to the lattice oxygen desorption.<sup>10</sup> It is difficult to reduce NO which is stable at higher temperatures (above 300 °C) and therefore difficult to reduce it to N<sub>2</sub>.<sup>11</sup> Thus, NO reduction would be favored at lower temperatures. Incorporation of precious metals such as Rh in cobalt spinel lattice is found to be effective in stabilizing its structure and phase.<sup>10</sup> Since silver belongs to the Cu and Au family, which is closely related to precious group metals, its incorporation in cobalt oxide is studied for NO reduction. Preliminary studies are carried out to understand the effect of moisture and oxygen on the silver substituted catalysts.

## **EXPERIMENTAL**

Ag<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> (x= 0.1, 0.2, 0.3) were synthesised by citric acid assisted sol-gel method. Cobalt (II) nitrate hexa-hydrate (Sigma Aldrich, ≥ 99.0) and silver nitrate (Sigma Aldrich, ≥ 99.0) were dissolved in stoichiometric amount in water. To this solution, citric acid (Thomas Baker, AR) in 1: 1 molar ratio (Co/citric acid) was added and stirred for one hour at room temperature. The solution was then evaporated at 120 °C which resulted in the formation of a pink foamy mass. This was then ground using mortar and pestle and calcined at 600 °C in air for 8 h.

The spinel phase of the catalysts powder samples was identified using X-ray powder diffractometer (Rigaku Ultima IV) with Cu-Ka source. TEM images were recorded with the help of PHILIPS CM 200 electron microscope. Elementary studies were performed to check the presence of silver using Energy Dispersive X-ray spectroscopy on JEOL JSM 6360 LV scanning microscope (SEM/EDS). BET surface electron area measurements and CO chemisorptions were performed using QUANTACHROME AUTOSORB IQ-MP-C surface area analyzer. Prior to the BET analysis, samples were degassed at 120 °C for three hours and nitrogen adsorption was performed at liquid nitrogen temperatures. Chemisorption of CO was performed at room temperature using 0.15 g of catalyst. Samples were initially heated to 100 °C under N<sub>2</sub> flow, cooled and CO was passed at the flow rate of 60 ml min<sup>-1</sup>.

Redox reaction between NO and CO was performed in a continuous flow, fixed bed glass reactor. About 1.5 g of the catalyst was loaded in the glass reactor supported in between the quartz wool. Moisture and adsorbed oxygen was removed by passing stream of  $N_2$  flow at the rate of 20 ml h<sup>-1</sup> at 100 °C for 15 min. Catalyst bed was cooled down at room temperature and then CO was flushed over the catalyst at the rate of 4 ml min<sup>-1</sup>

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for 10 min. Catalytic activity was measured as a function of temperature using 5% CO and 5% NO in Argon at the rate of 5000 ml h<sup>-1</sup>. Controlled heating of the furnace was done using temperature programmer at the rate of 2 °C min<sup>-1</sup>. Individual gas flow rates were maintained by gas flow meters and precision needle valves. Conversion of NO and CO was monitored by employing an online Gas Chromatograph with Molecular sieve 13x and Porapak Q columns using TCD detector.

Stability test of catalysts in presence and absence of moisture and oxygen was carried with the same feed gas composition for 10 h. For the stability test in the presence of moisture and oxygen, 2.5% moisture and 2.5%  $O_2$  were introduced in the original feed gas composition.

#### **RESULTS AND DISCUSSION**

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Figure 1. a) XRD pattern of silver substituted catalyst and b) TEM image of  $Ag_{0.2}Co_{2.8}O_4$ .

Monophasic formation of Ag substituted spinel cobalt oxide is seen and the XRD pattern matches with JCPDS card No. 00-042-1467 (Figure 1a). The diffraction pattern shows peaks at 111 (~18.9°), 220 (~31.3°), 311 (~36.8°), 222 (~38.56°), 400 (~4.8°), 511 (~59.3°), 440 (~65.2°) and 533 (~78.5°) respectively, which indicates the cubic phase formation. No extra reflection of Ag or Ag<sub>2</sub>O is observed for doped catalysts. Broadening of the peaks is attributed to the poor crystallinity and nano size particle nature of the catalysts. An increase in lattice parameter was observed with increase in silver substitution. Higher doping of Ag was attempted (Ag<sub>0.5</sub>Co<sub>2.5</sub>O<sub>4</sub>) under same preparative conditions but resulted in biphasic composition (shown in supplementary Figure 1). Presence of silver is confirmed by SEM/EDS studies. TEM images indicate the formation of spherical and plate like nano particles ranging from 10 - 25 nm. Representative TEM image of Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub> is given in Figure 1b. BET surface area

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**Figure 2.** Chemisorption of CO at room temperature (25 °C).

measurements carried out at liquid nitrogen temperature indicates high surface area of about 106, 105 and 104 m<sup>2</sup>g<sup>-1</sup> for Ag<sub>0.1</sub>Co<sub>2.9</sub>O<sub>4</sub>, Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub> and Ag<sub>0.3</sub>Co<sub>2.7</sub>O<sub>4</sub> respectively, whereas pristine surface area of about 56 m<sup>2</sup>g<sup>-1</sup> is observed for Co<sub>3</sub>O<sub>4</sub>. **Figure 2** shows the CO chemisorptions result performed at room temperature. Enhancement in CO adsorption with increase in Ag substitution is observed. This shows that electron rich elements like Ag facilitate CO chemisorptions which increase linearly with increased CO partial pressure.

Nitric oxide conversion plots are presented in Figure 3. Results clearly indicate that silver substitution greatly enhances the activity of NO reduction by CO as compared to the pristine catalyst. 100% NO conversion was observed at 120 °C for  $Ag_{0.3}Co_{2.7}O_4$  catalyst which is found to be the best among the tested catalysts and is reported for the first time over such catalyst system. 100% conversion (T<sub>100</sub>) for Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub> is observed at 150 °C. Catalyst activity is tested for three catalytic cycles without any regeneration process and the data is found to be reproducible with no loss in activity. Formation of N<sub>2</sub>O in lower concentration is observed during the activity test (supplementary Table 1). It is a well-established fact that at low temperatures selectivity for  $N_2$  over  $N_2O$  is less due to the partial reduction of NO in such a catalytic reaction. Increase in Ag substitution improved the selectivity for N<sub>2</sub>, as evident from the decrease or no N<sub>2</sub>O formation at low temperatures. CO conversion is observed in line with NO conversion in all the experiments. Higher amount of Ag substituted composition  $Ag_{0.5}Co_{2.5}O_4$  (biphasic) is also tested for catalytic activity but shows lower activity than Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub> catalyst.

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Figure 3. NO conversion over all the catalyst in feed gas composition 5% NO, 5% CO in Ar at 5000 ml  $h^{-1}$ .

Catalyst stability tests for  $Ag_{0.3}Co_{2.7}O_4$  at 120 °C in different reaction environments are shown in **Figure 4**. As evident from the figure, catalysts show excellent stability in the reaction test conditions as there is no fall in the activity observed with respect to time up to 10 h. Catalyst stability in presence of moisture and oxygen is investigated. A marginal decrease in activity due to the presence of moisture and  $O_2$  is observed. Similar trend is also seen for  $Ag_{0.2}Co_{2.8}O_4$  catalyst (Supplementary **Figure 6**). Moisture has no effect on selectivity for N<sub>2</sub>. In the presence of oxygen, N<sub>2</sub> selectivity is reduced due to the N<sub>2</sub>O formation. Since O<sub>2</sub> oxidizes both NO and CO oxidation, complete reduction of NO to N<sub>2</sub> becomes difficult.

Ag belong to the group of metals having outer electronic configuration  $ns^2$  (n - 1)d<sup>9</sup> (like Cu and Au) for which good activity at low temperatures is reported. These metals are closely related to platinum group of metals which are usually found to be highly active for NO reduction due to their electronegative nature which helps in strengthening the



**Figure 4.** Catalyst stability test of  $Ag_{0.3}Co_{2.7}O_4$  for NO conversion in the reaction mixture for 10 h at 120 °C, also in presence of moisture and  $O_2$  in Ar at flow rate of 5000 ml h<sup>-1</sup>.

chemical bond with CO and NO via back bonding.<sup>12</sup> CO adsorption studies show enhancement in CO adsorption with increase in Ag substitution which is probably due to the back bonding ability of Ag. Stronger CO adsorption result in desorption of CO as CO2, since CO takes lattice oxygen as explained by Mar's - Van Krevelen mechanism which reduces the oxide catalyst surface. NO has ability to re-oxidize the catalyst surface by dissociative adsorption of NO which can result in  $N_2$  and  $N_2O$  formation. Selective  $N_2$  formation is observed when NO dissociate completely over the oxide surface and re-oxidize the reduced catalyst site. Whereas, partial dissociation of NO results in N<sub>2</sub>O formation. Thorough investigations are needed to explain the observed experimental results. From the catalytic study, it is observed that Ag incorporation improves the catalysts' activity drastically may be due to its high affinity for CO adsorption, small particle size and higher surface area as compared to the pristine catalyst.

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#### CONCLUSIONS

Ag substituted catalysts were prepared by citric acid assisted sol-gel method. Prepared catalysts were found to be 10 - 25 nm in size. BET surface area measurements indicate catalysts to be of high surface area in the range of 104 to 106 m<sup>2</sup>g<sup>-1</sup>. XRD and SEM/EDS studies indicate that silver is incorporated in appropriate concentration in spinel cobalt oxide but higher concentration results in biphasic compound. Ag substitution significantly improved the catalytic activity for NO-CO redox reaction. CO chemisorption at room temperature showed an enhancement in CO adsorption with silver substitution. Substituted catalysts were found to be active at low temperature. Among the tested catalysts  $Ag_{0.3}Co_{2.7}O_4$  gave complete conversion of NO at 120 °C, which is novel among the few best catalysts reported in the literature. Increase in Ag substitution reduced N<sub>2</sub>O formation at low temperatures. Catalysts also showed excellent reproducibility for NO reduction reaction with same activity without regeneration. N<sub>2</sub>O formation was not observed above 150 °C for Ag<sub>0.2</sub>Co<sub>2.8</sub>O<sub>4</sub> indicating good selectivity for N2. Catalysts have showed excellent stability for the NO-CO reaction for 10 h. Low level of moisture did not show substantial decrease in the activity. However, marginal fall in activity was observed with introduction of oxygen in the catalytic system. It is concluded that, Ag substituted spinel cobalt oxide are novel for NO-CO redox reaction and highly active under various reaction conditions studied.

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