

# DEVELOPMENT OF GREEN Ag/Al<sub>2</sub>O<sub>3</sub> CATALYST BY MECHANOCHEMICAL METHOD FOR LOW TEMPERATURE H<sub>2</sub>-LPG-SCR OF LEAN NO<sub>x</sub>

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## ABSTRACT

Emission regulations for diesel cars are becoming stricter, especially for NO<sub>x</sub> emissions. Various devices are available for NO<sub>x</sub> abatement such as NSCR, EGR, SCR, LNT, etc. But none of the methods is equivocally accepted for 100% NO<sub>x</sub> reduction from diesel exhaust. SCR is a potential method to convert NO<sub>x</sub> to N<sub>2</sub> by reductant under rich-O<sub>2</sub> diesel exhaust. Different types of catalysts including noble metals, zeolite, spinels, hydrotalcite, metal oxides, etc. are found effective under strict conditions for diverse reductants (NH<sub>3</sub>/urea/HC/H<sub>2</sub>, etc.) for SCR of NO<sub>x</sub>. But none of the catalyst-reductant combination came up to be limitation free. Therefore, the present paper aimed to develop a total environmental friendly method to achieve the NO<sub>x</sub> emission standard for diesel and lean-burn gasoline vehicles at low temperature by combining altogether a novel approach. The approach involves H<sub>2</sub>-HC-SCR of lean NO<sub>x</sub> over nano-size Ag/Al<sub>2</sub>O<sub>3</sub> green catalyst using LPG reductant. LPG was chosen a reducing agent as it leads to a strong decrease in the Gibbs free energy values of NO reduction to N<sub>2</sub>. The catalysts were characterized by N<sub>2</sub>-sorption, XRD, FTIR and SEM. The best catalyst among the prepared catalysts showed 100% NO conversion at 195°C.

**Keywords:** Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst, NO Reduction, Reactive Calcination, LPG Reductant

## I. INTRODUCTION

NO<sub>x</sub> reduction for lean burn engines exhaust after-treatment is currently an intense area of research. Recently, the emission regulations for NO<sub>x</sub> from diesel light duty vehicles has been fixed at 80mg km<sup>-1</sup> by the September 2014 Euro-VI regulations as compared to previous 180mg km<sup>-1</sup> corresponding to 2011 Euro-V regulations (Gill, 2012). Various control techniques are available for NO<sub>x</sub> abatement such as NSCR, EGR, SCR, LNT, etc. But none of the methods is equivocally accepted for 100% NO<sub>x</sub> reduction from diesel exhaust. SCR is a potential method to convert NO<sub>x</sub> to N<sub>2</sub> by reductant under rich-O<sub>2</sub> diesel exhaust. Different types of catalysts including noble metals, zeolite, spinels, hydrotalcite, metal oxides, etc. are found effective under strict conditions for diverse reductants (NH<sub>3</sub>/urea/HC/H<sub>2</sub>, etc.). Yet, these catalysts have their own specific limitations and are not sufficiently active below 300°C. It is therefore, imperative to develop a new, green and low cost de-NO<sub>x</sub> catalyst using an apposite reductant effective at low temperature.

Ag/Al<sub>2</sub>O<sub>3</sub> is a unique catalyst reported to be highly active in hydrogen assisted hydrocarbon selective catalytic reduction (H<sub>2</sub>-HC-SCR) of lean NO<sub>x</sub> emissions. It is well known that the silver phase, as well as the performance of the catalyst for lean NO<sub>x</sub> reduction, is sensitive to the method of preparation and amount of silver loading. The recent studies pointed out that silver oxide and metallic silver is favoured as the active phase (Korhonen et al., 2011). Alumina is found to be the support of choice with 2 wt% silver as optimal for wet-impregnated catalysts. However, their lack of activity below 350°C still remains a problem. Selection of an appropriate reductant may act as a good support system with Ag/Al<sub>2</sub>O<sub>3</sub> for NO reduction at low temperature.

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<sub>2</sub> than other reductants (PaÅrvulescu et al. 1998) (Table 1).

**Table 1. Gibbs free energy at 500K for reduction of NO in the presence of various reductants**

Reductant	H <sub>2</sub>	CO	NH <sub>3</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>
-ΔG <sub>r</sub> (kJ/mol)	605.8	646.3	367.5	543.9	603.1	557.7

Methods of catalyst preparation are also an important aspect in order to synthesis the desired catalyst and that too economically. Solvent-free mechano-chemical method of catalyst synthesis is an approach to provide cleaner alternatives to the conventional solution-based methods of preparation. Therefore, in the present work, mechano-chemical technique was used to prepare nano-size 2%Ag/Al<sub>2</sub>O<sub>3</sub> green catalyst using Ag<sub>2</sub>O powder in a planetary ball mill, rather than the conventional multistep solvent-based routes. This technique has the potential to provide more sustainable preparative route to catalysts than the conventional multistep solvent-based routes.

Therefore, the present paper aimed to develop a total environmental friendly method to achieve the NO<sub>x</sub> emission standard for diesel and lean-burn gasoline vehicles at low temperature by combining altogether a novel approach. The approach involves H<sub>2</sub>-HC-SCR of lean NO<sub>x</sub> over nano-size Ag/Al<sub>2</sub>O<sub>3</sub> green catalyst using LPG reductant. 2%Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by 1) impregnation method (Ag<sub>IA</sub>) and 2) mechano-chemical method (Ag<sub>MA</sub>) and both the catalysts were calcined in air at 500°C. Further, the better catalyst was calcined by a novel reactive calcination route at 500°C in a 4.5%CO-air mixture (Prasad and Singh, 2013).

## II. EXPERIMENTAL

### 2.1 Catalyst Preparation

The Ag/Al<sub>2</sub>O<sub>3</sub> catalyst containing 2.0 weight % Ag was prepared by wet-impregnation of commercial γ-Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar, surface area 255 m<sup>2</sup>g<sup>-1</sup>) with an aqueous solution of AgNO<sub>3</sub>. AgNO<sub>3</sub> was dissolved in distilled water, required amount of this solution was slowly added to γ-Al<sub>2</sub>O<sub>3</sub> under vigorous stirring. Excess water was evaporated at 80 °C on a hot plate. The solid mass dried at 110 °C overnight and calcined at 500 °C for 1 h.

Ag/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by ball-milling Ag<sub>2</sub>O as the Ag precursor. Accurately weighed powder of the Ag precursors (Sigma Aldrich) and 2.00 g of γ-Al<sub>2</sub>O<sub>3</sub> (Sigma Aldrich) to obtain a silver loading of 2 wt % were well-mixed by agate mortar and pestle. The resulting physical mixture was placed into a 150 cm<sup>3</sup> grinding jar with

tungsten carbide inside lining. Seven 10-mm-diameter stainless steel grinding balls were used for grinding taking ball: catalyst ratio 10:1 by weight. Milling was performed in a VB ceramic Planetary Ball Mill at a rotation speed of 500 rpm for 15 min. The resulting powders were calcined at either 550 for 2 h in air (Gill, 2012). Further, reactive calcination (RC) method described elsewhere (Prasad and Singh, 2013) in which precursor was calcined in a specific chemically reactive, 4.5% CO-air mixture was also used. The nomenclatures of the catalysts were as follows:

**Table 2. Nomenclature of catalysts**

Catalyst	Preparation method
Ag <sub>MR</sub>	Ball-milled/RC
Ag <sub>MA</sub>	Ball milled/calcined in air
Ag <sub>IA</sub>	Impregnated/calcined in air

## 2.2 Characterisation

Textural characterization of the catalyst samples was done by nitrogen adsorption at -196 °C using Micromeritics ASAP 2020 analyzer. X-ray diffraction (XRD) patterns of the catalysts were collected on 18 kV rotating anode Rigaku powder diffractometer, using CuK $\alpha$  radiation for phase identification of the catalysts. Fourier transform spectroscopy (FTIR) of the prepared catalyst was recorded in the range of 400-4000 cm<sup>-1</sup> on Shimadzu 8400 FTIR spectrometer with KBr pellets at room temperature. In present study, the surface morphology was determined with FEI Quanta 200 scanning electron microscope (SEM) instrument. An accelerating voltage of 30kV and magnification of 1000X was applied.

## 2.3 Catalytic Activity Measurement

The experiments were performed in a fixed bed, tubular reactor under the following conditions: 100 mg catalyst diluted to 1ml with alumina; feed gas 60 ml/min, consisted of 500ppm NO, 1000ppm LPG, 10% O<sub>2</sub>, 1% H<sub>2</sub>, and Ar balance and pressure = 1 atm. The reaction was carried out in the temperature range of ambient to the temperature till 100% NO conversion was attained. The compositions of inlet and outlet gases were measured with the help of NO analyzer (Technovation, series-89).

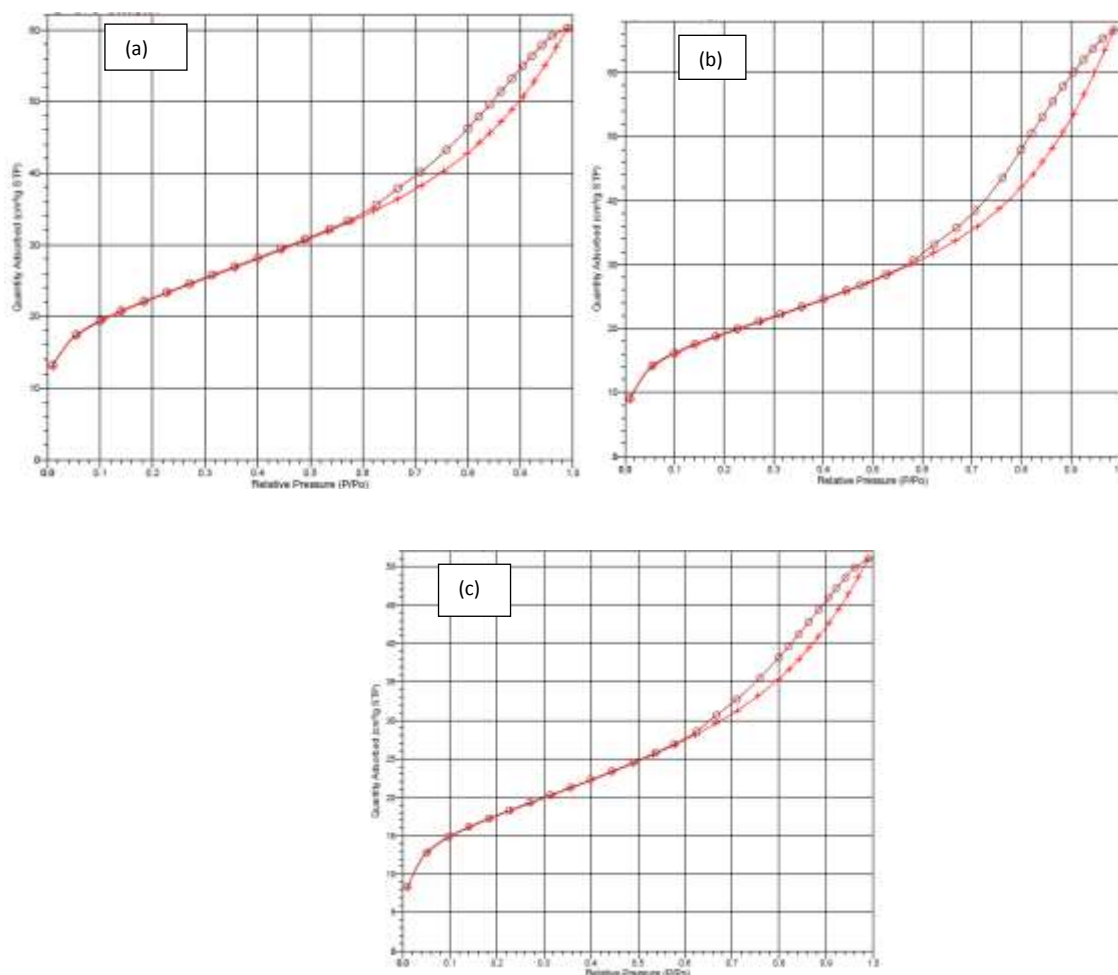
## III. RESULT AND DISCUSSION

### 3.1 Textural Characterization

The BET surface areas of various catalysts are summarized in Table 3. The results show that for all Ag catalyst samples, the specific surface areas are in the range from 60-80 m<sup>2</sup>/g. The Ag<sub>MR</sub> catalyst prepared by ball milling and calcined by RC method exhibited the highest surface area, 79.02 m<sup>2</sup>/g, indicating a favorable interaction between silver species and the support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The mean pore diameter is also quite low for Ag<sub>MR</sub>, 55 Å as compared to rest of the samples. Adsorption and desorption isotherms of nitrogen show that the catalyst samples are mesoporous material (Fig. 1 a,b,c). In mesoporous materials due to larger pores more number of molecules interacts with each other, and they show better catalytic properties (Kyriienko et al., 2013).

**Table 3. Textural Characterization of Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst**

Catalyst	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Aver. pore Diameter (Å)
Ag <sub>MR</sub>	79.02	0.081	55.46
Ag <sub>MA</sub>	68.45	0.089	67.90
Ag <sub>IA</sub>	61.92	0.065	60.65

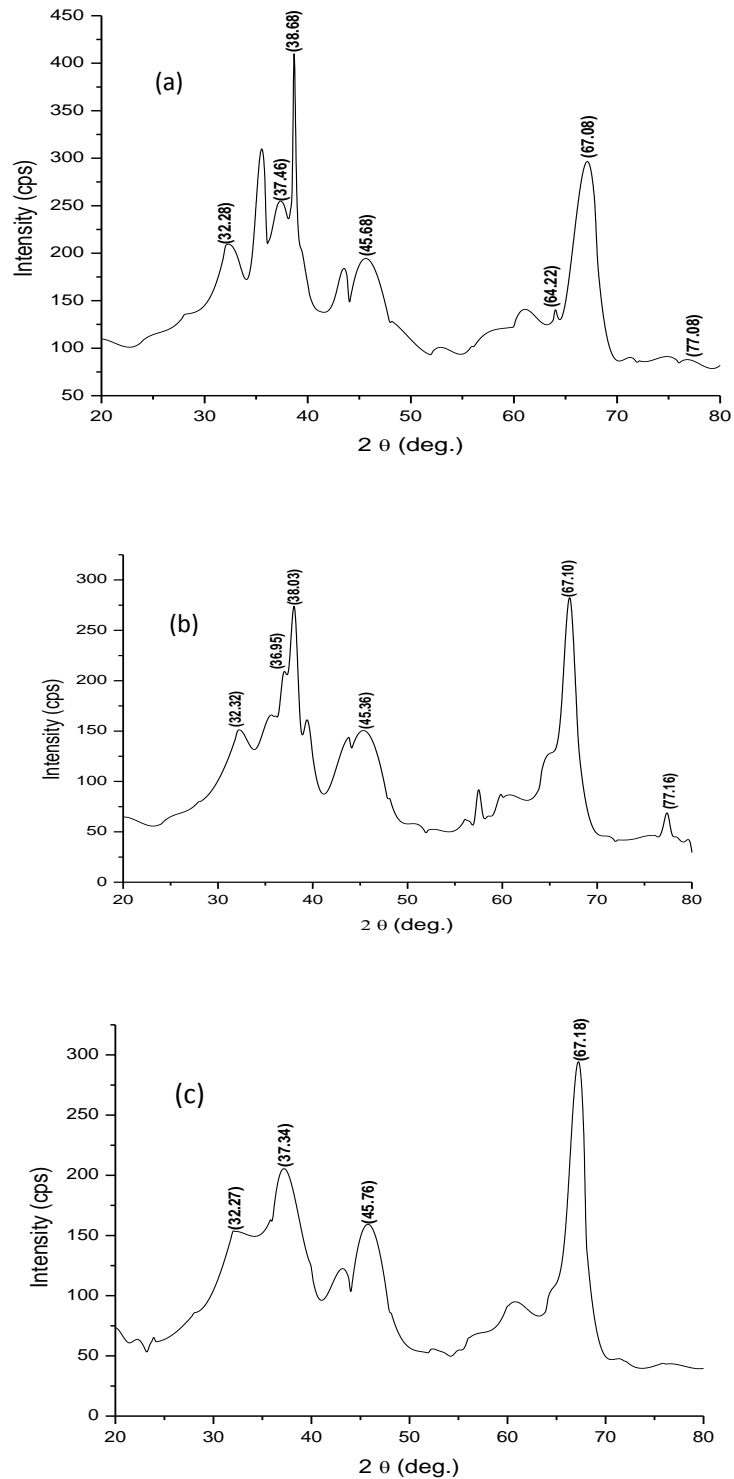


**Fig. 1 Adsorption-desorption curve of (a) Ag<sub>MR</sub> (b) Ag<sub>MA</sub> (c) Ag<sub>IA</sub>**

### 3.2 X-Ray Diffraction Analysis (XRD)

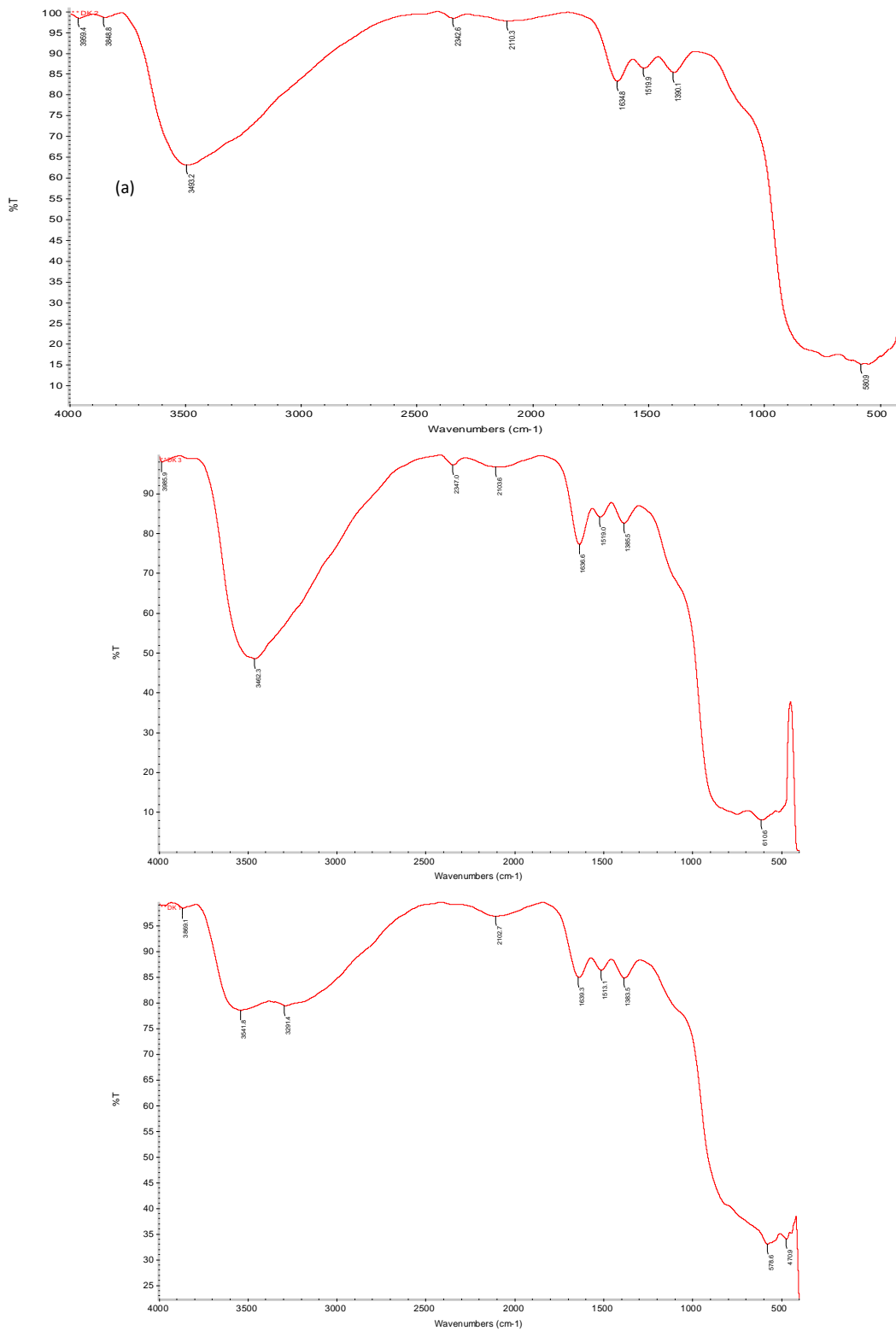
XRD pattern of Ag-Al<sub>2</sub>O<sub>3</sub> composite are shown in fig. 2. In XRD patterns of the catalysts, much significant, sharper and broad peak of alumina based on peaks at  $2\theta \approx 45.8^\circ$  and  $67.18^\circ$  were observed (Zhang et al., 2010). In all the samples weak diffraction lines of metallic silver were found at  $2\theta \approx 37.2^\circ$  whereas peaks at  $2\theta \approx 38.2^\circ$ ,  $77.6^\circ$  were present only in samples Ag<sub>MR</sub> and Ag<sub>MA</sub>. Additional strong peak at  $2\theta \approx 38.1^\circ$  and mild peak at  $2\theta \approx 64.5^\circ$  of metallic silver were observed exclusively in Ag<sub>MR</sub> (JCPDS 04-0783). No silver aluminate lines were detected, this

may be due to the small amount of silver and high dispersion. Significant peak at  $2\theta = 32.4$  indicates presence of  $\text{Ag}_2\text{O}$  phases in all the samples (JCPDS 41-1104) (She and Flytzani-Stephanopoulos, 2006).



**Fig. 2 XRD pattern of (a)  $\text{Ag}_{\text{MR}}$  (b)  $\text{Ag}_{\text{MA}}$  (c)  $\text{Ag}_{\text{IA}}$**

### 3.3 Fourier Transform Infrared Spectroscopy (FTIR)



**Fig. 3 FTIR spectra of (a) Ag<sub>MR</sub> (b) Ag<sub>MA</sub> (c) Ag<sub>IA</sub>**

In the FTIR spectra several peaks appear in the range  $3900\text{-}3000\text{ cm}^{-1}$ , which are owing to OH stretching vibrations (Fig. 3 a,b,c). The OH configurations possess different properties as a consequence of their different net charges, and one property that is influenced is the acidity (Sazama et al. 2005). The peak distribution is similar for all samples investigated. The surface acidity will hence not be the cause for the differences in catalytic performance observed for the different samples.

### 3.4 Scanning Electron Microscopy (SEM)

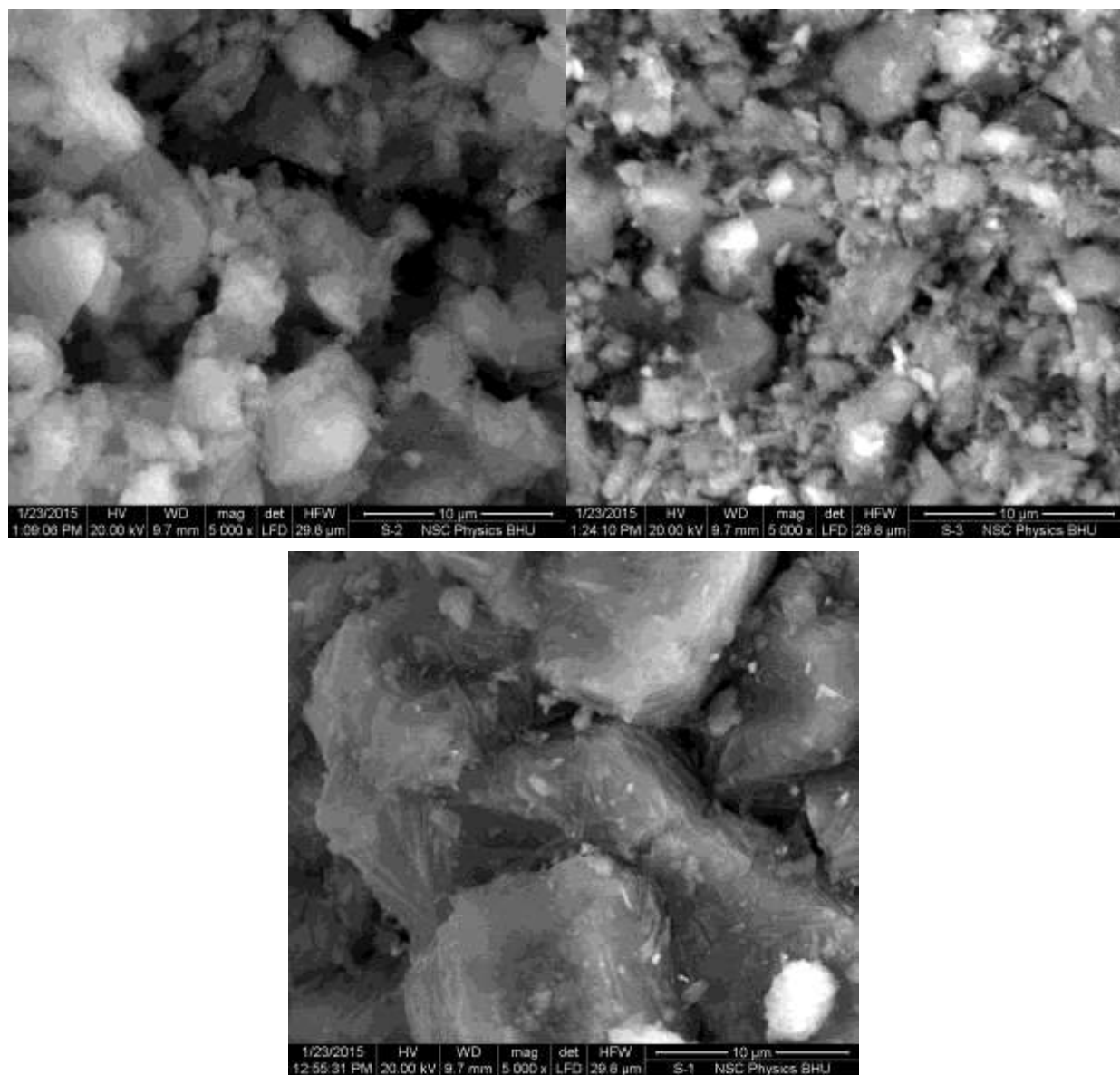
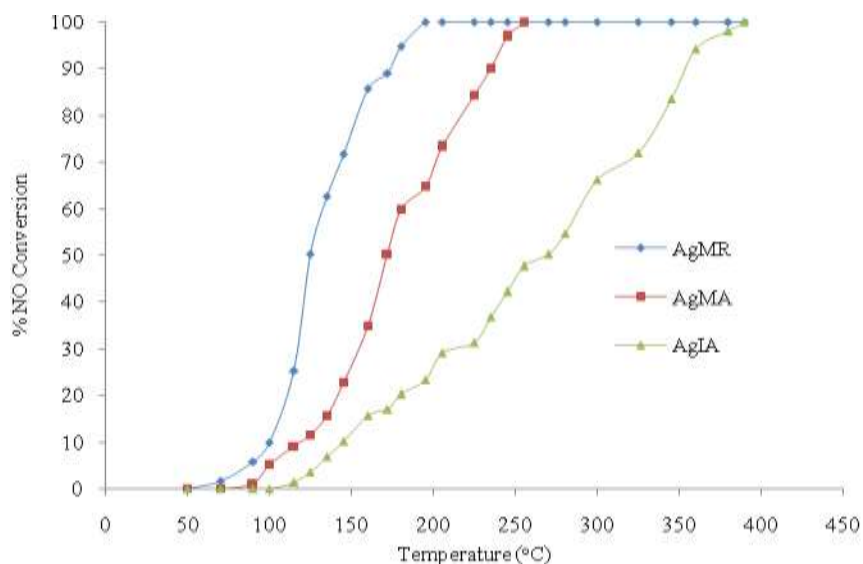


Fig. 4 SEM micrographs of (a) Ag<sub>MR</sub> (b) Ag<sub>MA</sub> (c) Ag<sub>IA</sub>

In SEM micrographs (Fig. 4 a,b,c) it is clearly visible that silver particles are in good contact with the alumina matrix. The silver particles are quite large in the impregnated sample, compared to the ball milled samples. It was also observed that silver particles are visible on the alumina matrix in case of Ag<sub>IA</sub> (Fig. 4c) whereas it is well dispersed in ball milled samples, so one can conclude that silver is uniformly distributed over the surface of Al<sub>2</sub>O<sub>3</sub> in the Ag<sub>MR</sub> and Ag<sub>MA</sub> samples.

### 3.5 Catalytic Activity Measurement



**Fig. 5 Temperature Vs NO conversion over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts**

The ball milled catalyst calcined by reactive calcination denoted by Ag<sub>MR</sub>, showed the best performance compared to Ag<sub>MA</sub> and Ag<sub>IA</sub> (table 4), giving 100% NO conversion at 195°C. The complete NO conversion to N<sub>2</sub> was maintained up to 390°C. The light off temperatures for NO conversion over the catalyst samples are given in table 4.

**Table 4. Light off temperatures of NO over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts**

	T <sub>i</sub> (°C)	T <sub>50</sub> (°C)	T <sub>100</sub> (°C)
Ag <sub>MR</sub>	70	125	195
Ag <sub>MA</sub>	90	172	255
Ag <sub>IA</sub>	115	270	390

It is observed by many authors [Kamolpoph et al. 2011, Korhonen et al., 2011, Ghude et al., 2013] that the NO<sub>x</sub> reduction is not only connected to an optimized silver loading, but also to the nature of the reductants. 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<sub>2</sub> than other reductants. The SCR reaction over Ag-Al<sub>2</sub>O<sub>3</sub> catalysts is



most likely dependent on two factors: the ability to reduce NO<sub>x</sub> to N<sub>2</sub> and to activate (partially oxidize) the reducing agent, i.e. the hydrocarbon (Klingstedt, 2009). Metallic silver supported on alumina is active for the combustion of hydrocarbons and oxidation of NO to NO<sub>2</sub> (Koebel et al., 2000), whereas oxidized silver, present in the form of e.g. silver ions, silver aluminate or oxides, is shown to promote the formation of N<sub>2</sub> during HC-SCR conditions.

This implies that samples active for NO<sub>x</sub> reduction most likely contain silver in metallic and oxidized/ionic state, very finely distributed throughout the alumina matrix. Together, the results from the textural characterisation, XRD and SEM analyses suggest that the Ag<sub>MR</sub> samples contain more non-metallic silver, finely dispersed throughout the alumina matrix compared to the rest of the samples. It is clear that preparation via ball milling combined with reactive calcination facilitates the dispersion of the silver species into the alumina matrix. Whereas, preparation via impregnation results in silver distributed only on the surface of the support, theoretically giving access to all silver deposited on the alumina. However, agglomeration of silver species forming metallic silver reduces the ratio of accessible silver, as the bulk silver does not take part in the HC-SCR reaction. Further, reactive calcination further facilitates dispersion of metal over support, prevents agglomeration of particles as well as preserves active site of the catalyst by averting uncontrolled oxidation.

#### IV. CONCLUSION

Ag/Al<sub>2</sub>O<sub>3</sub> green catalyst has been synthesized by a total environmental friendly approach by planetary ball milling followed by the reactive calcination for the H<sub>2</sub>-HC-SCR of lean NO<sub>x</sub> using LPG as a reductant for the first time. Reactive calcination further helps in improving the activity of the catalyst. As a result of combination of high activity catalyst and apposite reductant, NO<sub>x</sub> conversion is achieved at low temperature. Therefore, it can be concluded that Ag<sub>MR</sub> catalyst has the potential to achieve the goal of NO<sub>x</sub> emission standard from diesel, petrol as well as LPG-fuelled vehicles using H<sub>2</sub>-LPG-SCR. It is hoped that the H<sub>2</sub>-LPG-SCR using Ag/Al<sub>2</sub>O<sub>3</sub> can be considered as a breakthrough NO<sub>x</sub> control technology in favor of the present Urea-SCR.

#### V. ACKNOWLEDGMENTS

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