ISSN: 0976-3376

Available Online at http://www.journalajst.com

ASIAN JOURNAL OF SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology
Vol. 08, Issue, 01, pp.4087-4092, January, 2017

RESEARCH ARTICLE

PROMOTIONAL EFFECTS OF Co AND Ce ON V-W-Ti CATALYST FOR SELECTIVE CATALYTIC REDUCTION OF NO

[1]Ashish R. Kavaiya, [1]Deepak Yadav, [2]Pratichi Singh and *[1]Ram Prasad

[1]Department of Chemical Engineering and Technology, IIT (BHU), Varanasi 221005, India
[2]Enviroment Science Division, Institute of Sciences, BHU, Varanasi 221005, India

ARTICLE INFO

Article History:
Received 20th October, 2016
Received in revised form
15th November, 2016
Accepted 25th December, 2016
Published online 31st January, 2017

Key words:
NOx, $V_1W_9Ti_{90}$,
$Co_{0.01}V_{0.99}W_9Ti_{90}$,
$Ce_{0.01}V_{0.99}W_9Ti_{90}$,
Promoter,
Low temperature SCR.

ABSTRACT

NO has been identified as a major pollutant causing various concerns like, health, acid rain, greenhouse gas, photochemical smog, etc. Different environmental legislatives have forced to control NO emissions around the globe. Selective catalytic reduction (SCR) of NO has been emerged out as the best prominent NO control technique. Three, V-W-Ti-catalysts ($V_1W_9Ti_{90}$, $Co_{0.01}V_{0.99}W_9Ti_{90}$, $Ce_{0.01}V_{0.99}W_9Ti_{90}$) were prepared by wet impregnation method with and without promoter (Co or Ce) in a minute amount. The catalysts were characterized by various technics such as XRD, SEM, and EDX. The influence of promoters and reductants (NH_3, LPG, H_2-LPG) was investigated for NO reduction over the SCR catalysts. The catalyst activity was evaluated in tubular flow reactor under the following experimental conditions: catalyst = 200mg, NO = 500ppm, O_2=8%, NH_3= 1.0% in Ar, GHSV =30,000 h^{-1}.The inlet and outlet gases of the reactor were analyzed by NOx chemiluminescence and online GC. The catalyst activity was dependent on the reductants and promoters used. The catalyst, $Co_{0.01}V_{0.99}W_9Ti_{90}$ exhibited the best activity of 99.8% NO reduction at 310 °C with H_2-LPG reductant. The activity order of the catalyst is as follows: $Co_{0.01}V_{0.99}W_9Ti_{90} > Ce_{0.01}V_{0.99}W_9Ti_{90} > V_1W_9Ti_{90}$. The performance order of the reductants is as follows: H_2-LPG>LPG>NH_3.

INTRODUCTION

Nitric oxides (NOx) emissions from vehicle exhaust are accountable for severe health and environment threat as it originates acid rain, photochemical smog and global warming (L. Chen *et al*, 2011). Stringent environment legislation force to lower down NOx emissions from vehicle tail pipes. Selective catalytic reduction (SCR) is the most promising technique for NOx reduction. Various types of catalyst and reducing agents are reported in the literature (M. Jabłońska *et al*, 2016). Many types of catalysts including noble metals, base metals, mixed metals, spinel, perovskite, hydrotalcite, etc. were studied for NOx SCR reaction (C. Liu *et al*, 2016, M. Jabłońska *et al*, 2016).Several reductants such as NH_3, urea, HC, H_2-HC, etc. were used to reduce NOx (H. Hamada *et al*, 2012).The exhaust composition of NOx mainly include nitric oxide (NO ~95%), nitrogen dioxide (NO_2 ~ 4%) and nitrous oxide (N_2O~1%) (X. Yang *et al*, 2013). For light and heavy duty diesel vehicles NOx emission limit severely decline in order to achieve present emission control legislation. Since, 2014 Euro-6 emission legislation reduced NOx emissions by 55% as compared to Euro-5 for light duty vehicle (LDV) as depicted in Table 1.

In order to comply with the stringent legal requirements, great deal of research works have been carried out to find high performance catalysts together with worthy reductants as a comprehensive solution for NOx reduction under lean conditions. Transition metal oxides have attracted a considerable interest in heterogeneous catalysis owing to their low price and good redox properties e.g. V_2O_5, Co_3O_4, MnO_2, NiO, CeO_2, TiO_2 and CuOx (X. Wang *et al*, 2015). Among these supported and promoted catalysts, V_2O_5-WO_3/TiO_2 (L. J. Alemany *et al*, 1995), Mn/TiO_2 (P. G. Smirniotis *et al*, 2006), Fe/TiO_2 (R. Q. Long *et al*, 2002), Cu/TiO_2 (G. Ramis *et al*, 1995), Cr/TiO_2 (H. Schneider *et al*, 1995), and MnOx-CeO_2 (G. Qi *et al*, 2003), have also been extensively studied for SCR of NOx. V_2O_5-WO_3/TiO_2 (V-W-Ti) has been widely accepted as a commercial catalyst (L. Chen *et al*, 2009). Vanadia(V_2O_5) is the active phase in V-W-Ti catalyst, whereas Tungsten (W) as a promoter stabilizes titania (TiO_2), also favors V spreading on the catalyst surface, and enhances catalyst acidity (L. Chen *et al*, 2011). However, this commercial catalyst is competent over a tapered temperature window (300-400 °C). Addition of promoters in the catalyst of V-W-Ti can reduce the temperature and advance its performance by tuning of surface properties. The promoters used are transition metal (Co), rare earth (La, Ce) and noble metals (Pd, Pt, Rh) (L. Obalová *et al*, 2013).

Corresponding author: Ram Prasad,
Department of Chemical Engineering and Technology, IIT (BHU), Varanasi 221005, India.

To improve the activity along with stability enhancement of V-W-Ti, Ceria (CeO_2) has been studied due to its oxygen storage and redox properties as shown in three way catalyst (TWC) during gasoline engine exhaust control. CeO_2 stores and releases oxygen via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions, respectively (B. M. Reddy *et al*, 2003). Ceria enhances the oxidization of NO to NO_2 and then increase the activity of the SCR of NO by ammonia (L. Chen *et al*, 2009). If the NO in the NOx gas is partially oxidized to NO_2 so that an equi-molar NO/NO_2 ratio is formed very high increase in activity at low temperature is observed, thus the process is known as "fast SCR". SCR process of de-NOx various Reductants are used like NH_3, Urea, HC, CO, H_2, Ethanol, Mono Ethanolamine, etc. Generally, V_2O_5-WO_3 (MO_3)/TiO_2 is employed as NH_3-SCR catalysts (A. Grossale *et al*, 2008). However, many problems occur when using the NH_3-SCR technology, namely NH_3 slip (emissions of unreacted toxic ammonia), catalyst deterioration, ash odor, air heater fouling, and a high running cost (G. G. Olympiou *et al*, 2011).

Table 1. Euro norms for NOx emissions for light duty and heavy duty vehicles

Light Duty Vehicle (mg/km)						Heavy Duty Vehicle(mg/kWh)					
Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	Euro 6	Euro I	Euro II	Euro III	Euro IV	Euro V	Euro VI
1992	1996	2000	2005	2009	2014	2000	2009	2009	2009	2009	2014
-	-	500-780	250-330	180-230	80	8000	2000-7000	5000	3500	2000	400

Currently in automobiles AUS 32 (aqueous urea solution, containing 32.5% urea, also known as AdBlue®) is used as reductant for the control of NOx reduction (F. Birkhold *et al*, 2007). This method also produces the ammonia (NH_3) on hydrolysis of urea so that same problem occurs as NH_3-SCR process. Hydrocarbon-SCR (HC-SCR) is a de-NOx system that uses hydrocarbon as the reducing agent and onboard fuel as the reductant. Consequently, no need exists to use another tank to supply the reducing agent, which simplify the system. H_2-SCR has many advantages; for instance, hydrogen as reductant does not induce any second pollutants and has high activity to reduce NOx efficiently at the lowest possible temperature (S. S. Kim *et al*, 2010; M. Machida *et al*, 2001). In industrial sites where H_2 is easy available, H_2-SCR is regarded as a possible substitute for NH_3-SCR. The catalyst is the most central technology in any H_2-SCRprocess, and its performance directly affects the removal of nitrogen oxides (X. Cai *et al.* 2016). In this experimental work, abundantly available low cost materials were used to synthesize M-VWTi catalysts with and without promoters (M = Co or Ce) and the reducing agents of choices were selected as NH_3, LPG, H_2-LPG.The activity and N_2 selectivity of the different M□VWTi catalysts were evaluated for SCR of NO using different reductants.

MATERIALS AND METHODS

All the precursor used in the catalyst preparation are all of Analytical grade like ammoniummetavanadate (NH_4VO_3), oxalic acid($C_2H_2O_4$), sodium tungstate ($Na_2WO_4.2H_2O$), conc. HCl, cobalt nitrate ($Co(NO_3)_2.6H_2O$), cerium nitrate ($Ce(NO_3)_2.6H_2O$), TiO_2 powder, etc. with 99% of purity.

Catalyst Preparation: The catalyst (V-W-Ti) prepared by wet impregnation method for the present experimental work. V_2O_5:WO_3:TiO_2:: 1:9:90 shows mass percentage and can be abbreviated as V_1W_9/Ti_{90}. Sodium tungstate ($Na_2WO_4.2H_2O$) was used to prepare tungsten oxide (WO_3). Ammonium metavanadate (NH_4VO_3), prepared tungsten oxide (WO_3) mixed in the oxalic acid ($C_2H_2O_4$) in desired proportions then impregnated over commercial TiO_2. In 3.406g of sodium tungstate ($Na_2WO_4.2H_2O$) conc. HCl was added to form white precipitate. It is then washed 4-5 times with distilled water. Light yellow precipitate was obtained, which was dried at 110 °C for 12 h to get light yellow powder obtained. 25.21g oxalic acid added to 200 ml water stirred and mixed. 0.2571g of ammonium metavanadate (NH_4VO_3) was added to oxalic acid yellow colored solution formed. 1 mol% of V has been doped with different dopents namely transition metals Co and rare earth metal Ce to enhance NO SCR performance of catalyst. After that, 0.8g of WO_3 was added to the solution. It turned into dark yellow and then after sometime into fluorescent green color, stirred for 30 min. Subsequently TiO_2 powder was added and the solution again turned into white color powdery like solution, stirred for 7 h.

The solution is heated to 110 °C for 12 h followed by calcination at 500°C for 4 h in air.

Experimental Set Up and Activity Measurement

The gas mixture flow through a downstream flow tubular reactor was used to evaluate the catalytic performance of 200 mg V-W-Ti catalysts. The configuration of the reactor system has been reported in a previous publication (R. Prasad *et al*, 2009). The catalyst was diluted to 1 ml with alumina support over the glass wool as compact fixed bed. Tests of the SCR activity were carried out in a fixed-bed quartz-reactor vertically placed in the split open furnace for reaction temperature control. Type K thermocouples (0.02 in. diameter) are placed at base of the catalyst bed for temperature control and measurement at the reaction site (catalyst bed).Briefly, in the experimental set up all the gas flow rates of gases were monitored with the help of digital gas flow meters in mL min^{-1}. The catalytic experiments were carried out under steady state conditions (25-550°C). Generally, the reactor was heated to the desired temperature with the help of a microprocessor based temperature controller. A temperature control of ±0.5 °C was achieved. The gaseous reactants and products concentrations passing through the catalyst bed were analyzed by an online gas chromatograph (Nucon series 5765) equipped with NOx analyzer, Porapack Q-column, methaniser and FID detector. All the gas mixture flow lines were silicon tubing with proper joints and Ts along with moisture traps to absorb moisture. Catalysts with particle size 100–150 mesh, under detailed lean reaction gases containing 500 ppm NO, 1% NH_3, 1.0% H_2 and 1% LPG, 8% O_2 and rest Ar. All the gases supplied by Inox Air products Ltd. in cylinders and with UHP grade. Prior to the gas mixture passing through the catalyst bed inside the reactor was passed through moisture traps with total gas flow rate at 60 mL min^{-1}. In view to take precautionary measures for mercaptan free LPG, surpass it through sodium plumbite solution followed by $CaCl_2$ tower to free it from moisture. The analysis of 0.5% NO cylinder (Inox Air products Ltd.) with 99.9% purity was used for experimental purposes. The fractional conversion of NO was evaluated using Ecophysics CLD 62 chemiluminescence calculated by the concentration displayed inside NOx analyzer by the following formula:

$$X_{NOx}\,(\%) = \frac{NO_{inlet} - NO_{outlet}}{NO_{inlet}} X\ 100$$

RESULTS AND DISCUSSIONS

The SCR activities of different catalysts were evaluated at wide temperature range of 25-550 °C using NH_3, LPG and H_2-LPG as reductants. The SCR activity was significantly enhanced at lower temperature ends using H_2-LPG, along with LPG and conventional NH_3 reductant over V-W-Ti catalyst shown in Fig. 1.

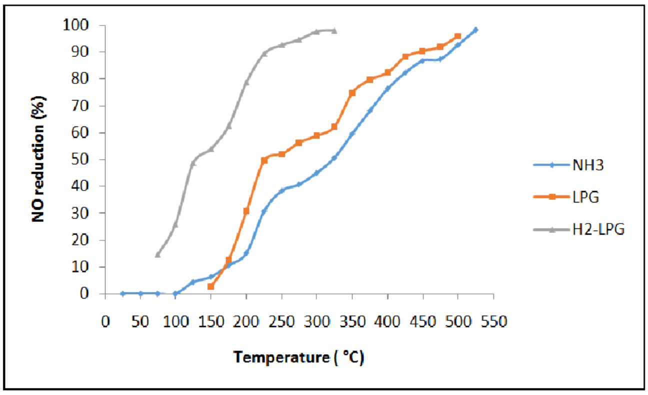

Fig. 1. NO reduction over VWTi catalyst

The SCR activities of $Co_{0.01}V_{0.99}W_9Ti_{90}$ over different reductants (NH_3, LPG, and H_2-LPG) are shown in Fig. 2.

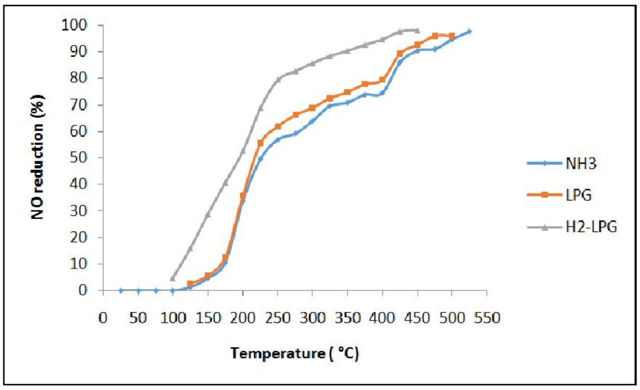

Fig. 2. NO reduction over $Co_{0.01}V_{0.99}W_9\ Ti_{90}$ catalyst

The potential use of LPG as reducing agent is a better alternative to the other reductants as it leads to a strong decrease in the Gibbs free energy values of NO reduction to N_2 than other reductants. NO-SCR conversion using $Ce_{0.01}V_{0.99}W_9\ Ti_{90}$ catalyst using (NH_3, LPG, H_2-LPG) as reductants are demonstrated in Fig. 3.The SCR reaction over $Ag-Al_2O_3$ catalysts is most likely dependent on two factors: the ability to reduce NOx to N_2 and to activate (partially oxidize) the reducing agent, i.e. the hydrocarbon (Klingstedt *et al*, 2009).

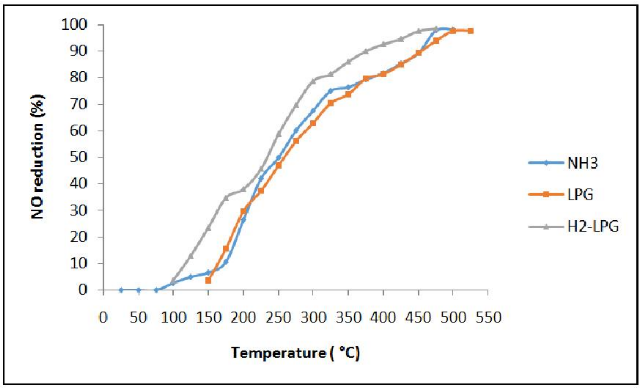

Fig. 3 NO reduction over $Ce_{0.01}V_{0.99}W_9\ Ti_{90}$ catalyst

It is clear that Co promoter facilitates the dispersion of the catalyst over the support matrix. The complete NO conversion to N_2 was maintained up to 390°C. The light off temperatures for NO conversion over the catalyst samples are given in table 2. It is observed by many authors (Kamolphop *et al*, 2011, S. Korhonen *et al*, 2011; Ghude *et al*, 2013) that the NO reduction is not only connected to an optimized silver loading, but also to the nature of the reductants.

Table 2. Light off temperatures of NO over $V_1W_9\ Ti_{90}$ catalysts

Catalyst	Reductant	NO reduction (%)		
		T_i	T_{50}	T_f
$V_1W_9\ Ti_{90}$	NH_3	140	230	510/ 97.6
	LPG	135	290	490/96.1
	H_2-LPG	120	150	470/ 98.0
$Co_{0.01}V_{0.99}W_9Ti_{90}$	NH_3	135	210	415/ 98.0
	LPG	145	190	375/96.3
	H_2-LPG	60	130	310/ 99.8
$Ce_{0.01}V_{0.99}W_9Ti_{90}$	NH_3	110	250	460/ 98.0
	LPG	145	260	530/97.5
	H_2-LPG	95	190	480/98.5

The wet impregnation catalyst using Co as promoter denoted by $Co_{0.01}V_{0.99}W_9Ti_{90}$, showed the best performance compared over $Ce_{0.01}V_{0.99}W_9Ti_{90}$ and $V_1W_9Ti_{90}$ (Table 1), showed its best activity 99.8% NO reduction at 310°C.

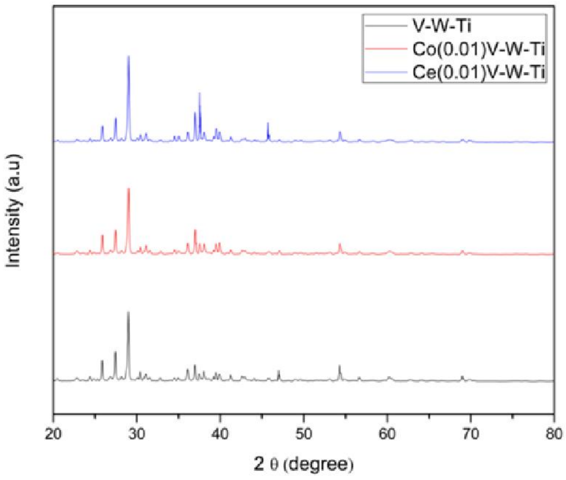

Fig. 4. XRD patterns of $V_1W_9Ti_{90}$, $Co_{0.01}V_{0.99}W_9Ti_{90}$, and $Ce_{0.01}V_{0.99}W_9Ti_{90}$

Catalyst Characterization

X-ray diffraction (XRD): X-Ray diffractogram of the three catalysts (V-W-Ti, Co-V-W-Ti and Ce-V-W-Ti) were confirmed by wide-angle XRD. XRD studies were carried out to identify the phases of the catalyst samples synthesized by coprecipitation method is shown in Fig. 1. The characteristics reflections showed diffraction peaks at 2θ= 28.987°, 27.425°, 25.827°, 36.926°, 36.103°, and 38.014° could be primarily attributed to a spinel structure JCPDS card no. #32-0297 ascribed/ corresponds to the (200), (111), (311), (440), (511), (220), (400), (222) and (422) phase structure of $MnCo_2O_4$, respectively. These diffraction peaks indicated the presence of V_9O_{17} crystallites. These diffractographs noticed diffraction peaks with lowering intensity by adding promoters Ce to less while Co to greater extent indicated the presence of nano-crystallites. The sharp peaks in Catalyst X-ray crystallograph indicate relatively crystalline nature of the catalyst and formation of average crystallites size of 120.2 Å. The diffraction peaks correspond to [PDF#85-1514] the catalyst can be observed, and to better understand the phase transformation, diffractograms of catalysts is incorporated in Fig. 4.

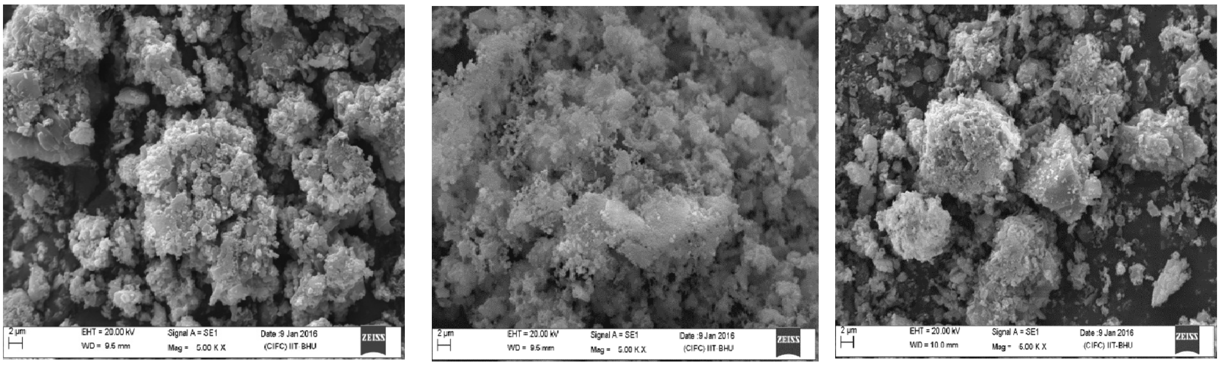

Fig. 5. SEM image of (a) $V_1W_9Ti_{90}$;(b) $Co_{0.01}V_{0.99}W_9Ti_{90}$;(c) $Ce_{0.01}V_{0.99}W_9Ti_{90}$;

Table 3. Weight % and atomic % (EDX elemental data) for$V_1W_9Ti_{90}$, $Co_{0.01}V_{0.99}W_9Ti_{90}$, $Ce_{0.01}V_{0.99}W_9Ti_{90}$

	$V_1W_9Ti_{90}$		$Co_{0.01}V_{0.99}W_9Ti_{90}$		$Ce_{0.01}V_{0.99}W_9Ti_{90}$	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
O K	62.89	85.33	71.76	89.3	52.6	79.82
Ti K	29.78	13.49	23.88	9.92	36.24	18.37
V K	1.02	0.43	0.84	0.33	0.79	0.38
W M	6.32	0.75	0.3	0.1	8.85	0.26
Ce L/ Co K	-	-	3.23	0.35	1.53	1.17
Total	100		100		100	

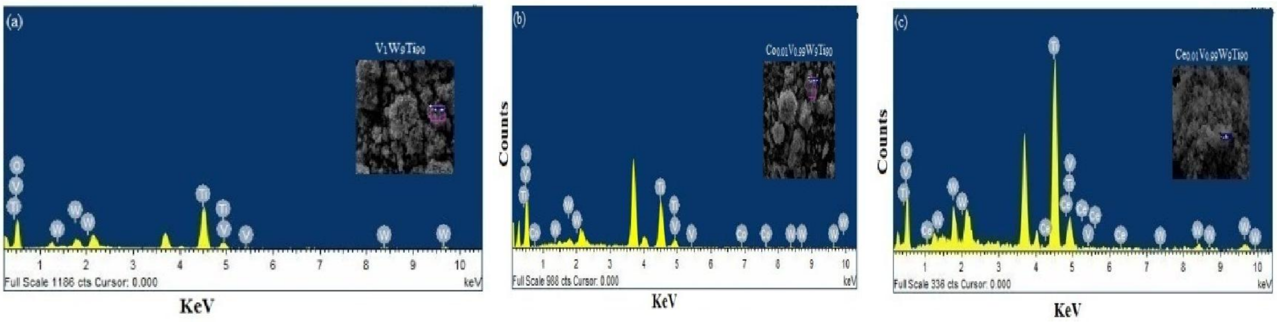

Fig. 6. EDX spectrum and elemental micrographs of (a) $V_1W_9Ti_{90}$;(b) $Co_{0.01}V_{0.99}W_9Ti_{90}$; (c) $Ce_{0.01}V_{0.99}W_9Ti_{90}$

Scanning Electron Micrographs (SEM)

SEM micrographs showed the morphology of all three catalysts as shown in Fig. 5. The SEM micrograph images of respective catalysts are composed of the diverse, discrete and disperse irregular particles having different microstructures and non-uniform size distribution of catalyst particles. But the particle structure of V-W-Ti (Co) is somewhat hazy structure compared to other two. This could be the reason for its exceptionally high low temperature NO reduction capacity and may be due to considerable effect of its particle size and morphology of the catalyst. The micrographs of these three catalysts showed clearly differences in the morphology of these three catalysts. The granular particles calculated by "Image J software" range between 0.96 and 11.59 nm. The particles shown in SEM micrograph comprised grains of course, fine and finest sizes. In the meantime particle size of $Co_{0.01}V_{0.99}W_9Ti_{90}$ and $Ce_{0.01}V_{0.99}W_9Ti_{90}$was a little smaller than that of VWTi, indicating that Co and Ce doping could somewhat decrease the particle size of the catalyst.

Energy Dispersive X-ray (EDX)

The elemental compositions of the three catalysts were examined by energy dispersive X-ray (EDX) measurements. (EDX) results from different regions of micrographs depicts that all the samples were pure due to presence of O, Ti, V, W, Ce and Co peaks and no other element present in the spectra as shown in Fig. 6. EDX spectrum of the $Co_{0.1}V_{0.9}W_9Ti_{90}$ sample gives signal peaks of Co, V, W, Ti and O elements with their respective Co/V ratio and Ce/V ratio in Table 3.

Conclusion

Co doped catalysts are accountable for maximum NO reduction over $V_1W_9Ti_{90}$ catalytic active site. All the catalysts prepared by wet impregnation method shows appreciably good performance for the reduction of NO emissions whether in presence or absence of hydrogen. Impregnation of 0.1 mol% Co on gives 99.8% NO conversion but the hydrogen effect in observed so it is beneficial to run the experiment without H_2. $Co_{0.1}V_{0.9}W_9Ti_{90}$ catalyst shows better NO emission control than other five catalysts at comparable operating parameters. H_2-LPG-SCR of NO, using LPG as a reductant used over $Co_{0.1}V_{0.9}W_9Ti_{90}$ catalyst for first time. Promoters help to improve the activity of the catalyst. As a result of combination of high activity catalyst and apposite reductant, NO conversion is achieved at relatively low temperature in V-W-Ti catalyst operating range. Therefore, it can be concluded that $Co_{0.1}V_{0.9}W_9Ti_{90}$ catalyst has the better potential to achieve the goal of NO emission standard from diesel and lean burn vehicles' exhaust using H_2-LPG SCR.

Acknowledgments

The authors gratefully acknowledge the support characterization given to the research work by Department of Chemical Engineering And Technology, IIT (BHU), Varanasi, India is duly acknowledged for various characterization facilities of the catalysts.

REFERENCES

Alemany, L. J., Lietti, L. and Ferlazzo, N. J. 1995. Reactivity and Physicochemical Characterization of V_2O_5-WO_3/TiO_2 De-NO_x Catalysts, *Journal of Catalysis,* Vol. 155, No. 19, pp. 117-130

Birkhold, F., U. Meingast, P. Wassermann, and O. Deutschmann. 2007. Modeling and simulation of the injection of urea-water-solution for automotive SCR DeNOx-systems. *Applied Catalysis B Environmental*, Vol. 70, pp. 119-127

Cai, X., Sun, W., Xu, C., Cao, L. and Yang, J. 2016. Highly selective catalytic reduction of NO via SO_2/ H_2O-tolerant spinel catalysts at low temperature, *Environmental Science Pollution Research International*, Vol. 18, pp. 18609-18620

Chen, L., Li, J. and Ge, M. 2009. Promotional Effect of Ce-doped V_2O_5-WO_3/TiO_2 with Low Vanadium Loadings for Selective Catalytic Reduction of NOx by NH_3, *Journal Physical Chemistry C*, Vol. 113, No. 50, pp. 21177-21184

Chen, L., Li, J. and Ge, M. 2011. The poisoning effect of alkali metals doping over nano V_2O5 – WO_3/ TiO_2 catalysts on selective catalytic reduction of NOx by NH_3, *Chemical Engineering Journal*, Vol. 170, No. 2-3, pp. 531–537

Ghude, S. D., Kulkarni, S. H., Jena, C., Gabriele, G. P., Beig, G. and Fadnavis, S. 2013. Application of satellite observations for identifying regions of dominant sources of nitrogen oxides over the Indian Subcontinent, *Journal of Geophysical Research: Atmospheres*, Vol. 118, pp. 1075–1089.

Grossale, A. I. Nova, and E. Tronconi, 2008. Study of a Fe–zeolite-based sys- tem as NH_3-SCR catalyst for diesel exhaust after treatment, *Catalysis Today*, Vol. 136, pp. 18–27

Hamada, H. and Haneda, M. 2012. A review of selective catalytic reduction of nitrogen oxides with hydrogen and carbon monoxide, *Applied Catalysis A, General,* Vol. 421-422, pp. 1–13

Jabłońska, M. and Palkovits, R. 2016. Nitrogen oxide removal over hydrotalcite-derived mixed metal oxides, *Catalysis Science Technology,* Vol. 6, pp. 49-72

Kamolphop, U., Taylor, S.F.R., Breen, J. P., Burch, R., Delgado, J. J., Hardacre, S. C., Hengrasmee, S. and S. L. James. 2011. Low-Temperature Selective Catalytic Reduction (SCR) of NO_x with *n*-Octane Using Solvent-Free Mechanochemically Prepared Ag/Al_2O_3 Catalysts, *ACS Catalysis*, Vol. 1, pp. 1257–1262

Kim, S. S. and Hong, S. C. 2010. Relationship between the surface characteristics of Pt catalyst and catalytic performance on the H_2-SCR, *Journal of Industrial and Engineering Chemistry*, Vol. 16, pp. 992–996

Klingstedt, F., Eranen, K., Lindfors, L., Andersson, S., Cider, L. and Landberg, 2004. A highly active Ag/alumina catalytic converter for continuous HC-SCR during lean-burn conditions: from laboratory to full-scale vehicle tests, *Topics in Catalysis*, Vol. 30-31, pp. 27-30

Korhonen, S. T., Beale, A. M., Newton, M. A. and Weckhuysen, B. M. 2011. New Insights into the Active Surface Species of Silver Alumina Catalysts in the Selective Catalytic Reduction of NO, *Journal Physical Chemistry C,* Vol. 115, pp. 885–896

Liu, C., Shi, J., Gao, C. and Niu, C. 2016. Manganese oxide-based catalysts for low-temperature selective catalytic reduction of NO x with NH 3: A review, *Applied Catalysis A General,* Vol. 522, pp. 54–69.

Long, R. Q. and Yang, R. T. 2002. Selective Catalytic Oxidation of Ammonia to Nitrogen over Fe_2O_3–TiO_2Prepared with a Sol–Gel Method, *Journal of Catalysis*, Vol. 207, pp. 158-165

Machida, M., Ikeda, S., Kurogi, D. and Kijima, T. 2001. Low temperature catalytic NOx–H_2 reactions over Pt/TiO_2-ZrO_2 in an excess oxygen, *Applied Catalysis B Environmental*, Vol. 35, pp. 107–116

Obalová, L., Karásková, K., Wach, A., Kustrowski, P. and K. Mamulová-kutláková, 2013. Alkali metals as promoters in Co–Mn–Al mixed oxide for N_2O decomposition. *Applied Catalysis A,* Vol. 462-463, pp. 227–235

Olympiou, G. G. and Efstathiou, A. M. 2011. Industrial NOx control via H_2-SCR on a novel supported-Pt nanocatalyst. *Chemical Engineering Journal*, Vol. 170, pp. 424–432

Prasad, R. and Rattan, G. 2009. Design of a Compact and Versatile Bench Scale Tubular Reactor. *Bulletin of Chemical Reaction Engineering and Catalysis*, Vol. 4, No. 1, pp. 5-9

Qi, G. and Yang, R. T. 2013. Performance and kinetics study for low-temperature SCR of NO with NH_3over MnO_x–CeO_2 catalyst. *Journal of Catalysis*, Vol. 217, pp. 434-441

Ramis, G., Yi, L. and Busca, G. 1995. Adsorption, Activation, and Oxidation of Ammonia over SCR Catalysts, *Journal of Catalysis*, Vol. 157, pp. 523-535

Reddy, B. M. and Khan, A. 2003. Structural Characterization of CeO_2-TiO_2 and V_2O_5 / CeO_2-TiO_2 Catalysts by Raman and XPS Techniques. *Journal Physical Chemistry B,* Vol. 107, pp. 5162–5167

Schneider, H., Maciejewski, M. and Kohler, K. 1995. Chromia Supported on Titania: VI. Properties of Different Chromium Oxide Phases in the Catalytic Reduction of NO by NH_3 Studied by *in Situ* Diffuse Reflectance FTIR Spectroscopy, *Journal of Catalysis*, Vol. 157, pp. 312-320

Smirniotis, P. G., Sreekanth, P. M. and Pena, D. A. 2006. Manganese Oxide Catalysts Supported on TiO_2, Al_2O_3, and SiO_2:A Comparison for Low-Temperature SCR of NO with NH_3, *Industrial and Engineering Chemistry Research,* Vol. 45, pp. 6436-6443

Wang, X., Wen, W., Su, Y. and Wang, R. 2015. RSC Advances In fluence of transition metals (M ¼ Co , Fe and Mn) on ordered mesoporous CuM / CeO_2 catalysts and with H_2. *RSC Advances,* Vol. 5, pp. 63135–63141

Yang, X., Zhu, H., Yang, L., Long, X. and Yuan, W. 2013. A Study on the Reduction of $[Fe(III)\text{-}EDTA]^-$ Catalyzed with Activated Carbon in a Fixed-Bed, *Environmental Progress Sustainable Energy*, Vol. 32, No. 2, pp. 206–212

****