ABSTRACT

With rise in environmental awareness, strict restrictions are being introduced worldwide as a result of rapid urbanization that have seriously affected the atmosphere. Nitrogen oxides (NO_x) emitted from the power plants and automobiles are regarded as major sources of atmospheric contamination and are the main causes of acid rain, greenhouse effect, and photochemical smog. Several technologies including three-way catalyst, selective catalytic reduction **(**SCR), non-selective catalytic reduction **(**NSCR), and selective non-catalytic reduction (SNCR) are implemented for the NO_x abatement.

The SCR process using NH_3 as reducing agent has been commercially employed in stationary sources where NO_x is effectively converted into N_2 using the suitable catalysts. The most widely used catalyst for NH_3-SCR in the industry is V_2O_5-WO_3 (MoO_3)/TiO_2 (VWTi). However, the catalysts have a relatively high and narrow working window (300–400°C) and it is not suitable for low-temperature denitration (250°C) of flue gases emitted from steel, cement, glass, and other industries (<250°C). At the same time, the high cost of tungsten and high toxicity of vanadium further limit the application of this catalyst. Therefore, developing a new low-cost, V-free, low-temperature de-NO_x catalyst is very important. Even though current SCR systems achieve 90% of NO_x conversion, they have certain limitations such as poor NO_x conversion below 150°C, constant refill of liquid reducing agent, space constraints, catalytic poisoning and freezing of reducing agent, and poor cold start.

The primary focus of the present study is to improve the low-temperature NO_x conversion of the NH_3-SCR systems. CeO_2 has shown excellent results in the past. Ceria can switch its normal oxidation state, $Ce^{3+} \leftrightarrow Ce^{4+}$, which is crucial for the NO_x reduction reaction. Many researchers have reported ceria as good automotive support due to its oxygen storage capacity. Manganese

based catalysts have also shown high catalytic activity due to significant redox ability and surface acidity, which may be due to the interconversion of Mn^{n+} ions with different valences, which improves the low-temperature SCR performance.

This work aims to study the effect of support morphologies, different MnO_x oxides on CeO_2 support, the crystal structure of MnO_2 on CeO_2 supports in the catalysts, and their impact on NO_x conversion. This work is divided into three categories:

(1) Effect of CeO_2 support morphology (nanorod, nanocube, and nanopolyhedral)

(2) Effect of different oxides of manganese in the MnO_x/CeO_2 catalyst

(3) Effect of MnO_2 crystal phases in the MnO_2/CeO_2 catalyst

In the first section the different CeO_2 morphologies (nanorod, nanocube, and nanopolyhedral) were synthesized by hydrothermal techniques. In the second section, different oxides of Manganese (MnO_2, MnO, Mn_2O_3) were impregnated on CeO_2-nanorod using the wet-impregnation method. In the third section, the different crystal structures of MnO_2 (α, β, γ, and δ) were impregnated on CeO_2-nanorod using the wet-impregnation method. The supports and catalysts were characterized via nitrogen adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), hydrogen-temperature-programmed reduction (H_2-TPR), and Raman spectroscopy.

Initially, the effect of different CeO_2 morphologies supports (nanorod, nanocube, and nanopolyhedral) was evaluated for NO_x reduction. The CeO_2-nanorod showed the best (48%) NO_x reduction activity in the range of 200-300°C. Furthermore, the effect of different oxides of Manganese supported on ceria nanorod catalysts were tested for NO_x reduction. It was found that MnO_2/CeO_2-nanorod catalysts showed the highest NO_x conversion. Compared to bare CeO_2 support, the MnO_x/CeO_2 catalyst greatly enhances the SCR activity with a wide

temperature range (100-400°C). The experimental results showed that the MnO_2/CeO_2-Nanaorod gave the maximum NO conversion (65%) and N_2 selectivity (89%) among all catalysts. Further, the MnO_2/CeO_2-NR catalyst was studied for the effect of MnO_2 loading, and more than 90% NO conversion and N_2 selectivity was obtained in the temperature range of 250 to 300°C, when MnO_x loading reached to 17 wt.%. Finally different crystal effects of MnO_2 on the MnO_2/CeO_2-nanorod catalysts were anaylzed. The activity results showed that is the 200–300°C temperature range, the α-MnO_2/CeO_2-nanorod has the maximum NO conversion and N_2 selectivity. It showed the highest NO conversion (75%) and N_2 selectivity (86%) at 250 °C.