Selective Catalytic Reduction of NO_x with NH₃ over Mn₂O₃ supported with different morphology of CeO₂ Catalysts

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Abstract

Three different morphologies of CeO₂ supports (NP, NC, and NR) were prepared by hydrothermal method and further Mn₂O₃ is impregnated on CeO₂ supports using wet-impregnation methods, and their activity for NO reduction using NH₃-SCR technique is analysed. The prepared catalysts and supports are further characterized through scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and transmission electron microscopy (TEM), and Brunauer–Emmett–Teller (BET). The catalytic performance of Mn₂O₃/CeO₂-NP has shown the highest conversion (76.06 %) compared to the other two catalysts in the temperature range of 50 - 450°C.

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KEYWORDS

Mn₂O₃, CeO₂ morphology, NH₃-SCR.

INTRODUCTION

The exponential growth of population and industrialization led to the emission of various pollutants in the environment, causes adverse effects on our environment and subsequently leading to climate change. Nitrogen oxides (NO_x), one of the major air pollutants, emitted from mobile and stationary sources cause genuine environmental issues, such as photochemical smog, acid rain, ozone depletion, and greenhouse effects.^{1,2} At present, various strict environmental legislations are being implemented worldwide to reduce the

concentration of NO_x before releasing it into the environment.^{1,3} There are many techniques, such as non-selective catalytic reduction (NSCR)³, selective catalytic reduction (SCR)^{4,5}, photocatalytic^{6,7} etc., out of which selective catalytic reduction with ammonia (NH_3 -SCR) is one of the most efficient methods for NO_x reduction. It is more useful for exhaust emissions from stationary sources. In this process, NO_x emissions are converted into water vapors and nitrogen gas molecules as depicted in equations (1) and (2)^{8,9}.

V_2O_5 - WO_3 / TiO_2 based catalysts are widely used in NH_3 -SCR due to their cost effectiveness, best de-nitration efficiency, good sulfur resistance within a temperature range of 300-400°C. Though, there are certain disadvantages of vanadium-based catalysts such as its narrow temperature window, the high toxicity of V_2O_5 , high oxidation activity towards SO_2 converted into SO_3 , and N_2O production at higher temperatures^{10,11,12}. The gases exhausted from stationary sources, for example, steel, cement, and glass plants are in a temperature range of 100–200degC^{13,14}. Therefore, extra energy is needed to heat the exhaust gasses to give good performance by NH_3 -SCR catalysts^{15,16}. Therefore, there is a need to develop a suitable catalyst whose performance should be high at the low-temperature range of 100-300°C.

Mn-based catalysts have been thoroughly explored for the reduction of NO_x by NH_3 -SCR in the last few years due to their excellent low-temperature catalytic activity^{17,18,19}. It has been observed that MnO_x - CeO_2 catalysts, among the many bimetallic oxides, have a lot of potential owing to the high oxygen storage capacity of CeO_2 ^{16, 23}. In addition, some other properties such as morphology and microstructure of catalysts also influence the catalytic activity and selectivity by changing active site pore structure and dispersion^{8,9,12}. Chao et al. found that MnO_x - CeO_2 - Al_2O_3 catalysts showed high NO_x conversion and strong redox ability at low temperatures²⁵. Li et al. synthesized Mesoporous MnO_x - CeO_2 composites²⁶, which gave better performance for NO_x conversion as well as exhibited significant resistance to SO_2 , and H_2O . Yiran et al. synthesized MnCoO_x catalysts with hollow nanotube structure²⁷, which exhibited high NO_x conversion at 150°C even under the co-existence of inhibitors like H_2O , SO_2 , and alkali metals. The template-based methods are also found to be useful for NO_x reduction, Liu et al. compared the performances of Mn-Ce oxide prepared with surfactant-template (ST) and co-precipitation (CP) methods. The activity results showed that the catalyst prepared by ST methods exhibited much better NO_x reduction and high SO_2 and H_2O resistance in comparison to catalyst prepared by CP method at the temperature range of 100-200°C¹⁸.

From above discussion it can be conclude that efforts in the area of improving morphology of the overall structures or supports in order to gain promising support-metal interaction is very much of interest. Working in this direction, a series of supported Mn_2O_3 / CeO_2 with different support morphologies, were successfully synthesized to study the support morphology influence on metal-support interaction.

EXPERIMENTAL

Materials and methods

All chemicals and gases were procured commercially and used without any additional processing. Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.0%), Sodium hydroxide (NaOH , 98%), ethanol (99%), and Manganese nitrate tetra-hydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, [?] 97%) were purchased from SRL Pvt. Ltd., Chemika-biochemika-reagents, SD fine-chemical limited and Sigma-Aldrich Factory, respectively. NH_3 (1000 ppm, Ar balanced), NO (1000 ppm, Ar balanced), O_2 (6 vol %, Ar balanced), N_2 (99.999%) were used in the activity valuation experiments for NO_x conversion.

Catalyst preparation

Three different morphologies (Nanorod, Nanocube, and Nanoparticle) of ceria supports were prepared using hydrothermal process by varying the synthesis parameters such as C_{NaOH} (mole), temperature (0C) and reaction time (hr) as shown in Table1. An aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mmol) is mixed with a precipitant NaOH solution of varying concentration at room temperature for one hr under continuous stirring to obtain uniform mixture. After this, the prepared mixtures were transferred into a Teflon-lined

autoclave (100 ml) at varied reaction temperatures and reaction times, anticipating different morphological structures. The formed hydrothermal precipitate in the autoclave was cooled down to room temperature and then washed several times with ethanol and de-ionized to eliminate any possible ionic impurities. After that, the thoroughly washed precipitates were dried at 65°C overnight and air calcined at 500°C for 4 hr, resulting in formation of different CeO₂ supports denoted as CeO₂-NR, CeO₂-NC, and CeO₂-NP in the manuscript. Further, Manganese (III) oxide was employed as a metal oxide precursor and was impregnated on the support using the wet-impregnation process. An aqueous solution of prepared CeO₂ supports (CeO₂-NR, CeO₂-NC, and CeO₂-NP) were mixed with a particular amount of commercial Mn₂O₃ (10 wt%).

TABLE 1 . Different condition for CeO₂ supports synthesis

C NaOH (mole)	Temperature(°C)	Time (hr)	Shape
7	100	12	CeO ₂ -NR
15	180	24	CeO ₂ -NC
10	130	24	CeO ₂ NP

The obtained mixtures were agitated until the metal oxide and support were evenly mixed, and then the solutions were dried overnight at 100°C and air calcined for 4 hr at 350°C. The resultant impregnated catalysts are denoted as Mn₂O₃/CeO₂-NR, Mn₂O₃/CeO₂-NC, and Mn₂O₃/CeO₂-NP in this manuscript for reference.

3.3 Characterization

The X-Ray Diffraction system (Rigaku Miniflex 600) was used to obtain XRD patterns of the catalysts (RIGAKU Corporation). A nickel filtered Cu Ka radiation source was used in an X-ray diffraction apparatus. The intensity data were taken at a scanning rate of 5°/min in the range of 10°[?]2θ[?]80°. The crystallite sizes of the catalysts were calculated using the Scherrer equation, and the crystalline phases of the materials were established by comparing the XRD patterns to reference data from the International Center for Diffraction Data (ICDD) files.

The specific surface area and pore volume of the prepared catalysts were determined using N₂ physisorption at 77°K liquid nitrogen temperature (Micromeritics ASAP 2020, USA). The samples were degassed at 300°C for 5 hours to N₂ physisorption.

The atomic surface of catalysts was analyzed using X-ray photoelectron spectroscopy (XPS), which was evaluated using Al Ka radiation by an X-ray photoelectron spectroscopy (AMICUS, Kratos Analytical) (1486.6 eV). The binding energies of O 1s, Mn 2p, and Ce 3d were calibrated using the C 1s peak's binding energy (284.8 eV) as a reference and origin software was used to de-convolute the spectra.

To determine the morphology and particles size distribution of the supports and catalysts transmission electron microscopic (TEM) images were taken with a JEOL JEM-2100 system operated at 200 KV. The SEM images of the catalysts were obtained after scanning by the surface SEM: EVO 18-20-45 system electron-microscope. In a pulse chemi sorb 2705, H₂-TPR was employed to analyze the reducibility of the catalysts (Micromeritics, USA). The catalysts were reduced using a hydrogen (5 %H₂/Ar) and a temperature range of 100 to 700°C at a ramp rate of 10°C/min.

3.4 Catalytic performance:

The catalytic reduction was performed in an Inconel tubular reactor (length 500 mm x ID 12 mm), as shown in Figure 1. The composition of gases used was 1000 ppm NO, 1000 ppm NH₃, 6 vol % O₂ and flows into the reactor with 100 ml min⁻¹, corresponding to gas hour space velocity (GHSV) of 13000 h⁻¹. The mass flow controller (Bronkhorst) were used to control the gas flow rate. The thermocouple, connected to the PID controller and inserted inside the reactor was used to monitor the reaction temperature. For the catalytic test, the reaction temperature was performed in the range of 50–500°C, and product gases were analyzed by NO

analyzer (UNIPHOS ENVIROTRONIC Pvt Ltd, India) and gas chromatography (Centurion Scientific, 5800 model). The activity and selectivity measurements were done based on the equations (3) and (4) as given below:

$$\text{NO conversion (\%)} = \left(\frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \right) \times 100\% \quad (3)$$

$$\text{N}_2 \text{ selectivity (\%)} = \left(\frac{\text{N}_2}{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}} \right) \times 100 \quad (4)$$

FIGURE 1. Schematic diagram of NH₃-SCR experimental setup

RESULTS AND DISCUSSION

XRD

The XRD pattern of CeO₂-NR, CeO₂-NP, CeO₂-NC, Mn₂O₃, Mn₂O₃/CeO₂-NR, Mn₂O₃/CeO₂-NC, and Mn₂O₃/CeO₂-NP are shown in Figure 2. The diffraction peaks observed at 28.360, 32.700, 47.130, 55.900, 58.730, 69.150, 76.410 and 78.760 corresponding to (111), (200), (220), (311), (222), (400), (331) and (420) crystal plane of ceria respectively and it is cubic face-centered (a=b=c=5.412 Å) (JCPDS 81,0792). In case of pure Mn₂O₃, the peaks at 23.1090, 32.9190, 38.2200, 45.090, 49.290, 55.120 and 65.800 corresponding to (211), (222), (400), (332), (431), (440), and (622) crystal planes respectively were observed, ascribing to cubic body-centered type crystal structures (a=b=c=9.420 Å) (JCPDS 89, 2809)^{2,9}. It indicated that all samples are crystalline in nature. The average crystal size of supports and catalysts was calculated by the Scherrer equation and is shown in Table 2. CeO₂-NP showed the smallest crystal size, whereas CeO₂-NR has the largest crystal size. The orders of crystal size of CeO₂ morphology are as follows: CeO₂-NP > CeO₂-NC > CeO₂-NR.

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FIGURE 2. XRD pattern of catalysts (A) CeO₂-NR, (B) CeO₂-NC (C), CeO₂-NP

(D), Mn₂O₃/CeO₂-NR, (E) Mn₂O₃/CeO₂-NC (F), Mn₂O₃/CeO₂-NP and (G) Mn₂O₃ catalysts.

The impregnation of Mn₂O₃ over improved the crystal size of all the catalysts. It may be due to the shared cubic structure of Mn₂O₃ with ceria morphology. There are no diffraction peaks observed related to Mn₂O₃ in all the samples, shows that Mn₂O₃ is highly dispersed over the CeO₂ supports^{8,11}. The smaller crystal size is possibly associated with the high specific surface area as correlated with BET data.

TABLE 2. Crystal size of CeO₂, Mn₂O₃ and Mn₂O₃/CeO₂ Samples

Sample	Crystal size (nm)	Average particle size (nm)
CeO ₂ -NR	12.2	55
CeO ₂ -NC	11.2	35
CeO ₂ -NP	07.4	11
Mn ₂ O ₃	35.2	—
Mn ₂ O ₃ /CeO ₂ -NR	13.0	80
Mn ₂ O ₃ /CeO ₂ -NC	12.4	77
Mn ₂ O ₃ /CeO ₂ -NP	08.3	24

BET

The specific surface area, pore size, and pore volume of the Mn₂O₃ impregnated on different CeO₂ morphology are listed in Table 3. The specific surface area of Mn₂O₃/CeO₂-NR, Mn₂O₃/CeO₂-NC, and

Mn₂O₃/CeO₂-NP are 22.699, 30.253, and 34.352m²/g, respectively. Mn₂O₃/CeO₂-NP shows the highest specific surface area and pore volume compared to the other two catalysts, and this is due to its lower crystalline nature and lower average particle size, as also evident by XRD and SEM results described later. This shows that the cubic and rod arrangement of atoms of CeO₂ are more compact compared to CeO₂-NP. The loading effect of Mn₂O₃ (5, 10, and 15 %) over CeO₂ is shown in Table 3. The 10 wt% Mn₂O₃ over CeO₂ shows more surface area and pore volume than 5 and 15 wt %, this is maybe due to the combined effect of CeO₂ and Mn₂O₃'s properties^{11,23}. But 15 wt % loading inhibits the surface property due to surface coverage of CeO₂ by more Mn₂O₃ atoms.

TABLE 3. BET of Mn₂O₃/CeO₂ catalyst

Sample	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	Pore size (nm)
10 wt%Mn ₂ O ₃ /CeO ₂ -NR	22.69	0.126	8.76
10 wt%Mn ₂ O ₃ /CeO ₂ -NC	30.45	0.211	6.51
10 wt%Mn ₂ O ₃ /CeO ₂ -NP	34.53	0.290	5.73
5 wt%Mn ₂ O ₃ /CeO ₂ -NP	31.23	0.270	6.32
15 wt%Mn ₂ O ₃ /CeO ₂ -NP	29.57	0.257	6.87

5.3 XPS

The elements that exist within a material (elemental composition) are covering its surface and oxidation states in the material were identified using X-ray photoelectron spectroscopy (XPS), with the spectrum of this study shown in Figure 3.

The Ce 3d spectra of the catalysts are shown in Figure 3 (A). All catalysts were de-convoluted into six peaks, which were represented as u^o, uⁱ, uⁱⁱ, v^o, vⁱ, and vⁱⁱ. The spin-orbit doublet peak's series represented by u and v respectively denote the Ce 3d3/2, and Ce 3d5/2 states. According to analyzed catalysts, it was found that both Ce³⁺ and Ce⁴⁺ ions are dispersed in the catalysts. In these peaks u^o (901.48 eV), and vdeg (883.29 eV) are ascribed to Ce³⁺ ions XPS peaks, while uⁱ (907.78 eV), uⁱⁱ (917.18 eV), vⁱ (888.88 eV) and vⁱⁱ (897.88 eV) are ascribed to Ce⁴⁺ ions species

²⁹. De-convoluted split peaks confirm the presence of Ce³⁺ and Ce⁴⁺ ions in the CeO₂ oxides. The proportion of lattice oxygen and surface ion contents of Ce³⁺ had a significant effect on the performance of the catalyst. The percentage evaluation of Ce³⁺ state is calculated as,

$$\text{Ce}^{3+} \% = \left(\frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}} \right) \times 100 \quad (5)$$

Table 4 shows that Mn₂O₃/CeO₂-NP had the highest Ce³⁺ concentration among all particle-base catalysts.

FIGURE 3. XPS spectra of (A) Ce 3d, (B) O 1s, and (C) Mn 2p catalysts.

TABLE 4 . Atomic ratios of the catalysts by XPS spectra

Catalysts	$\left(\frac{\text{Ce}^{3+}}{\text{Ce}^{3+}+\text{Ce}^{4+}}\right)$	$\left(\frac{\text{O}_\alpha}{\text{O}_\alpha+\text{O}_\beta}\right)$	$\left(\frac{\text{Mn}^{4+}}{\text{Mn}^{4+}+\text{Mn}^{3+}}\right)$
Mn ₂ O ₃ /CeO ₂ -NR	0.3896	0.7022	0.7156
Mn ₂ O ₃ /CeO ₂ -NP	0.4353	0.7331	0.7621
Mn ₂ O ₃ /CeO ₂ -NC	0.4102	0.7276	0.7431

The de-convoluted O 1s spectra of Mn₂O₃/CeO₂ catalysts show two peaks marked as O_α and O_β, respectively, as shown in Figure 3(B). The first one is caused by lattice oxygen species, whereas second is caused by chemisorbed oxygen^{14,16,29}. It is widely known that chemisorbed adsorb oxygen on defective catalyst sites has a high migratory potential, which helps in oxidization^{3,5,6}. The relative concentration of O_α (O_α / (O_α + O_β)) is calculated, and are shown in Table 4. The Oxygen content of Mn₂O₃/CeO₂ catalysts is ranked as: Mn₂O₃/CeO₂-NP > Mn₂O₃/CeO₂-NC > Mn₂O₃/CeO₂-NR. It is implying that Mn₂O₃/CeO₂-NR has the more chemisorbed oxygen species.

As seen in Figure3(C), the Mn 2p region consists of two peaks, Mn 2p3/2 with binding energy (BE) of approximately 643.7 eV and Mn2p1/2 with a binding energy of about 655.3 eV which are made up of Mn⁴⁺ and Mn³⁺, indicating that Mn is in the mixed-valence state that is in Mn³⁺ and Mn⁴⁺ form^{30,31,32}. For three catalysts, the Mn³⁺/(Mn³⁺+Mn⁴⁺) content ratio is calculated and found that Mn₂O₃/CeO₂-NP has highest Mn⁴⁺ contents. The Mn⁴⁺ is catalyst's primary valence that play substantial role in the reduction reaction³⁰.

5.4 TEM

TEM characterization is used to analyze the morphology structures and average particle size of synthe-

sized CeO_2 -NR, CeO_2 -NP, and CeO_2 -NC and $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NR, $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NP, and $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NC catalysts. Figure 4 showed that the hydrothermal approach successfully synthesizes CeO_2 supported morphologies such as CeO_2 -NR, CeO_2 -NC, and CeO_2 -NP^{33,34}. It exhibited that after impregnating Mn_2O_3 over CeO_2 supports, all supports kept their original morphologies (Figure 4.D, E, and F), as confirmed by the SEM and EDX data. This shows that the Mn_2O_3 is dispersed over CeO_2 morphology-based supports. The textural parameters of all catalysts are shown in Table 3. The $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NP sample had the smallest average particle size and the highest surface area out of the three catalysts, making it potentially beneficial for the NH_3 -SCR reaction, followed by $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NR and $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NC. The particle size of $\text{Mn}_2\text{O}_3/\text{CeO}_2$ -NP is the highest, while the specific surface area is the smallest; it shows a correlation of BET surface area with TEM particle size data.

FIGURE 4 . TEM images of supports, catalysts, and used catalysts (A) CeO₂-NP, (B) CeO₂-NC, (C) CeO₂-NR, (D) Mn₂O₃/CeO₂-NP, (E), Mn₂O₃/CeO₂-NC, (F) Mn₂O₃/CeO₂-NR, (G) Mn₂O₃/CeO₂ -NP, (H) Mn₂O₃/CeO₂-NC, and (I) Mn₂O₃/CeO₂-NR

5.5 SEM-EDX

The SEM and EDX images of CeO₂-NR, CeO₂-NC, and CeO₂-NP and catalysts: Mn₂O₃/CeO₂-NR, Mn₂O₃/CeO₂-NP, and Mn₂O₃/CeO₂-NC synthesized by the wet-impregnation method shown in Figure 5. Comparing the SEM images of all catalysts and their supports, it is clear that Mn₂O₃ is impregnated over the supports and also confirmed in EDX data (C), (F), and (I). Comparing B, E, and H, it can be found that impregnation of Mn₂O₃ over CeO₂-NP made the morphology of CeO₂-NP more homogeneous and thus showing the high dispersion of active components (Mn₂O₃) over the surface of CeO₂-NP. It is observed that Mn₂O₃/CeO₂-NP and Mn₂O₃/CeO₂-NC have less roughness and un-uniformity compared with Mn₂O₃/CeO₂-NR. The surface got rougher, thereby increasing the catalyst's specific surface area and providing additional reaction sites. BET and TEM data confirmed that Mn₂O₃/CeO₂-NP has a high surface area and a homogeneous distribution of Mn₂O₃.

5.6 H₂-TPR

H₂-TPR of the samples are shown in Figure 6. Nano-rod shape of CeO₂ shows the slightly higher reduction temperature (360 and 450) compared to Nano-particle (298 and 400) and Nano-cube CeO₂ (295 and 402). It is related to the reduction of surface Ce⁴⁺ to Ce³⁺. At low temperatures, CeO₂-NR had weaker reduction peaks than CeO₂-NC and CeO₂-NP subsequently, indicating weaker redox capability. It shows that the atoms in Nano-rod arranged more strongly than the cube and particle state of CeO₂, show more peaks area and hence more hydrogen consumption in reduction¹². The reduction peaks at low temperature shifted to higher temperature after the impregnation of 10 wt% Mn₂O₃ over Ceria's morphology-based support. The Mn₂O₃ state shows two reduction peaks at 421 and 519, and both are higher than Ceria with broader peaks. It can shift the reduction performance of catalyst over 350, with broadening the range.

FIGURE 5. SEM and EDX images of CeO_2 supports and $\text{Mn}_2\text{O}_3/\text{CeO}_2$ catalysts

FIGURE 6. H₂-TPR profile Mn₂O₃, CeO₂-NR, Mn₂O₃/CeO₂-NR, CeO₂-NC, Mn₂O₃/CeO₂-NC, CeO₂-NP, Mn₂O₃/CeO₂-NP

5.7 Catalytic Performance and Discussion

5.7.1 NO catalytic activity

The NO_x conversion activity and N₂ selectivity of 10 wt% Mn₂O₃ based CeO₂ morphology of NP, NR, and NC catalysts in temperature range of 50 – 450 are in figure 7. Figure 7(A) shows the NH₃-SCR activity of Mn₂O₃/CeO₂ catalysts at various temperatures. The morphologies of CeO₂ catalyst regulate the NO_x reduction performance of NH₃-SCR. NO_x conversion was done in the following order at temperatures below 350°C; Mn₂O₃/CeO₂-NP > Mn₂O₃/CeO₂-NC > Mn₂O₃/CeO₂-NR. The Mn₂O₃/CeO₂-NP catalyst has the maximum NH₃-SCR activity, with a NO_x conversion of about 76.03% at 100-450°C. Even though all Mn₂O₃/CeO₂ catalysts had the same Mn₂O₃ loadings, NH₃-SCR catalytic efficiency depended on CeO₂ morphology. Mn₂O₃/CeO₂-NP catalysts showed the highest NO_x conversion activity above 300°C due to the more BET surface area and pore volume and caused significant active sites and response time for reaction. One other reason is the XPS deconvolution data of Mn₂O₃/CeO₂-NP catalysts show an excellent quantity of Ce³⁺, adsorbed oxygen, and Mn⁴⁺ states in Mn₂O₃/CeO₂-NP catalysts; 0.4353, 0.733, and 0.7621, respectively.

The figure 7(B) shows the N₂ selectivity profile of catalysts. It can be observed that the N₂ selectivity is approximate follow the NO_x conversion profile of catalysts. At lower temperatures, it shows very little activity as like selectivity. These surface properties are helpful in ammonia adsorption and further NO_x reduction. Among all three catalysts, Mn₂O₃/CeO₂-NP showed the best NO_x conversion shown in figure 7.

5.7.2 Effect of Mn₂O₃ loading on NH₃-SCR performance

It is well known that the activity of the catalyst is the function of active sites of loaded metals and support. Here, to optimize the loading, prepared the 5, 10, and 15 wt.% Mn₂O₃ over CeO₂-NP. The 10 wt% Mn₂O₃/CeO₂-NP shows the highest NO_x conversion activity and N₂ selectivity approx. 78% and 84% at 350. This may be due to more active surface area and required pore volume for the NO_x reduction to N₂ conversion. At 5 and 15 wt% loading, there are less active sites for NO_x conversion may be due to fewer Mn₂O₃ or presence in cluster form and hence insignificant for the reaction. The 15 wt% Mn₂O₃/CeO₂-NP shows the highest N₂ selectivity compared to 5 and 10 wt% Mn₂O₃ loading over CeO₂-NP. There is no clear information about this, but it may be due to the required BET surface area, pore-volume, and other chemical properties of catalysts.

FIGURE 7. NO conversion at temperature range 50 to 450°C. Reaction conditions: NO, NH₃=1000 ppm, O₂=6 vol%, N₂ balance, and GHSV =13,000 h⁻¹

FIGURE 8. NO conversion at temperature range 50 to 450°C. Reaction conditions: NO, NH_3 =1000 ppm, O_2 =6 vol%, N_2 balance, and GHSV =13,000 h^{-1}

CONCLUSIONS

The effect of bare CeO₂ support with varied morphology and metal-support interaction in Mn₂O₃/CeO₂ based catalysts for NH₃-SCR of NO has been studied. The Mn₂O₃/CeO₂-NP catalyst synthesized showed the highest catalytic performance among the other Mn₂O₃/CeO₂-NR, Mn₂O₃/CeO₂-NP, and Mn₂O₃/CeO₂-NC catalysts, with around 76.03% NO conversion at 50-450°C. The lowest crystal size of Mn₂O₃/CeO₂-NP (8.3 nm) and the highest specific surface area (34.53 m²/gm), facilitated the better dispersion Mn₂O₃ species (Mn⁴⁺=76.21%) and creation of more surface defects. As a result, Mn₂O₃/CeO₂-NP exhibited very high surface oxygen content (73.31%) and appreciable redox capacity as evident by XPS and H₂-TPR analysis. Thus, it is concluded favourable morphology of the support led to the desirable interaction with the metal, exhibiting support morphology effect on metal. In addition, the use of CeO₂ with Mn₂O₃ showed positive synergism, revealing desirable metal-support interaction system for NO_x reduction by NH₃ SCR reaction.

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