

CHAPTER – 4

Results and Discussion

4.1. Comparison of methods of catalyst preparation

Three different MnCO_2O_4 catalysts were prepared by CP, NC and DCP methods and calcined in air in a muffle furnace at 450°C for 4 h. The comparative activities of these three catalysts for SCR of NO using NH_3 reductant are shown in Figure 4.1 and their characteristics light off temperatures (LOT) are given in Table 4.1. The SCR activity is defined in terms of NO conversion and the LOT is demarcated as T_{10} , T_{50} and T_{max} corresponding the 10%, 50% and max% conversion of NO respectively.

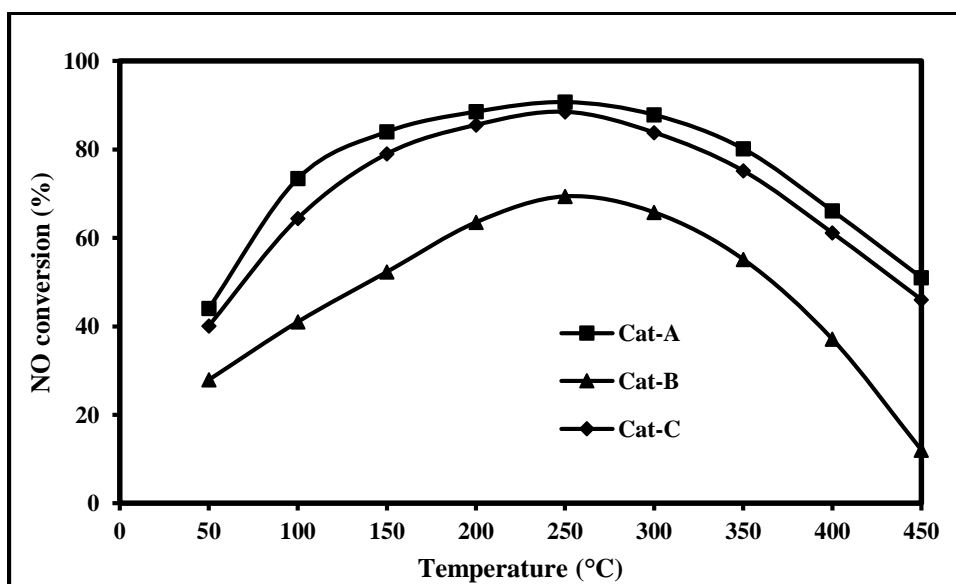


Figure 4.1. SCR activity of NO over catalysts: Cat-A, Cat-B, Cat-C (500 ppm NO, 1000 ppm NH_3 , 8% O_2 in Ar, GHSV = 30000 h^{-1}).

It is very clear from the figure 4.1 that the catalyst prepared by NC method showed the best activity for NO reduction. This may be due to difference in their textural and morphological characteristics as reflected by smaller crystallite size and higher surface area of NC produced catalyst. The supported catalyst prepared DCP method showed the activity in between unsupported catalysts produced by NC and CP methods. The activity of supported Cat-C

prepared by DCP is comparable with one synthesized by NC method (Cat-B). Thus, the order of preparation methods of the catalysts for NO reduction activity was as follows: NC \approx DCP > CP. However, NC method is tedious, very costly and difficult to prepare supported catalyst. Therefore, for further experiments, DCP method was selected to formulate catalysts for additional improvement of NO reduction performance.

Table 4.1. Light-off characteristics of Cat-A, Cat-B and Cat-C for NO reduction.

Catalyst	Light off characteristics			
	T ₁₀	T ₅₀	T _{max}	X _{NO} (%)
Cat-A	15	75	256	90.74
Cat-B	24	143	252	69.46
Cat-C	13	87	254	88.53

From Figure 4.1 and table 4.1, it can be seen that the activities of catalysts for NO reduction with NH₃ show the maxima in each case around 254°C. The maximum NO reduction achieved over Cat-A, Cat-B and Cat-C were 90.74%, 69.46% and 88.5% at the respective T_{max}. The order of NO conversion Cat-A, Cat-B and Cat-C using NH₃ reductant is as follows: Cat-A \approx Cat-C > Cat-B.

4.2. Effect of calcination strategies on activity of the catalyst for SCR of NO

The precursor of supported catalyst prepared by DCP method was divided into three parts and then each part was calcined under three different strategies of stagnant air (SA), flowing air (FA) and in a reactive mixture of CO-air mixture called as reactive calcination (RC). They were named as Cat-C_{SA}, Cat-C_{FA} and Cat-C_{RC}, where suffixes represent corresponding

calcination strategy. The comparative activities of these three catalysts for SCR of NO using NH_3 reductant are shown in Figure 4.2 and their characteristics LOT are given in Table 4.2.

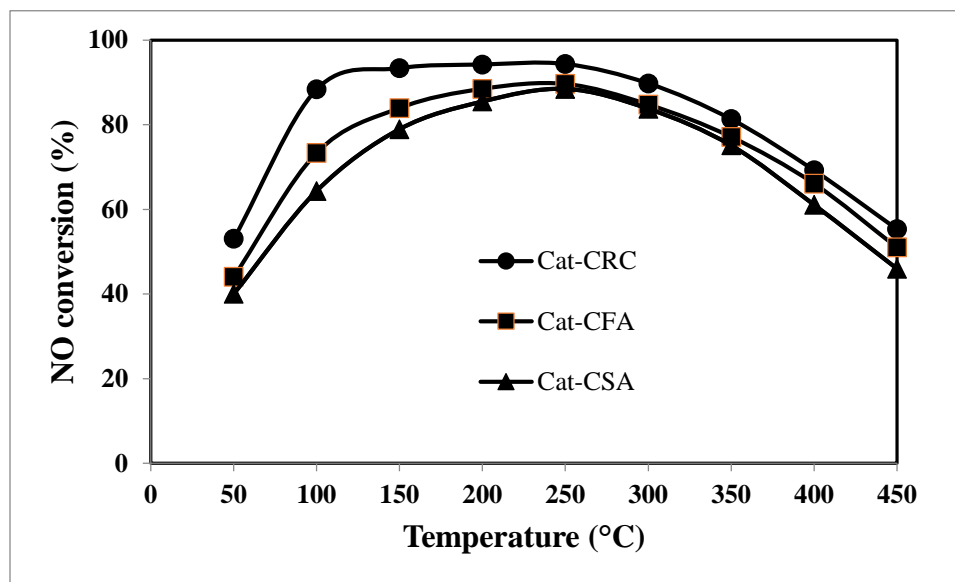


Figure 4.2 Effect of calcination strategies (SA, FA, RC) of DCP prepared catalysts on NO reduction activity with different reductants (500 ppm NO, 1000 ppm NH_3 , 8% O_2 in Ar, GHSV = 30000 h^{-1}).

It can be visualized that Cat- C_{RC} calcined via RC route showed the best activity for NO reduction ($X_{\text{max}}=94.4\%/ 243^\circ\text{C}$) with NH_3 (Figure 4.2). The light off characteristics shown in table 4.2 revealed that the catalyst prepared by calcination in stagnant air (Cat- C_{SA}) the lowest activity and the activity of Cat- C_{FA} (flowing air) showed the intermediate activity.

Table 4.2. Light-off characteristics of Cat- C_{SA} , Cat- C_{FA} and Cat- C_{RC} for NO reduction.

Catalyst	Light off characteristics			
	T_{10}	T_{50}	T_{max}	$X_{\text{NO}} (\%)$
Cat- C_{SA}	13	87	254	88.53
Cat- C_{FA}	18	75	258	89.68
Cat- C_{RC}	12	63	243	94.42

The maximum NO reduction achieved over Cat-C_{SA}, Cat-C_{FA} and Cat-C_{RC} were 88.53%, 89.68% and 94.42% at the respective T_{max} mentioned in table 3.2. The order of catalytic activity for NO conversion using NH₃ reductant is as follows: Cat-C_{RC} > Cat-C_{FA} > Cat-C_{SA}. The order of calcination strategies for production of catalyst for SCR of NO was as follows: RC > FA > SA. It can be concluded that RC route of the catalyst precursor is the best calcination strategy. Therefore, for further experiments, RC route was selected for the production of catalysts for NO reduction.

4.3. Selection of reducing agent for SCR of NO_x

Different reductants, NH₃, H₂, C₃H₈, H₂-NH₃, H₂-C₃H₈, were used for NO reduction over the selected Cat-C_{RC} for the choice of the best one. The catalytic activities using different reductants for SCR of NO are compared in Figure 4.3. The corresponding characteristics LOT of the catalysts are shown in table 4.3. It can be seen from the figure and table that the catalytic activity of the catalyst Cat-C_{RC} with H₂-C₃H₈ is the highest among other reductants. The maximum NO conversion using C₃H₈ reductant was 70.90% at 256°C. Whereas, NO reduction achieved was the highest, 98.71% at 203°C with H₂ assisted C₃H₈. Here, the promoting effect of 1% H₂ in the reductant is obviously reflected.

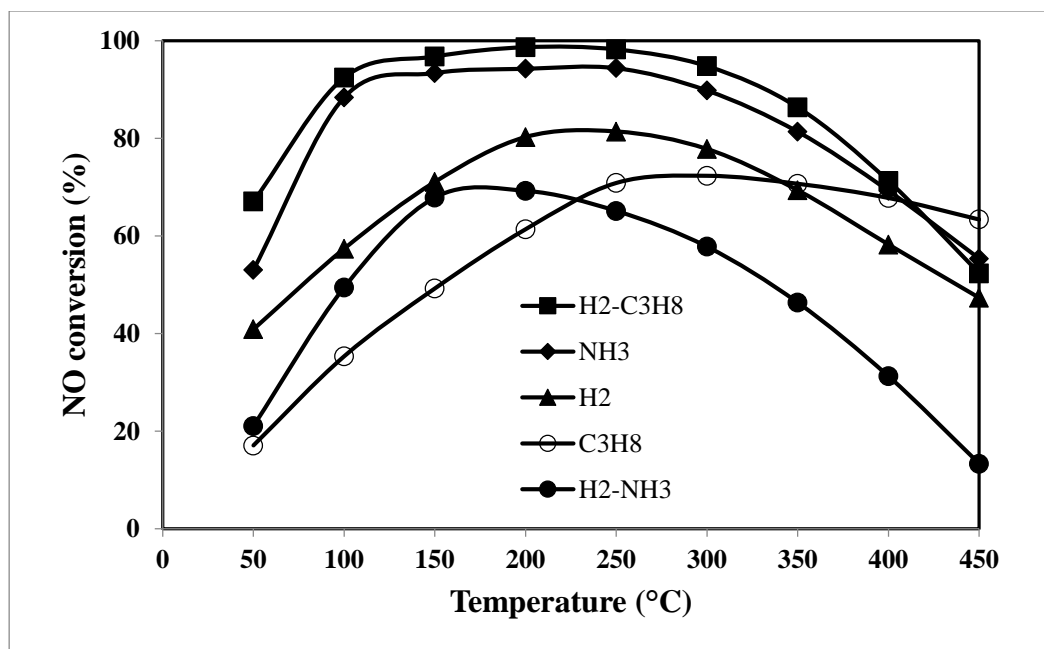


Figure 4.3 Effect of different reductants on DCP prepared catalyst Cat-E for NO reduction activity (500 ppm NO, 8% O₂ in Ar, GHSV = 30000 h⁻¹) with reductants 1% H₂; 1000 ppm NH₃; 1000 ppm C₃H₈; 1% H₂-1000 ppm NH₃; and 1% H₂-1000 ppm C₃H₈.

Table 4.3. Light-off characteristics of Cat-C_{RC} for NO reduction using different reductants.

Reactant	Light-off characteristics			
	T ₁₀	T ₅₀	T _{max}	X _{NO} (%)
NH ₃	17	55	258	94.40
H ₂	29	63	249	81.20
C ₃ H ₈	25	157	256	70.90
H ₂ -NH ₃	31	100	205	69.27
H ₂ -C ₃ H ₈	13	72	203	98.70

When, H₂ was used as reducing agent itself, the catalytic activity was not as high as when it was used as H₂-C₃H₈, but found it to be quite satisfactory i.e. 81.2% NO conversion at 249°C

(Table 4.3). The T_{50} for NO reduction using H_2 and C_3H_8 individually over Cat- C_{RC} was 63 and 157°C respectively, while it was intermediate value (72°C) with $H_2-C_3H_8$.

The maximum NO conversion of 69.27% was achieved at 205°C using H_2-NH_3 over Cat- C_{RC} while the effect of H_2 addition was prominent with C_3H_8 leading to 98.7% NO reduction at 203°C. Thus, the order of reductants based on their efficiency over Cat- C_{RC} is as follows: $H_2-C_3H_8 > NH_3 > H_2 > H_2-NH_3 > C_3H_8$. The reason for the best activity with $H_2-C_3H_8$ reductant might be due to the ease of breaking of H-C bonds which is the rate-determining step in HC-SCR that initiates the reaction [19]. When C_3H_8 is used as a reductant, the lower mean energy of the H-C bond enables oxidation, which in turn assists this rate-determining step, and hence the overall HC-SCR reaction proceeds rapidly [4,14]. The addition of H_2 further increased the breaking of H-C and C-C bonds due to the generation of reactive radicals, even at low temperatures [19]. It has been reported earlier by us that the RC leads to better dispersion and the high surface area which are the positive outcome in terms of the activity of catalyst for NO reduction [44]. Therefore, for further studies $H_2-C_3H_8$ was selected as reductant.

4.4. Comparison of catalytic activity of various transition metals cobaltites

NO conversion with $H_2-C_3H_8$ reductant was studied over various transition metals cobaltites; $MnCo_2O_4$, $CuCo_2O_4$ and $NiCo_2O_4$ and the results are shown in Figure 4.4. The characteristics light off temperature of the cobaltites are given in Table 4.4. The maximum NO conversions and corresponding temperatures obtained were 98.7%/ 203°C, 90.4%/ 248°C and 78.53%/ 253°C for $MnCo_2O_4$, $CuCo_2O_4$, and $NiCo_2O_4$, respectively (Figure 4.4, table 4.4).

The initiation temperatures, T_{10} for $CuCo_2O_4$, $MnCo_2O_4$ and $NiCo_2O_4$ were found to be 18°C, 12°C and 23°C respectively. The light off temperatures, T_{50} were attained at 63, 45 and 72°C

for CuCo_2O_4 , MnCo_2O_4 and NiCo_2O_4 respectively. Therefore, the catalyst activity order follows the following trend: $\text{MnCo}_2\text{O}_4 > \text{CuCo}_2\text{O}_4 > \text{NiCo}_2\text{O}_4$.

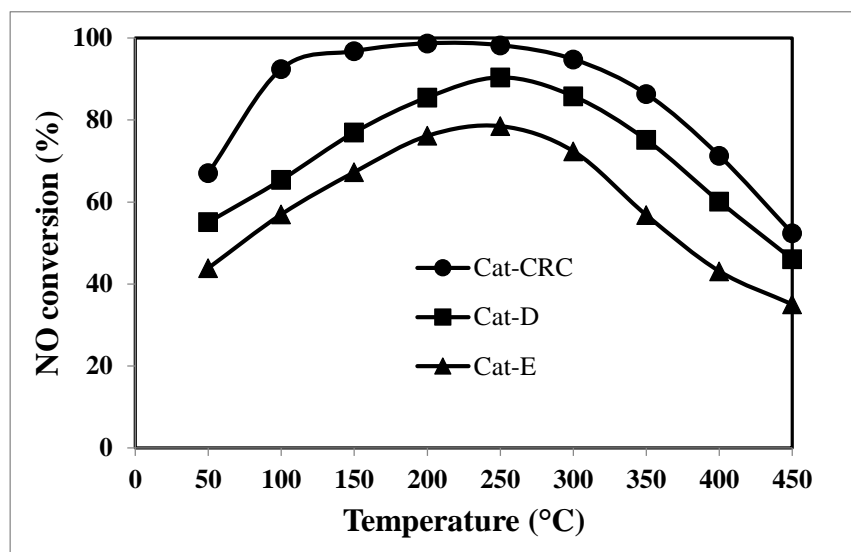


Figure 4.4. NO reduction with $\text{H}_2\text{-C}_3\text{H}_8$ reductant over different catalysts: Cat-CRC, Cat-D and Cat-E. Quantity of catalyst = 200 mg diluted with $\gamma\text{-Al}_2\text{O}_3$ to make volume 1 mL; Composition of feed mixture = 500 ppm NO, 1% H_2 -100 ppm C_3H_8 , 8% O_2 in Ar; Total flow rate = 100 mL/min. Temperature = ambient to 450°C; GHSV = 30000 h^{-1}

Table 4.4. Light-off characteristics of Cat-CRC, Cat-D and Cat-E with $\text{H}_2\text{-C}_3\text{H}_8$ reductant

Catalyst	Light off characteristics			
	T_{10}	T_{50}	T_{\max}	$X_{\text{NO}} (\%)$
Cat-CRC	13	45	203	98.7
Cat-D	18	63	248	90.4
Cat-E	23	72	253	78.53

Finally, it can be concluded that catalyst, 30% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ with $\text{H}_2\text{-C}_3\text{H}_8$ reducing agent was the best combination for NO reduction under the conditions studied.

4.5. Optimization of MnCo_2O_4 loading on $\gamma\text{-Al}_2\text{O}_3$

The comparative activities of five catalysts were varied from 10-50% loading of MnCo_2O_4 spinel on $\gamma\text{-Al}_2\text{O}_3$ for SCR of NO using $\text{H}_2\text{-C}_3\text{H}_8$ reductant are shown in Figure 4.5, their characteristics LOT are given in table 4.5. It can be seen from the figure that 30% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ showed the best NO-SCR activity, 89.70% NO reduction at 253°C with >80% NO reduction over wide temperature range of 150-400°C. The catalyst 50% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, Cat-I showed the least conversion 74.5%/251°C due to less amount of active metal present in the catalyst composition. Thus, the order of catalyst activity for NO reduction activity: 30% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, Cat-C_{RC}>40% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, Cat-G>50% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, Cat-F>20% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, Cat-H>10% $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, Cat-I.

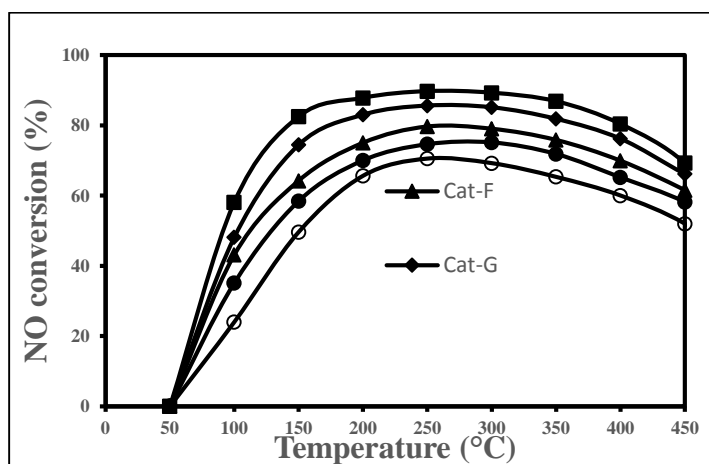


Figure 4.5. Optimization of MnCo_2O_4 loading on $\gamma\text{-Al}_2\text{O}_3$. Quantity of catalyst = 200 mg diluted with $\gamma\text{-Al}_2\text{O}_3$ to make volume 1 mL; Composition of feed mixture = 500 ppm NO, 1% H_2 -100 ppm C_3H_8 , 8% O_2 in Ar; Total flow rate = 100 mL/min. Temperature = ambient to 450 °C; GHSV = 30000 h^{-1}

Table 4.5. Characteristics LOT of (10-50%) $\text{MnCo}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ with $\text{H}_2\text{-C}_3\text{H}_8$ for SCR of NO

Catalyst	Light off characteristics			
	T_{10}	T_{50}	T_{\max}	$X_{\text{NO}} (\%)$
Cat-F	58	101	250	83.6

Cat-G	63	87	244	89.5
Cat-C _{RC}	9	68	249	89.7
Cat-H	70	135	308	79.1
Cat-I	74	138	247	74.5

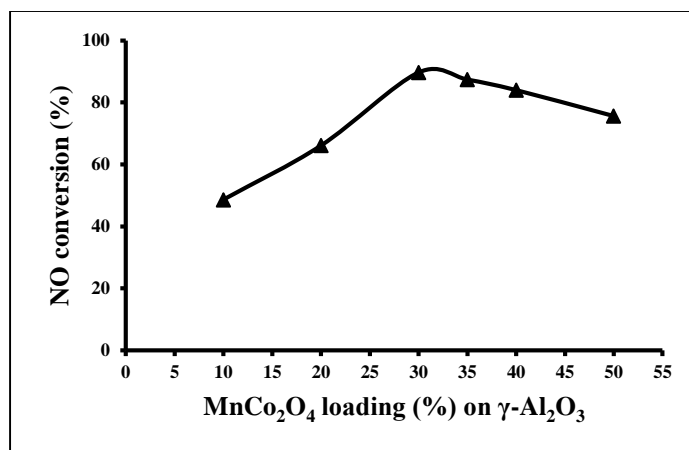


Figure 4.6. Optimization of MnCo₂O₄ loading on γ -Al₂O₃ for SCR of NO at 250°C

The optimization of MnCo₂O₄ loading on γ -Al₂O₃ for SCR of NO using H₂-C₃H₈ at 250°C is shown in Figure 3.6. It is clearly seen in the figure that the curve shows the maximum NO conversion of 91.3% at optimum loading of 32%. Therefore, for further improvement of the activity by Rh doping in the supported catalyst optimum loading of 32% MnCo₂O₄ on γ -Al₂O₃ was prepared and used.

4.6. Optimization of Rh doping in 32%MnCo₂O₄/ γ -Al₂O₃

The amount of Rh doping in 32%MnCo₂O₄/ γ -Al₂O₃ catalyst were varied as 0.1%, 0.2% and 0.3%; they were named as Cat-J, Cat-K, Cat-L, respectively. The NO conversions using H₂-C₃H₈ reductant over the three Rh promoted catalysts with increasing temperature were studied and the results are shown in Figure 4.7. The characteristics LOT of de-NO_x activity are given in Table 4.7.

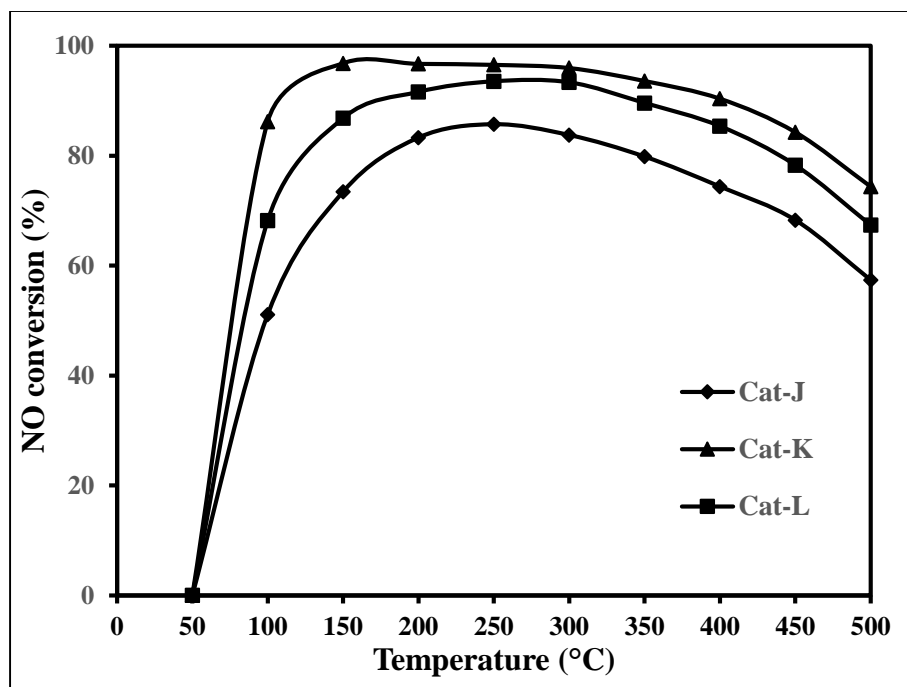


Figure 4.7. Optimization of Rh loading over 0.2%Rh.MnCo₂O₄/γ-Al₂O₃. Quantity of catalyst = 200 mg diluted with Al₂O₃ to make volume 1 mL; Composition of feed mixture = 500 ppm NO, 1% H₂-100 ppm C₃H₈, 8% O₂ in Ar; Total flow rate = 100 mL/min. Temperature = ambient to 450°C; GHSV = 30000 h⁻¹

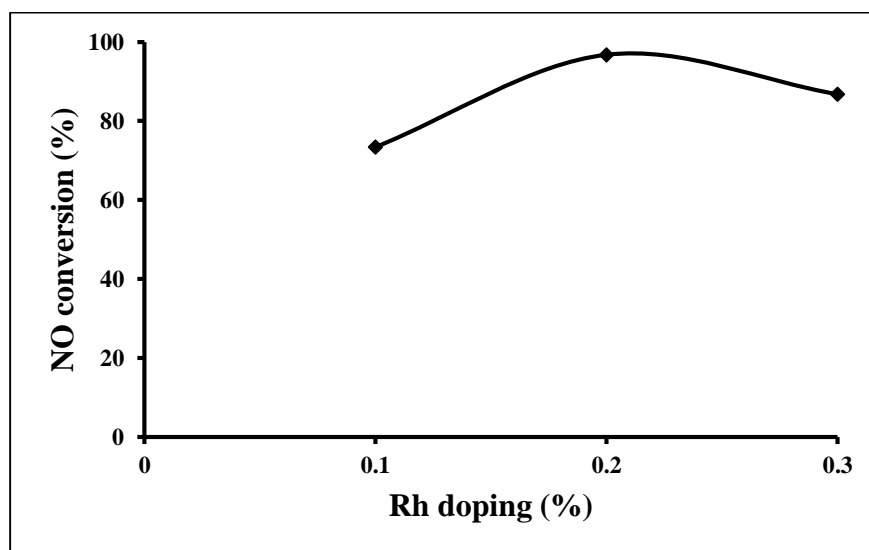


Figure 4.8. Optimization of Rh doping on MnCo₂O₄/γ-Al₂O₃ for SCR of NO at 150°C

It can be seen from the figure that Cat-K showed the best NO-SCR activity with H₂-C₃H₈. However, Cat-L exhibited comparable activity with Cat-K. Thus, the optimum doping of promoter in the catalyst was 0.2%Rh. The light off temperatures, T₅₀ were attained at 91, 67 and 135°C for Cat-J, Cat-K and Cat-L respectively. Thus, the order of catalyst activity for NO reduction activity: 0.2%Rh32%MnCo₂O₄/γ-Al₂O₃>0.1%Rh32%MnCo₂O₄/γ-Al₂O₃>0.3%Rh32%MnCo₂O₄/γ-Al₂O₃. Therefore, Cat-K was selected for further kinetics studies of SCR of NO using H₂-C₃H₈.

Table 4.6. Characteristics LOT of 0.2%Rh.32%MnCo₂O₄/γ-Al₂O₃ with H₂-C₃H₈ reductant

Catalyst	Light off Temperature			
	T ₁₀	T ₅₀	T _{max}	X _{NO} (%)
Cat-J	56	91	252	95.7
Cat-K	34	67	150	96.8
Cat-L	62	135	256	91.9

4.7. De-NO_x performance of the best formulated catalyst

The de-NO_x performance (activity, selectivity and stability) of the best formulated catalyst, Cat-K (0.2%Rh.32%MnCo₂O₄/γ-Al₂O₃) are shown in Figures 4.7-4.11. Catalyst activity was already discussed in section 4.6.

4.7.1. Catalyst Selectivity

The NO catalytic activity were performed for NO reduction and the negligible amount of NO₂ and N₂O were found in the product stream. Therefore, catalyst selectivity was shown in terms of N₂ only. In order to reduce awkwardness in the manuscript here we are presenting the graph of best catalyst selectivity (96.8%/150°C). The concentration of NO₂ and N₂O were found

negligible in the product stream during SCR of NO studies. Therefore, catalysts were highly selective towards N_2 .

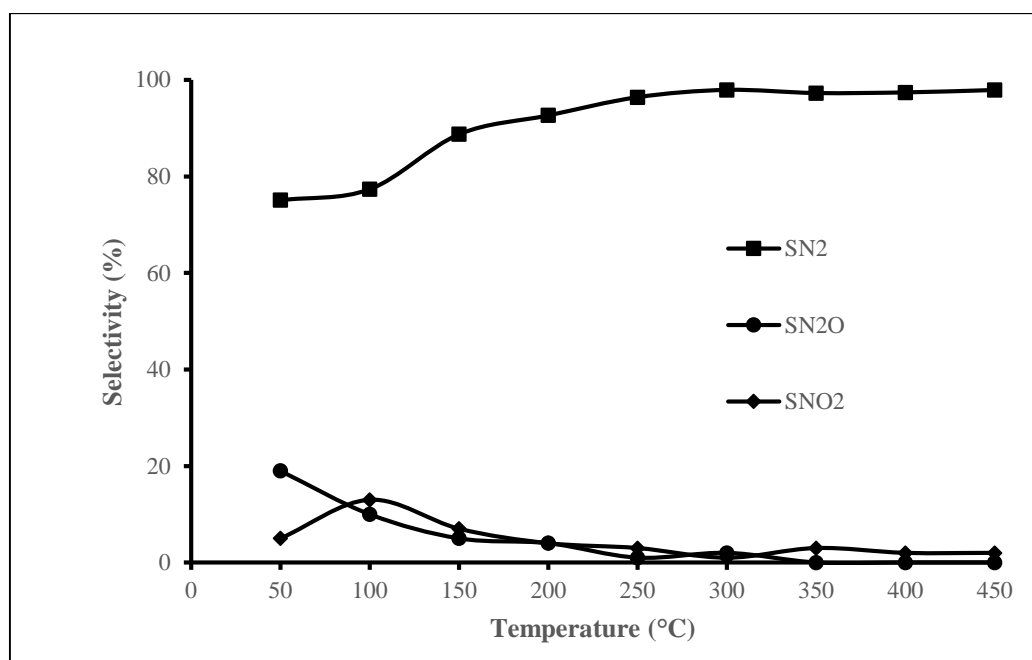


Figure 4.9. N_2 selectivity over Cat-K ($0.2\%Rh.32\%MnCo_2O_4/Al_2O_3$)_{RC} spinel catalyst. Quantity of catalyst = 200 mg diluted with Al_2O_3 to make volume 1 mL; Composition of feed mixture = 500 ppm NO, 1% H_2 -100 ppm C_3H_8 , 8% O_2 in Ar; Total flow rate = 100 mL/min. Temperature = ambient to 450°C; GHSV = 30000 h^{-1}

The various selectivity curves, N_2 selectivity (SN_2), N_2O selectivity (S_{N_2O}) and NO_2 selectivity (S_{NO_2}) for SCR of NO using H_2 - C_3H_8 over Cat-K are shown in Figure 4.9. It can be seen from the figure that the Cat-K is highly selective for N_2 and SN_2 increased with increase in temperature to ~100% above 300°C. A notable increase in S_{N_2} was obtained in the temperature range of 250-450°C. The highest value of SN_2O was 19% at 50°C which continuously decreased with increase in temperature to zero value at 350°C. It is evident from the figure that S_{NO_2} curve shows a maxima of 13% at 100°C and then decrease in with further increase in temperature to a minimum value of 2% above 400°C.

4.7.2. Stability tests of 0.2% Rh32%MnCo₂O₄/γ-Al₂O₃

4.7.2.1. Time on stream

The time on stream study for life test was done to check the stability of the catalyst at 150°C at which ~100% conversion occurred during SCR of NO using H₂-C₃H₈ over Cat-K in a continuous run for 50 h under the experimental conditions used for activity measurements and the results are shown in Figure 4.10.. It was found that practically no deactivation of the catalyst occurred and the conversion of NO remained ~100% over a period of 50 h with ~90% selectivity towards N₂.

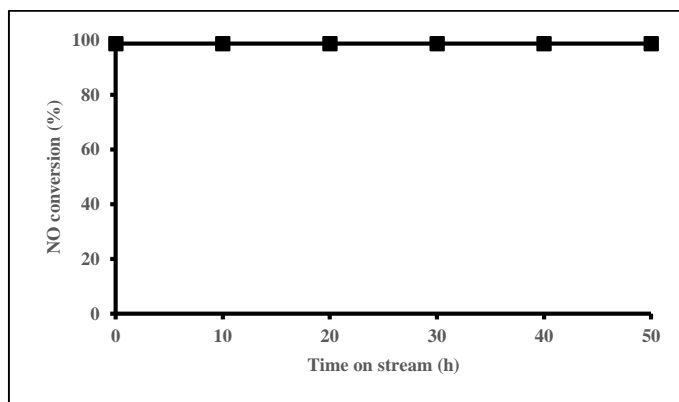


Figure 4.10. Constant temperature (150°C) stability test

4.7.2.2. Accelerated ageing

The accelerated aging test of the Cat-K was performed to evaluate the working stable temperature range under the reaction conditions. The test was performed at different steady temperatures (250, 350, 450, 550°C) starting from the lowest temperature of 150°C where complete conversions of NO occurred, up to 550°C with intermittent cooling to 150°C and measuring the NO conversion. In the first test, the temperature was raised from ambient to 150°C, and measured the NO conversion maintaining temperature for 5 h. In the second test,

the temperature was increased to 250°C at a rate of 10°C/min and maintained there for 5 h. Then, cooled to 150°C and NO conversion was measured. Similarly, the 3rd, 4th and 5th tests were done at 350, 450 and 550°C followed by cooling to 150°C, subsequently after each accelerated aging NO conversion was evaluated at 150°C. The results obtained are shown in the figure 4.11.

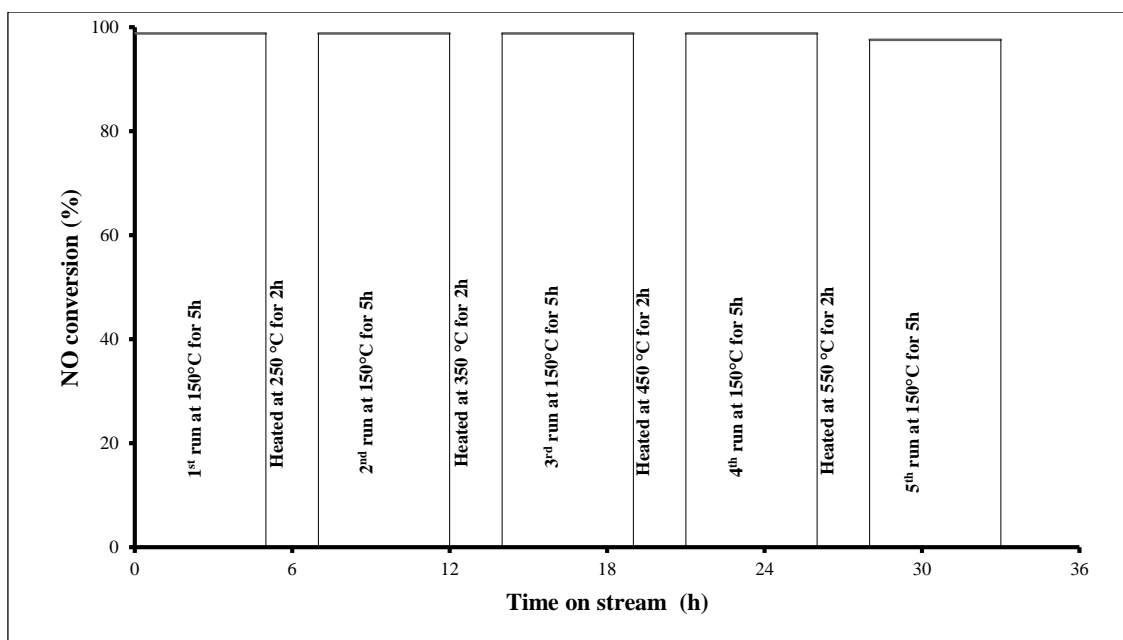


Figure 4.11. Accelerated ageing test

It is clear from the figure 4.11 that with accelerated ageing at different temperatures and then cooling to 150°C for measurement of NO conversion, there was practically no significant deactivation of the catalyst observed up to 450°C under the experimental conditions. However, there was a slight decrease of 1.2% in the activity of the catalyst after accelerated ageing at 550°C. Thus, the catalyst was stable within the exhaust temperature range of 150-450°C.

4.8. Comparison of the best Cat-K with commercial catalyst (VWTi)

Cat-K (0.2%Rh.32%MnCo₂O₄/γ-Al₂O₃) prepared by DCP by RC route showed the best NO-SCR activity (96.8%) NO reduction at 150°C. One can visualize from figure 4.12 that >90% NO conversion occurred over Cat-K using H₂-C₃H₈ reductant over a wide temperature range (100-400°C).

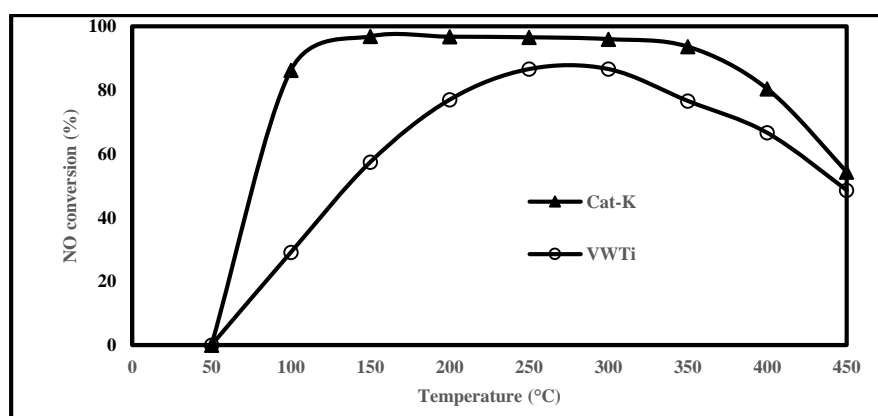


Figure 4.12. Comparison of the best Cat-K (0.2%Rh.32%MnCo₂O₄/ γ-Al₂O₃)_{RC} with commercial Cat-VWTi with H₂-C₃H₈ reductant for NO reduction.

The exceptionally high activity with high N₂ selectivity and good stability of Cat-K under the laboratory conditions were found. Characterization signified that Cat-K exhibited oxygen deficient structure, higher surface area (99.31m²/g) than commercial catalyst (V-W-Ti). Thus, Cat-K showed better SCR activity than commercial catalyst.

On the other hand, the commercial catalyst showed poorer NO-SCR activity exhibiting maximum conversion (86.6%) at 250°C. The characteristics LOT for Cat-K and commercial catalyst are given in table 4.7. For Cat-K the light temperature (T₅₀, 87°C) is less than that of V-W-Ti (140°C).

Table 4.7. Characteristics LOT of Cat-K and commercial catalyst (V-W-Ti) with H₂-C₃H₈ reductant

Catalyst	Light off Temperature			
	T ₁₀ (°C)	T ₅₀ (°C)	T _{max} (°C)	X _{NO} (%)
Cat-K	64	87	150	96.8
V-W-Ti	70	140	250	86.6

4.9. Comparison of H₂-LPG and H₂-C₃H₈ reductants for SCR of NO over Cat-K

In search of substitute for costly C₃H₈ reductant for SCR of NO_x, LPG was chosen because of the following reasons: Low cost, easy commercial availability, it has already been used as a cleaner fuel in >14 million vehicles plying around the world for light, medium and heavy duty applications [106]. Thus, LPG was chosen for comparative study with C₃H₈ under the mentioned previous operating conditions. The composition of an Indian LPG was determined by GC analysis experimentally in the laboratory. The typical chromatogram of the LPG is shown in Figure 4.13, which corresponds to 74.23% C₃H₈, 13.02% n-C₄H₁₀, 12.19% i-C₄H₁₀ and 0.55% C₂H₆.

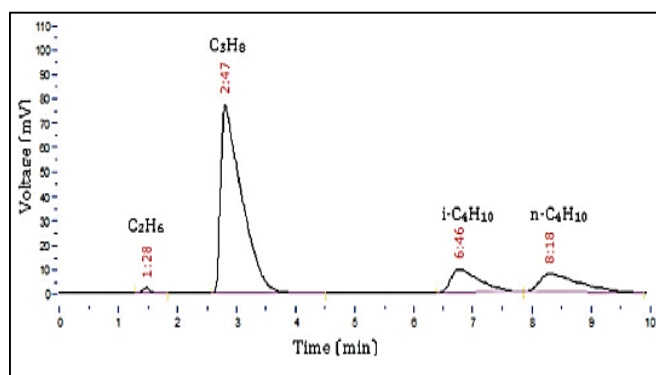


Figure 4.13. A typical GC chromatogram of LPG

The results of comparative studies on H₂-LPG and H₂-C₃H₈ reductants for SCR of NO over Cat-K are shown in figure 4.14 and characteristics LOT given in table 3.7.

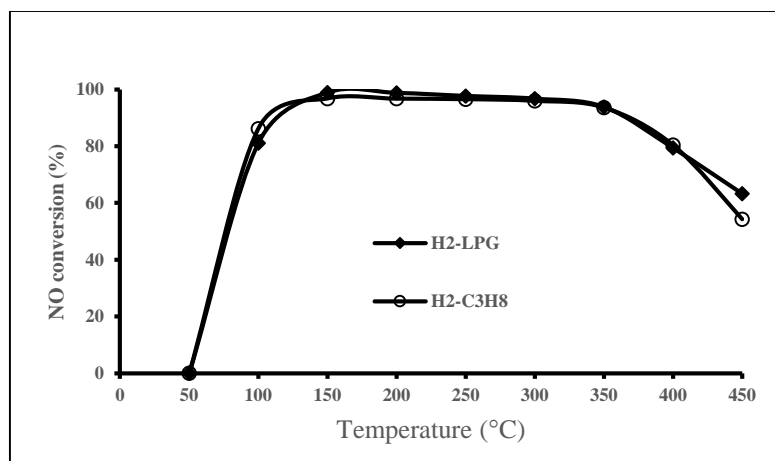


Figure. 4.14. C_3H_8 conversion (%) of Cat-K using $H_2-C_3H_8$ and H_2-LPG reductants (500 ppm NO, 1% H_2 -1000 ppm C_3H_8 , 1% H_2 -1000 ppm LPG, 8% O_2 in Ar, GHSV = 30000 h^{-1}).

Table 4.8. Characteristics LOT of Cat-K with $H_2-C_3H_8$ and H_2-LPG reductant

Reductant	Light off Temperature			
	T_{10}	T_{50}	T_{max}	X_{NO} (%)
$H_2-C_3H_8$	64	87	150	96.80
H_2-LPG	60	83	147	98.91

It is clearly seen that H_2-LPG showed higher NO conversion than $H_2-C_3H_8$. This may be due to synergistic effect of other constituents of LPG. Therefore, LPG has been suggested as potential reductant for SCR of NO_x .

Since, liquefied petroleum gas (LPG) constitutes $\approx 72\%$ C_3H_8 in India and it is low cost, easily available commercially. Therefore, for commercial feasibility studies, in place of $H_2-C_3H_8$, H_2-LPG was selected as reductant for SCR of NO over Cat-K.