Research Article

Studies on H₂-Assisted Liquefied Petroleum Gas Reduction of NO over Ag/Al₂O₃ Catalyst

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Abstract

Hydrocarbon-Selective catalytic reduction (HC-SCR) is one of the potential methods to remove NO_x emissions from diesel engine, lean burn petrol engines and natural gas engines exhaust. Ag/Al_2O_3 is a good catalyst for HC-SCR of NO_x under lean-burn conditions. Further, addition of small amount of H_2 is effective for enhancing HC-SCR activity. This effect is unique to silver and to specific Ag/support combinations, namely, $Ag/\gamma\text{-}Al_2O_3$. Various HC reductants, such as: octane, decane, dodecane and propane, have been reported in the literatures. Only a single study on LPG as a reductant over Cu-ZSM catalyst was reported. There was no work reported on H_2 assisted LPG over Ag/Al_2O_3 catalyst. Thus, this gap in the literature is filled with the present investigation of NO reduction over 2 wt.% Ag/Al_2O_3 catalyst using LPG reductant. The fresh and used catalyst was characterized by various techniques like low temperature N_2-adsorption, XRD, XPS and SEM. There was practically no change in the characteristics of the fresh and used catalyst. Two different reductants of CO and LPG were compared for SCR of NO over the catalyst without and with H_2-assisted. The experiments were performed in a fixed bed tubular flow reactor under the following conditions: 100mg catalyst; 0.13% NO, 2.5% LPG/CO, 1% H_2, 10% O_2, rest Ar; total flow rate 60 mL/min; temperature ambient 400 ºC and pressure 1 atm. Around 100% conversion of NO was achieved using LPG reductant. Light off temperature of NO reduction significantly reduced by H_2assisted LPG reductant. The maximum conversion of NO with CO was limited to 35.15% at temperature of 224 ºC and above. Whereas, 97.79 % NO conversion was achieved at 365 ºC with LPG reductant. While, the maximum conversions with H_2-LPG and H_2-CO reductants were 100 and 99.46% at 117 and 220 ºC, respectively. Therefore, H_2-LPG-SCR of NO_x over 2 wt.% Ag/Al_2O_3 catalyst system can be used to get 100% reduction at low temperature. Copyright © 2018 BCREC Group. All rights reserved

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1. Introduction

Selective catalytic reduction (SCR) is a potential method to remove NO_x under excess oxygen conditions such as diesel engine exhausts and lean burn engines. The two main aspects of SCR are reducing agent and NO_x reduction catalyst. Urea and ammonia are most exten-

sively used reductants. However, urea-SCR technology has serious drawbacks, such as an additional urea tank to be refilled periodically, heated to avoid freezing of the urea solution (urea-SCR) [1], and formation of high molecular weight products. Ergo, now a day hydrocarbons (HC) like those typically present in fuel mixtures are used as a reductant, such as: octane, decane, dodecane and propane [2-4], etc. Among the catalyst for NO_x reduction most extensively researched HC-SCR of NO_x catalysts are Ag/Al_2O_3. It is amongst the most active and se-

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lective catalyst in both laboratory and full-scale tests [5,6]. It has become clear that Ag/Al_2O_3 catalysts have several key advantages over other potential diesel-SCR catalysts, i.e. Cu-ZSM5 and Pt/Al_2O_3. Such advantages include low activity for SO_2 oxidation, relatively high thermal and hydrothermal durability (compared to Cu-ZSM5) and high selectivity to N_2 (contrasting Pt-based catalysts which form considerable quantities of N_2O) [7,8]. Further, addition of minute amount of H_2 to the reductant leads to a significant increase in NO_x reduction efficiency in presence of Ag/Al_2O_3 catalyst. This effect is unique to silver and to specific Ag/support combinations, namely Ag/γ-Al_2O_3 and Ag/MFI [2,9].

The role of each silver site in Ag/Al_2O_3 catalyst is much discussed topic leading to several articles [10-13], it is generally accepted that metallic silver has an oxidizing function and is thus responsible for activation of HC and NO_x. Small silver clusters and oxidized silver have been proposed to activate the NO_x reduction activity by partially oxidizing the reductant and promoting surface nitrate formation. Shimizu and Satsuma have summarized various silver states as active sites in their review and references therein [14]. The proportion of small silver clusters and metallic silver depends much on the silver loading and preparation technique. With impregnation methods, high silver loading tends to produce more metallic silver while low silver loading gives a higher proportion of small clusters of silver [15]. Sol-gel methods produce catalysts containing small silver clusters and oxidized silver which are more finely distributed in the alumina matrix [16,17].

One of the most challenging part in HC-SCR over Ag/Al_2O_3 catalysts is to understand the reaction mechanism of NO_x reduction, which is particularly complicated by the nature of hydrocarbons used that contribute to the formation of a number of intermediates (both spectators and active intermediates) during reaction. Several literature reports have addressed mechanistic aspects of NO_x reduction over Ag/Al_2O_3 [18-21]. Generally, the first step of HC-SCR is activation of NO and HC by O_2. NO and O_2 form NO_x surface species (nitrates and nitrites). Strongly adsorbed nitrate is known to self-inhibit the NO_x reduction at low temperature [22,23]. For activation of HC, the O_2 partially oxidizes the HC to form oxygenated HC surface components. Although the formation of oxygenated HC is generally agreed to occur, however, the structure and role of oxygenated HC surface compounds remains a subject of de-

bate in the literature [24].

Addition of hydrogen promotes the following reactions over Ag/Al_2O_3: (1) oxidation of NO to nitrate; (2) oxidation of NO to NO_2; (3) partial oxidation of C_3H_8 to acetone; and (4) oxidation of acetone with $NO+O_2$ mixture [19,25-27]. Some research groups believed that the catalytic activity was promoted by the reductive activation of O_2 with H_2 and the production of moderately agglomerated $Ag_{\delta+n}$ clusters on the catalyst surface [28]. Wichterlova and co-workers [29] proposed that hydrogen itself participates directly in the reaction mechanism. Similarly, Breen and co-workers [29] also investigated that "hydrogen effect" is due to a chemical effect and not the result of a change in the structure of the active site. Shibata et al. [30] claim that the rate of NO_x reduction in the SCR reaction is directly dependent on the rate of partial oxidation of the hydrocarbon to surface acetate and that hydrogen has a remarkable effect in promoting this oxidation reaction.

Wang *et al*. [31] studied SCR of NO_x over various trace noble metals (Pt, Au, or Pd) co-impregnated with Ag/Al_2O_3 catalysts and found that addition of small quantity of Pd to Ag/Al_2O_3 enhances NO_x reduction efficiency. D'Agostino *et al*. [32] have studied the SCR of NO_x in the presence of various reducing agents, namely toluene, n-octane and ethanol, over Ag/Al_2O_3 prepared by standard wet impregnation. In this paper they described a simple approach to characterizing the interaction energy of water and reducing agent so as to aid the selection of reducing agent and catalyst to be used in SCR conversions and found that reducing agents with weaker strength of surface interaction relative to water, such as hydrocarbons, show poorer activity compared to reducing agents with stronger strength of interaction, such as ethanol. Yu *et al*. [33] reported that NO_x reduction by hydrocarbons containing two- or three-carbon atoms was clearly promoted by H_2 at low temperatures, while this promotion effect of H_2 did not occur during the CH_4-SCR over Ag/Al_2O_3.

Therefore, in the present study LPG consisting ~72% C_3H_8 was used as a reductant. The potential use of LPG as reducing agent in the SCR of NO_x 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 [34]. Several advantageous features of LPG such as economical, portable, gaseous nature and readily available around the globe make it possible choice of lean de-NO_x reductant over gasoline and diesel or other HC reductants. However, there is very

limited literature is available for the use of liquefied petroleum gas (LPG) as a reductant [35].

Keeping in view the advantages of LPG and that fact that there is very limited literature available for the use of LPG as a reductant in SCR of NO_x, the present investigation was undertaken to evaluate LPG-SCR of lean NO_x over Ag/Al_2O_3 catalyst. To create a better understanding of the effect of reductants as well as H_2 addition to the reductant, CO and LPG with and without H_2 was also investigated over the Ag/Al_2O_3 catalysts.

2. Materials and Method

2.1 Catalyst preparation

The Ag/Al_2O_3 catalyst containing 2 wt.% Ag was prepared by wet-impregnation of commercial γ-Al_2O_3 (Alfa Aesar, surface area 255 $m^2.g^{-1}$) with an aqueous solution of $AgNO_3$ [36]. The precursor solution of the catalyst was dried overnight at 110 °C and calcined at 500 °C for 1 h.

2.2 Catalyst characterization

The 2 wt.% Ag/Al_2O_3 catalyst was characterized before and after the activity measurements by following techniques:

2.2.1 Textural characterization

BET surface area of the catalysts was measured by low temperature nitrogen adsorption at

Figure 1. Experimental setup for SCR of NO over Ag/Al_2O_3 catalysts: 1. NO cylinder, 2. Air cylinder, 3. Ar cylinder, 4. Reductant (H_2, LPG, CO) cylinder, 5. Digital gas flow meter, 6. Digital gas flow meter, 7. Hg safety device, 8. Moisture trap, 9. Reactor, 10. Split open furnace, 11. Condenser, 12. Microprocessor temperature controller, 13. Thermocouple, 14. Thermowell, 15. Chemiluminescence NO/ NO_x analyzer, 16. Gas chromatograph

-196 °C using a Micromeritics ASAP 2020 analyzer. Samples were degassed at 300 °C under vacuum prior to the measurement. The calculation was performed using the adsorption data in the relative pressure (p/p_o) range from 0.05 to 0.30, and the total volumes were determined from the amounts adsorbed at relative pressure, $p/p_o = 0.99$. The pore size distribution was calculated based on the desorption curve of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. The average pore diameter was defined as the position of the maximum in the pore-size distribution curve.

2.2.2 X-ray diffraction (XRD)

XRD measurements were conducted using a Rigaku Miniex DMAX-B diffractometer with a Cu-Kα radiation source, operated at 40 kV and 100 mA. Patterns were recorded in the θ range from 20° to 90° at 4 °/minute. The diffraction patterns have been indexed by comparison with the JCPDF files.

2.2.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS was performed on an Amicus scanning Auger microprobe using Mg-Ka X-ray source (h_c = 1253.6 eV) at a base pressure of 3×10^{-8} mbar operated at 120 W. The binding energies were calibrated using C 1s peak of contaminant carbon (BE = 284.6 eV) as standard, and quoted with a precision of ±0.2 eV. The collected data were analyzed using a nonlinear Shirley-type background. Atomic concentrations were evaluated by normalizing peak areas to the Scofield sensitivity factors.

2.2.4 Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEM) were recorded on Zeiss EVO 18 scanning electron microscope (SEM) instrument. An accelerating voltage of 15 kV and magnification of 1000X was applied.

2.3 Catalyst activity measurement

SCR of NO experiments were performed in a tubular reactor mounted in a split open tube furnace under the following conditions: 100 mg catalyst; gas composition consisting of 1250 ppm NO, 2.5% LPG/CO, 1% H_2, 10% O_2, rest Ar; total gas flow rate 60 mL/min; temperature from ambient to 400 °C and pressure 1 atm. The experimental setup used for the catalytic activity measurement is shown in Figure 1. It can be divided into following sections: feeding system consisting of gas cylinders and digital
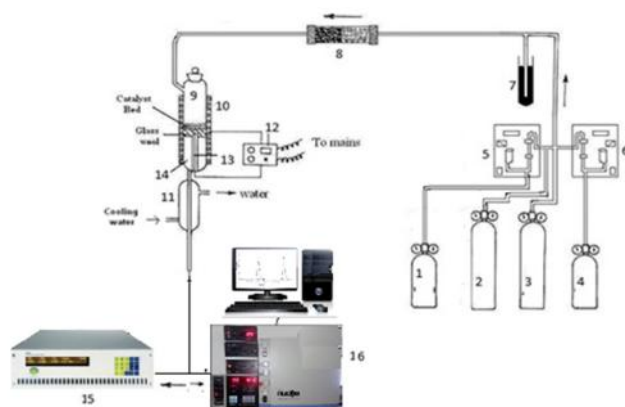
flow meters, tubular fixed bed reactor in split open furnace.

The compositions of inlet and outlet gases were measured with the help of an online gas chromatograph (Nucon, series-5765) and NO analyzer (Eco Physics CLD 62 chemiluminescence NO/NO_x). The CO, CO_2, and N_2 concentrations were measured by GC equipped with porapack Q-column/molecular sieve 5-A, methanizer, and FID/TCD detector. The temperature of the catalyst bed was measured using a K-type thermocouple. The measurement was done at steady state condition. The percent conversion of NO and CO was calculated by Equations 1 and 2, respectively.
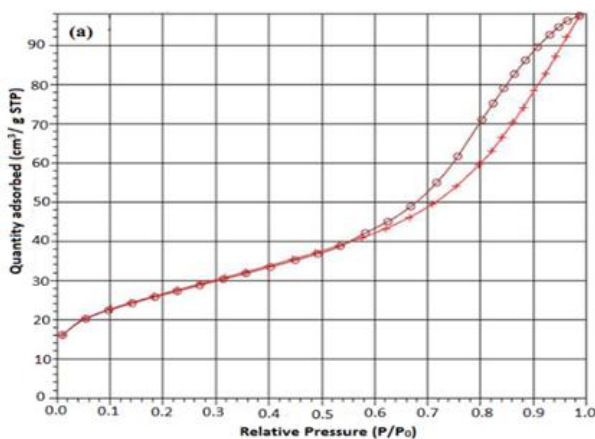
$$NO_{Conversion}\ (\%) = \frac{[NO_{inlet}] - [NO_{outlet}]}{[NO_{inlet}]} x100 \qquad (1)$$

$$CO_{Conversion}\ (\%) = \frac{[CO_{inlet}] - [CO_{outlet}]}{[CO_{inlet}]} x100 \qquad (2)$$

where, $[NO_{inlet}]$ and $[NO_{outlet}]$ are concentrations of NO at the inlet and outlet of the reactor, respectively. Similarly, $[CO_{inlet}]$ and $[CO_{outlet}]$ are concentrations of CO at the inlet and outlet of the reactor, respectively.

3. Results and Discussion

3.1 Catalyst characterization

3.1.1 Textural properties

The typical isotherms of fresh and used Ag/Al_2O_3 catalyst is shown in Figure 2 and textural properties are shown Table 1. It is of type IV isotherms according to IUPAC classification 1984, exhibit mesoporous pore size. In Ag/Al_2O_3 catalyst hysteresis loops occur at low relative pressures (~0.6) suggesting that catalyst contains cylindrical pores.

3.1.2 X-ray diffraction (XRD)

XRD pattern of $Ag-Al_2O_3$ composite are shown in Figure 3. In XRD patterns of the catalyst much significant, sharper and broad peak of Al_2O_3 was observed at $2\theta = 67.18°$ and $46.22°$. The Ag phase was observed at $2\theta = 37.2°$ which correspond to the (111) lattice planes of metallic Ag, this might because that Ag species on the $Ag-Al_2O_3$ was crystalline phase (JCPDS 04-0783). Significant peak at $2\theta = 32.4°$ indicates presence of Ag_2O (111) phases in the sample (JCPDS 41-1104). The crystallite size of the catalyst was 1.0154 Å determined using Debye-Scherrer equation (Equation 3).
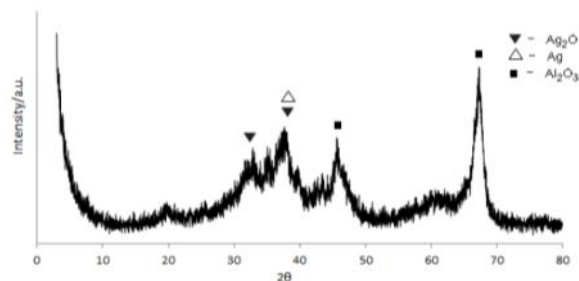
Table 1. Textural characterization of Ag/Al_2O_3 catalyst

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Avg. pore diameter (Å)
Ag/Al_2O_3 (Fresh)	93.13	0.151	64.80
Ag/Al_2O_3 (Used)	90.14	0.139	60.19

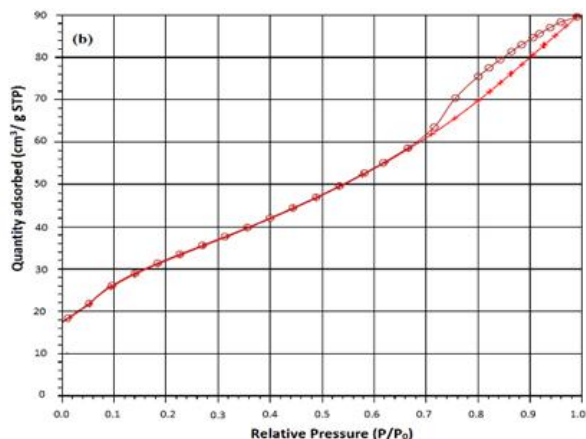**Figure 3.** XRD pattern of 2% Ag/Al_2O_3

Figure 2. Nitrogen adsorption-desorption isotherms on Ag/Al_2O_3: (a) Fresh, (b) Used catalyst

$$d = 0.89 \, \lambda/\beta \cos \theta \qquad (3)$$

where, d is the mean crystallite diameter (Å), λ is the X-ray wave length (1.54056 Å), β is the full width half maximum (FWHM) and θ is the Bragg-angle.

3.1.3 X-Ray Photoelectron Spectroscopy (XPS)

The Ag valence state of the supported Ag was characterized by high-resolution XPS, with the results shown in Figure 4 and summarized in Table 2. As can be seen in figure, the peaks of the Ag $3d_{5/2}$ binding energy for sample appeared at around 368.8-370.3 eV. This suggests that there are two different states of metallic silver on the surface, where the difference in binding energy between the two states can be explained by the difference of the charge effect. As reported by Hammond *et al.* [37] Ag is unusual in that its core-level photoemissions shift to lower binding energy with increasing oxidation state. The binding energy of Ag $3d_{5/2}$ in Ag-Al_2O_3, is 368.0, which are consistent with the binding energies of Ag $3d_{5/2}$ in Ag_2O, according to the literature values of 367.9 eV [37]. In addition, a shoulder at 368.5 eV for Ag/Al_2O_3 might be attributed to Ag^0 (Ag $3d_{5/2}$ = 368.4 eV) on the surface. Binding energy of Al $2p_{3/2}$ in Ag-Al_2O_3 appeared at 77.6 eV which might be binding energy of Al_2O_3.

3.1.4 Scanning Electron Microscopy (SEM)

The SEM micrographs of fresh and used Ag/Al_2O_3 catalysts is presented in Figure 5. The results are shown in the figure at magnification of 500 X. Agglomerates of γ-Al_2O_3 particles can be observed in SEM image of amorphous γ-Al_2O_3 in accordance with its pore volume (0.151 cm^3/g). At lower magnification the pictures reveal that Al_2O_3 clusters are almost regular spherical shape with diameters of 50-150 μm. The black shades surrounding the grey particles represent the fine inter-particles pores. At higher magnification intra-particles pores can be clearly visualized in the micrograph. Fine white and grey crystals clearly indicated that the silver was present in the metallic and oxide form respectively on Al_2O_3 surface at higher magnification. It is clear that silver was present in dispersed sate. Thus, SEM results are also in good agreement with that of the XRD findings. There was no noticeable change in the characteristics of the fresh and used 2 wt.% Ag/Al_2O_3 catalyst under the conditions studied in the present investigation.

Table 2. Binding energy of Ag/Al_2O_3 elements

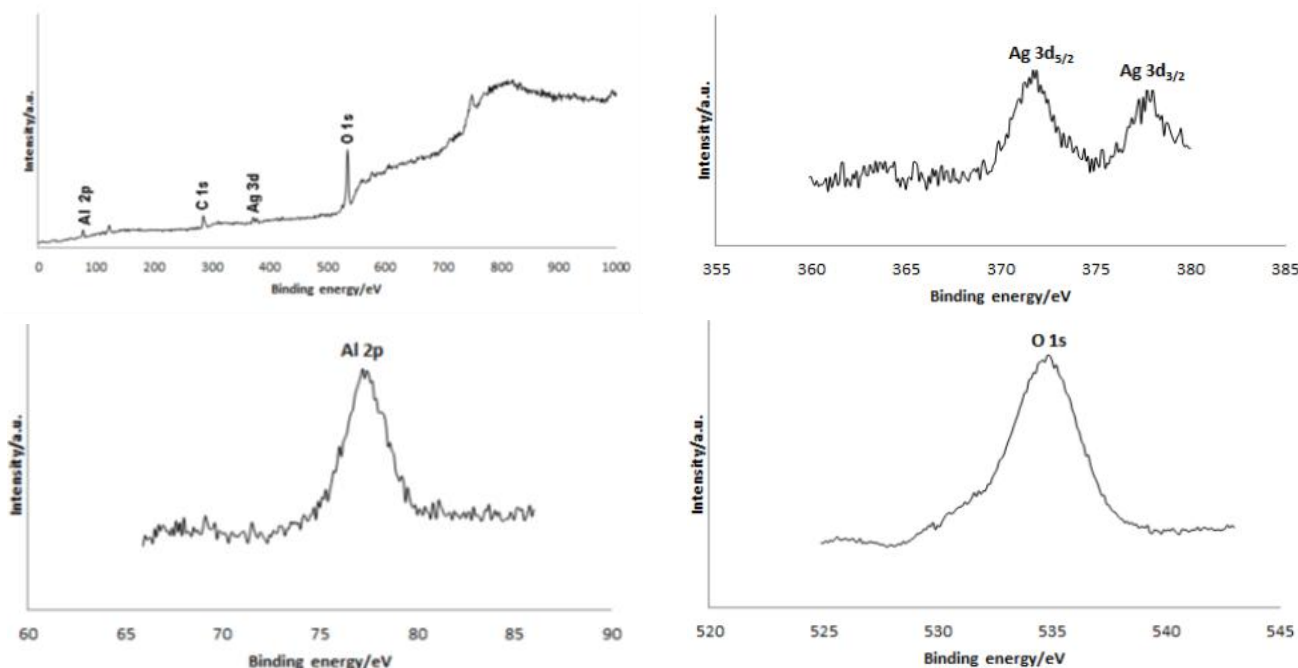| Catalyst	Components	Binding energy (eV)
Ag/Al_2O_3	Ag $3d_{5/2}$	371.9
		377.2
	Al $3d_{5/2}$	77
	O 1s	535

Figure 4. XPS spectra of Ag/Al_2O_3 elements

3.2 Catalyst activity measurement

3.2.1 Effect of CO and LPG reductant over Ag/Al₂O₃

As the feed gas in the present study contained two different reductants over Ag/Al$_2$O$_3$ catalysts, both kind of the reductant might contribute to the overall NO conversion [38]. In order to elucidate the individual effect of each kind of reductants and catalysts on the catalytic performance, first NO conversion over Ag/Al$_2$O$_3$ catalyst with LPG as well as CO was compared. It is very clear from the Figure 6 that the activity of the catalyst was greatly influenced by the type of reductant. The maximum conversion of NO with CO reductant was 35.15%, while this value (97.79 %) is relatively very high in case of LPG reductant. NO conversion with LPG reductant increased to the maximum conversion of 97.79% in two steps. In the first step 30% NO conversion was achieved at 269 ^{o}C. In the second step, with slight increase in temperature, conversion was suddenly in-
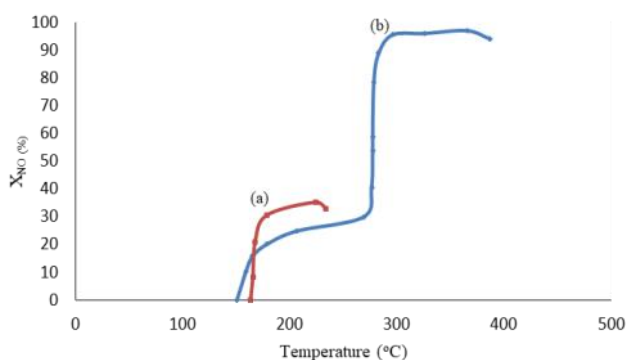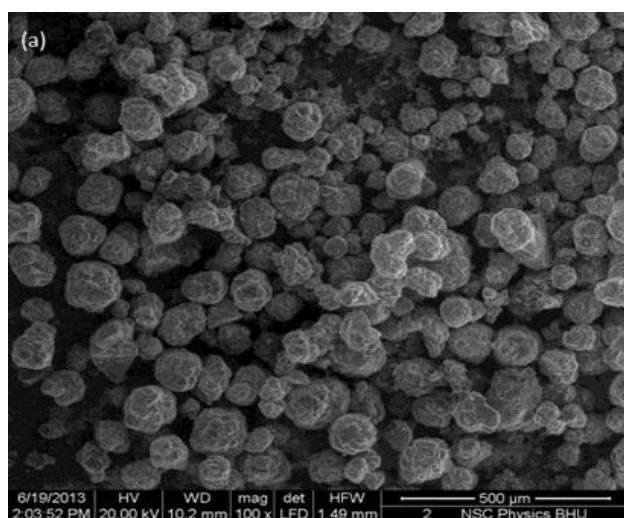

Figure 6. NO conversion over Ag/Al$_2$O$_3$ catalyst with (a) CO and (b) LPG

creased to the steady-state value of 97.79% in the temperature range 296-366 ^{o}C. After 366 ^{o}C NO conversion was decreased. Therefore, it is evident that LPG is better reductant than CO for NO conversion over Ag-Al$_2$O$_3$ catalyst.

3.2.2 Effect of H₂ addition on CO and LPG reductant over Ag/Al₂O₃

Figure 7 shows the NO reduction with CO and LPG reductants over Ag-Al$_2$O$_3$ catalyst in presence and absence of H$_2$. It is clearly observed that the addition of hydrogen in feed stream has remarkable effect on the activity of the catalyst with ~95% reduction below 100 ^{o}C. Though 100% conversion could be achieved with both the reductants but occurs at different temperatures. The maximum conversion of 100% of NO in presence of H$_2$ could be achieved with both the reductant. The temperature range for 100% NO reduction with CO reductant is narrower (108-160 ^{o}C) than LPG reductant. The maximum conversion with CO reductant without H$_2$ was only 35% at 224 ^{o}C, whereas in presence of H$_2$ this value is 100% at far below lower temperature of 108 ^{o}C.

With LPG reductant also 100% NO conversion could be achieved in presence of H$_2$ as well as in absence of H$_2$ at different temperatures (Figure 7). The 100% conversion with LPG reductant in presence of H$_2$ was achieved at far lower temperature (220 ^{o}C) than without H$_2$ at 366 ^{o}C. Reduction of NO with LPG also gives 97% conversion at the temperature 367 ^{o}C but the addition of hydrogen decreases the temperature approximately 150 ^{o}C.

Table 3 summarizes the experimental results for the catalyst tested using CO and LPG as reductant in presence and absence of H$_2$ to
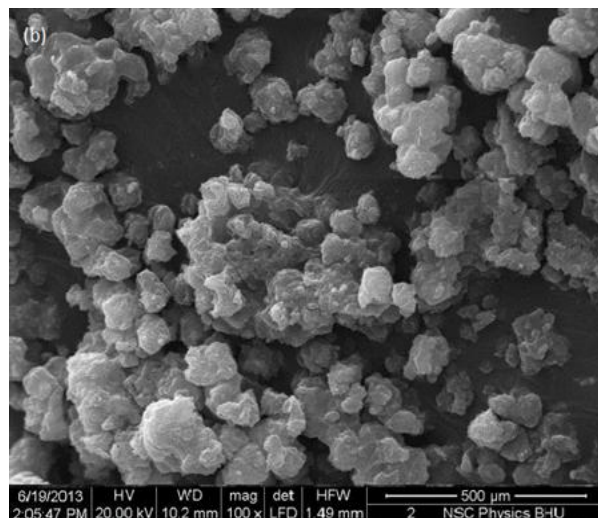

Figure 5. SEM micrographs of Ag/Al$_2$O$_3$ catalyst at different magnifications: a) fresh, b) used

the feed showing characteristic temperatures (T_i and T_{max}) for NO reduction. Complete NO conversion could be achieved specifically in presence of H_2. The table shows that Ag-Al$_2$O$_3$ catalyst initiation (T_i) as well as total NO conversion (T_{max}) occurred at lower temperatures of 60, for which these values were 107 and 304 ^{o}C respectively. Thus, Ag-Al$_2$O$_3$ behaves uniquely for NO reduction in presence of H_2.

The high catalytic performance of Ag/Al$_2$O$_3$ can be explained on the basis of Ag loading and the Ag physical and chemical states. It is reported by several authors that 2 wt.% Ag loading is optimum and contains Ag in the +1 oxidation state [40-42]. The same Ag loading is followed in the present experiment, resulting in formation of Ag$^+$ species as evidenced by XRD and XPS studies. It is reported in literature by Shibata *et al*. [39] that H_2 enhance the rate-determining step and prevents active sites from strongly adsorbed species (e.g. nitrates) at low temperature. H_2 addition results in a decreased activation energy for NO$_x$ reduction. Further, H_2 promotes indirectly the SCR-NO$_x$ through the changes in some states of the active catalyst but H_2 itself is not active as it is neither a reducing agent nor an intermediate species.

4. Conclusions

LPG is a better reductant in comparison to CO for NO reduction over Ag-Al$_2$O$_3$catalyst at low temperature. Addition of H_2 to the LPG, further reduces the NO reduction temperature. With LPG reductant 100% NO conversion can be achieved in presence of H_2 as well as in absence of H_2 but at different temperatures. The 100% conversion with LPG reductant in presence of H_2 was achieved at far lower temperature (117 ^{o}C) than without H_2 (220 ^{o}C). LPG has several advantages over other HCs such as easily available, economic market price and envi-

ronment friendly characteristics. LPG being gas at ambient condition no pump is required to feed it in the SCR unit. There is no noticeable change in the characteristics of the fresh and used 2 wt.% Ag/Al$_2$O$_3$ catalyst under the conditions studied in the present investigation. Therefore, it is proposed that H_2-LPG-SCR of NO$_x$ over Ag/Al$_2$O$_3$ catalyst is a good system for low temperature control of NO$_x$ emissions.

Acknowledgement

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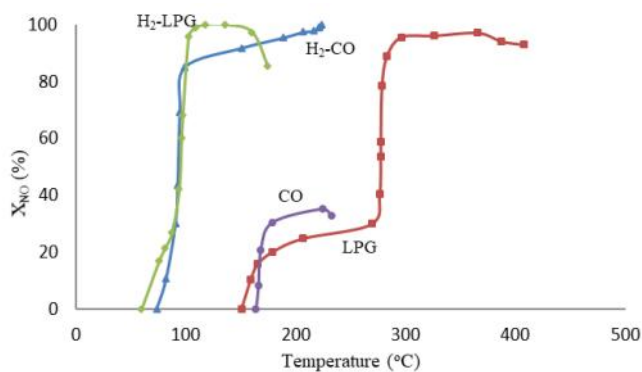

Figure 7. Comparison of with and without H_2-assisted NO-SCR over Ag/Al$_2$O$_3$ catalyst with (♦) H_2-LPG, (▲) H_2-CO, (●) CO and (▪) LPG

Table 3. Characteristic temperatures (T_i and T_{max}) for NO reduction over Ag-Al$_2$O$_3$ catalysts using CO and LPG as reductants with and without H_2-assisted

Reductant / Promoter	NO Reduction (%)	T_i (^{o}C)	T_{max} (^{o}C)
CO	35	163	224
LPG	97	150	365
CO and H_2	99	73	220
LPG and H_2	100	60	117

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