

COMMUNICATION

Low-temperature nitric oxide reduction over
silver-substituted cobalt oxide spinels†Cite this: *Catal. Sci. Technol.*, 2016,
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Catalytic reduction of NO by CO is performed over novel silver-substituted cobalt oxide nano-sized spinels, prepared via a citric acid-assisted sol-gel method. The catalysts are characterized by XRD, TEM, BET surface area measurements and CO chemisorption studies. Ag substitution in the cobalt oxide spinel lattice enhances CO chemisorption, hence the catalytic activity significantly. The prepared catalysts show excellent stability under the reaction conditions. The effect of moisture and oxygen dosage is studied for the reaction. The catalysts are found to be highly selective for N₂ over N₂O.

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 NH₃ as the reducing agent has been reported by many research groups.^{1,2} Unfortunately, NH₃ has to be added externally to exhaust treatment systems, thus its practical application is limited. CO is a very convenient reducing agent which is present in exhaust systems. The literature cites very few reports on low-temperature NO-CO reactions which have been achieved using Cu- and Au-based catalysts.³⁻⁶

Cobalt spinel compounds have been proven to be efficient in CO oxidation at low temperatures.^{7,8} Co₃O₄ 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.⁹ Thus, materials like cobalt oxide spinels can be good candidates for low-temperature nitric oxide reduction. As per L. Wang *et al.*, pristine Co₃O₄ undergoes a phase change to CoO under the reaction conditions due to lattice oxygen

desorption.¹⁰ It is difficult to reduce NO which is stable at higher temperatures (above 300 °C), therefore making it difficult to reduce to N₂.¹¹ Thus, NO reduction would be favored at lower temperatures. Incorporation of precious metals such as Rh in the cobalt spinel lattice is found to be effective in stabilizing its structure and phase.¹⁰ Since silver belongs to the Cu and Au family, which is closely related to the precious metal group, its incorporation into 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_xCo_{3-x}O₄ ($x = 0.1, 0.2, 0.3$) were synthesised by a citric acid-assisted sol-gel method. Cobalt(II) nitrate hexahydrate (Sigma Aldrich, ≥99.0%) and silver nitrate (Sigma Aldrich, ≥99.0%) were dissolved in stoichiometric amounts in water. To this solution, citric acid (Thomas Baker, AR) in a 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 a mortar and pestle, and calcined at 600 °C in air for 8 h.

The spinel phase of the catalyst powder samples was identified using an X-ray powder diffractometer (Rigaku Ultima IV) with a Cu-K α source. TEM images were recorded with the help of a PHILIPS CM 200 electron microscope. Elemental studies were performed to check the presence of silver using energy-dispersive X-ray spectroscopy on a JEOL JSM 6360LV scanning electron microscope (SEM/EDS). BET surface area measurements and CO chemisorption studies were performed using a QUANTACHROME AUTOSORB IQ-MP-C surface area analyzer. Prior to BET analysis, the 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 the catalyst. The

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samples were initially heated to 100 °C under N₂ flow, then cooled, and CO was passed at the flow rate of 60 ml min⁻¹.

The 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 into the glass reactor supported between quartz wool. Moisture and adsorbed oxygen were removed by passing a stream of N₂ at the rate of 20 ml h⁻¹ at 100 °C for 15 min. The catalyst bed was cooled down to room temperature, and then CO was flushed over the catalyst at the rate of 4 ml min⁻¹ for 10 min. The catalytic activity was measured as a function of temperature using 5% CO and 5% NO in argon at the rate of 5000 ml h⁻¹. Controlled heating of the furnace was carried out using a temperature programmer at the rate of 2 °C min⁻¹. Individual gas flow rates were maintained by using gas flow meters and precision needle valves. The conversion of NO and CO was monitored by employing an online gas chromatograph with Molecular Sieve 13X and Porapak Q columns using a TCD.

Stability tests of the catalysts in the presence and absence of moisture and oxygen were carried out 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% O₂ were introduced into the original feed gas composition.

Results and discussion

The monophasic formation of Ag-substituted cobalt oxide spinels is seen and the XRD pattern matches with JCPDS card no. 00-042-1467 (Fig. 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°), which indicates the cubic phase formation. No extra reflection of Ag or Ag₂O is observed for the doped catalysts. The broadening of the peaks is attributed to the poor crystallinity and nano-sized particle nature of the catalysts. An increase in lattice parameters was observed with the increase in silver substitution. Higher doping of Ag was attempted (Ag_{0.5}Co_{2.5}O₄) under the same preparative conditions but resulted in a biphasic composition (shown in Fig. S1†). The presence of silver is

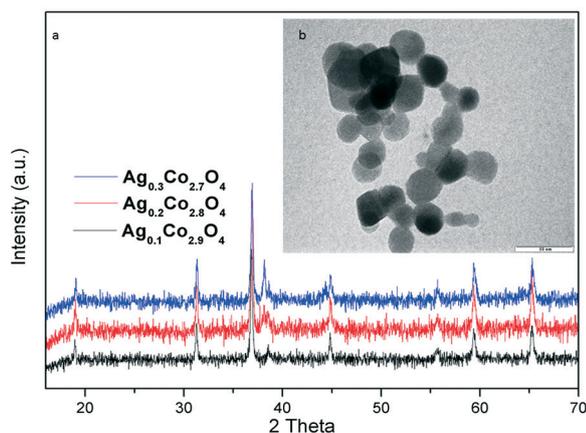


Fig. 1 (a) XRD pattern of the silver-substituted catalyst and (b) TEM image of Ag_{0.2}Co_{2.8}O₄.

confirmed by SEM/EDS studies. The TEM images indicate the formation of spherical and plate-like nanoparticles with sizes ranging from 10–25 nm. The representative TEM image of Ag_{0.2}Co_{2.8}O₄ is given in Fig. 1b. BET surface area measurements carried out at liquid nitrogen temperatures indicate high surface areas of about 106, 105 and 104 m² g⁻¹ for Ag_{0.1}Co_{2.9}O₄, Ag_{0.2}Co_{2.8}O₄ and Ag_{0.3}Co_{2.7}O₄, respectively, whereas a surface area of about 56 m² g⁻¹ is observed for pristine Co₃O₄. Fig. 2 shows the results of the CO chemisorption studies performed at room temperature. Enhancement in CO adsorption with an increase in Ag substitution is observed. This shows that electron-rich elements like Ag facilitate CO chemisorption which increases linearly with increasing CO partial pressure.

The nitric oxide conversion plots are presented in Fig. 3. The results clearly indicate that silver substitution greatly enhances the activity for NO reduction by CO as compared to the pristine catalyst. 100% NO conversion was observed at 120 °C for the Ag_{0.3}Co_{2.7}O₄ catalyst, which is found to be the best among the tested catalysts and is reported for the first time for such a catalyst system. 100% conversion (*T*₁₀₀) for Ag_{0.2}Co_{2.8}O₄ is observed at 150 °C. The catalytic activity is tested for three catalytic cycles without any regeneration process and the data are found to be reproducible with no loss in activity. Formation of N₂O in lower concentration is observed during the activity test (Table S1†). It is a well-established fact that at low temperatures, the selectivity for N₂ over N₂O is lower due to the partial reduction of NO in such a catalytic reaction. The increase in Ag substitution improved the selectivity for N₂, as evident from the decrease or absence of N₂O formation at low temperatures. CO conversion is observed in line with NO conversion in all the experiments. The Ag_{0.5}Co_{2.5}O₄ (biphasic) catalyst with a higher amount of Ag substituted is also tested for its catalytic activity but shows lower activity than the Ag_{0.2}Co_{2.8}O₄ catalyst.

The results of the catalyst stability tests for Ag_{0.3}Co_{2.7}O₄ at 120 °C in different reaction environments are shown in Fig. 4. As evident from the figure, the catalyst shows excellent stability under the reaction test conditions as there is no

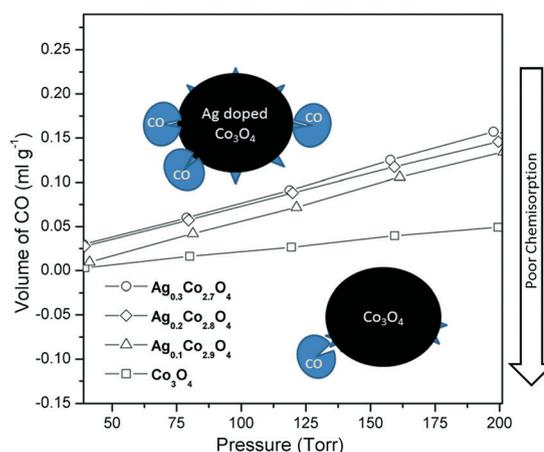


Fig. 2 Chemisorption of CO at room temperature (25 °C).

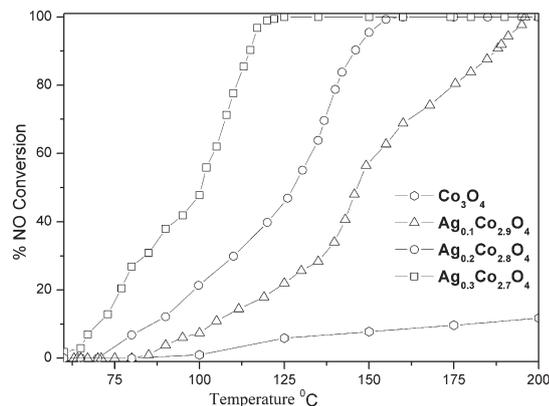


Fig. 3 NO conversion over all the catalysts in a feed gas composition of 5% NO and 5% CO in Ar at 5000 ml h⁻¹.

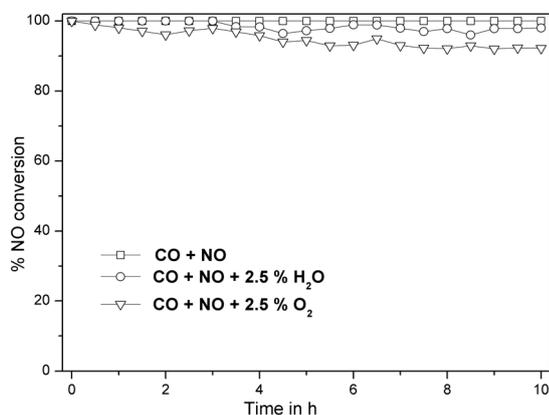


Fig. 4 Catalyst stability test of Ag_{0.3}Co_{2.7}O₄ for NO conversion in the reaction mixture for 10 h at 120 °C, and also in the presence of moisture and O₂ in Ar at the flow rate of 5000 ml h⁻¹.

observed decrease in activity with respect to time up to 10 h. The catalyst stability in the presence of moisture and oxygen is investigated. A marginal decrease in activity due to the presence of moisture and O₂ is observed. A similar trend is also seen for the Ag_{0.2}Co_{2.8}O₄ catalyst (Fig. S6[†]). Moisture has no effect on the selectivity for N₂. In the presence of oxygen, N₂ selectivity is reduced due to N₂O formation. Since O₂ oxidizes both NO and CO, complete reduction of NO to N₂ becomes difficult.

Ag belongs to the group of metals having the outer electronic configuration $ns^2(n-1)d^9$ (like Cu and Au) for which good activity at low temperatures is reported. These metals are closely related to the 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 chemical bond with CO and NO *via* backbonding.¹² CO adsorption studies show an enhancement in CO adsorption with the increase in Ag substitution, which is probably due to the backbonding ability of Ag. Stronger CO adsorption results in the desorption of CO as CO₂, since CO reacts with lattice oxygen, which reduces the oxide catalyst surface, as explained by the Mars–van Krevelen mechanism. NO has the

ability to re-oxidize the catalyst surface by dissociative adsorption which can result in N₂ and N₂O formation. Selective N₂ formation is observed when NO dissociates completely over the oxide surface and re-oxidizes the reduced catalyst site; whereas, partial dissociation of NO results in N₂O 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, which may be due to its high affinity for CO adsorption and small particle size, and their higher surface area compared to that of the pristine catalyst.

Conclusions

Ag-substituted catalysts were prepared by a citric acid-assisted sol–gel method. The prepared catalysts were found to be 10–25 nm in size. BET surface area measurements indicate that the catalysts have high surface areas in the range of 104 to 106 m² g⁻¹. XRD and SEM/EDS studies indicate that the incorporation of silver in an appropriate concentration results in the formation of monophasic Ag-substituted cobalt oxide spinels, while a higher concentration results in the formation of a biphasic compound. Ag substitution significantly improved the catalytic activity for the NO–CO redox reaction. CO chemisorption at room temperature showed an enhancement in CO adsorption with silver substitution. The substituted catalysts were found to be active at low temperatures. Among the tested catalysts, Ag_{0.3}Co_{2.7}O₄ exhibited complete conversion of NO at 120 °C, which is novel among the few best catalysts reported in the literature. The increase in Ag substitution reduced N₂O formation at low temperatures. The catalysts also showed excellent reproducibility for NO reduction with the same activity without regeneration. N₂O formation was not observed above 150 °C for Ag_{0.2}Co_{2.8}O₄, indicating its good selectivity for N₂. The catalysts have showed excellent stability for the NO–CO reaction for 10 h. The low levels of moisture did not induce a substantial decrease in activity. However, a marginal decrease in activity was observed with the introduction of oxygen into the catalytic system. It is concluded that Ag-substituted cobalt oxide spinels are novel for NO–CO redox reactions and highly active under various reaction conditions studied.

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