



# NO<sub>x</sub> storage behavior of BaO in different structural environment in NSR catalysts

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## Abstract

Barium oxide containing catalysts with different compositional and structural features have been prepared by impregnation and sol–gel technique for NO<sub>x</sub> storage reduction (NSR). Barium oxide supported on  $\gamma$ -alumina prepared by impregnation method exhibited better NO<sub>x</sub> storage reduction behavior compared to the catalysts prepared by sol–gel process. Barium oxide containing ceria/zirconia catalysts were also prepared without alumina, which showed lower NO<sub>x</sub> storage compared to alumina supported catalysts. In this case also the catalysts prepared by impregnation displayed better NO<sub>x</sub> storage behavior than the catalyst prepared by sol–gel process. The catalysts were characterized by X-ray diffraction analysis and BET surface area measurements. XRD and BET surface area measurements indicated the influence of structure and composition of the support on the NO<sub>x</sub> storage behavior of barium oxide.

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**Keywords:** deNO<sub>x</sub>; Storage-reduction; Barium oxide; NSR; Catalyst

## 1. Introduction

Internal combustion auto engines operating under lean burn conditions ( $A/F > 22$ ) are becoming more and more important because of its higher fuel efficiency and lower carbon dioxide emission. However the present three way catalyst (TWC) is ineffective for NO<sub>x</sub> removal from lean burn engine exhaust because of lower content of carbon monoxide and hydrocarbon required for the reduction as well as the higher content of oxygen in the exhaust gas [1]. Hence, development of a suitable catalyst for the removal of NO<sub>x</sub> from lean burn auto engine exhaust has attracted the major attention and various routes and catalyst compositions are being studied in academic as well as in industrial laboratories. Matsumoto [2–4] from Toyota Motor Corporation has developed barium oxide containing catalyst (1% Pt–Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>–BaO) [5] as NO<sub>x</sub> storage reduction catalyst (NSR) for removal of

NO<sub>x</sub> from lean burn auto engine exhaust. The NSR activity was studied using a cyclic sequence of feed, lean conditions for 120 s followed by rich conditions for 6–10 s. In lean cycle initially NO<sub>x</sub> is oxidized to NO<sub>2</sub> over platinum site and stored on the barium oxide as barium nitrate [2]. During lean cycle catalyst gets fully saturated and during the rich cycle a pulse of hydrocarbon reduces the stored barium nitrate to barium oxide and NO<sub>x</sub> in the form of nitrate is reduced to nitrogen. Thus, NO<sub>x</sub> storage reduction is carried out by operating the engine in dual mode (120 s lean followed by 10 s rich mode). Adopting this mode of operation Toyota has successfully operated NSR catalytic converter using Pt/Rh/Ba/TiO<sub>2</sub>/ZrO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst system, with 2 dm<sup>3</sup> hexagonal cell structure installed in a 2 dm<sup>3</sup> D-4 engine vehicle aged by driving 50,000 km in an urban area using the gasoline with low sulphur concentration (30 ppm sulphur) [3]. The NO<sub>x</sub> emission in this system after 50,000 km driving test was about one third that of conventional catalyst, as well as CO<sub>2</sub> emission was about 30% lower than that of conventional engine with conventional three-way catalyst.

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Various preparation techniques have been used in the literature for the preparation of barium containing NSR catalysts to obtain an efficient catalyst. A critical control on the preparation parameters is required to obtain better catalyst performances. Especially the dispersion of barium oxide and the nature of the catalyst support play important role in the catalytic activity. Barium oxide is initially dispersed on alumina support, which is further impregnated with ceria zirconia solution. The resulting material is calcined at 500 °C followed by impregnation of platinum salt on this catalyst to obtain the final catalyst for NSR application. The procedure is complex and it is believed that the barium oxide migrates to the surface of the catalyst so that the NO<sub>2</sub> can be stored as nitrate by reaction with surface barium oxide species [1]. Barium oxide phase is not very stable and it reacts with atmospheric carbon dioxide forming barium carbonate, however when NO<sub>2</sub> reacts with barium carbonate, CO<sub>2</sub> is liberated forming barium nitrate during NSR process, as stability of carbonate species is less compared to nitrate species [6].

Barium oxide, supported on high surface area alumina support prepared by either impregnation or by sol–gel gets dispersed on the surface whereas barium oxide supported on ceria zirconia is atomically dispersed into the support structure because of the formation of solid solutions with these oxides. The different structural environment of barium oxide on different supports has been investigated and related to its NO<sub>x</sub> storage behavior and the results of this investigation are presented here.

## 2. Experimental

### 2.1. Catalyst preparation

A set of five catalysts was prepared; in all these catalysts barium is in different environment by changing the support and also the precursors. The simplified preparation procedure for the set of five catalysts are mentioned below.

#### 2.1.1. NSR-1 and 2

For the preparation of NSR-1 catalyst both sol–gel and impregnation methods were used. Ceria–zirconia sol mixture was prepared by sol–gel method. Cerium nitrate (LOBA Chem.) (8.15 g) solution in water (10 ml) was added to zirconium nitrate (LOBA Chem.) solution (1.447 g in 5 ml water). This ceria–zirconia solution and barium nitrate (MERCK) (5.45 g) were added to the slurry of aluminum isopropoxide (ALDRICH) (51.2 g) in dry isopropyl alcohol. The slurry was initially dried at room temperature and then at 100 °C for 24 h. The resultant solid was powdered and calcined at 500 °C for 12 h. To the above catalyst (20 g), aqueous solution of chloro platinumic acid (H<sub>2</sub>PtCl<sub>6</sub> × H<sub>2</sub>O) (LOBA CHEM) (0.5 g) was added. It was dried in air at room temperature then at 100 °C. The catalyst was reduced in hydrogen at 350 °C for 5 h.

Similarly for preparation of NSR-2 catalyst the above procedure was followed except the solution of ceria–zirconia

and baria was added to boehmite (18.29 g) instead of aluminum isopropoxide to obtain slurry.

#### 2.1.2. NSR-3

For the preparation of NSR-3 catalyst both sol–gel and impregnation methods were used. Ceria–zirconia sol mixture was prepared by sol–gel method. Cerium nitrate (62.25 g) dissolved in 40 ml water was added drop wise to zirconium nitrate solution (11.58 g in 20 ml water). The resultant product was dried at room temperature and then at 100 °C. Barium hydroxide (MERCK) (16.45 g in 50 ml water) was then impregnated on this mixture. The catalyst was dried at room temperature and then at 100 °C for 24 h. The resultant solid was powdered and calcined at 500 °C for 12 h. To the above catalyst (40 g), aqueous solution of chloro platinumic acid (H<sub>2</sub>PtCl<sub>6</sub> × H<sub>2</sub>O) (1.0 g) was added. It was dried in air at room temperature and then at 100 °C. The catalyst was reduced in hydrogen at 350 °C for 5 h.

#### 2.1.3. NSR-4 and 5

NSR-4 catalyst was prepared by sol–gel method. Barium hydroxide (8.22 g) was dissolved in 20 ml water. This solution was added dropwise to a solution of zirconium butoxide (FLUKA) (62.28 g) in dry isopropyl alcohol (60 ml) with constant stirring. The resultant gel was dried at room temperature and then at 100 °C for 24 h. The solid obtained was powdered and calcined at 500 °C for 12 h. An aqueous solution of chloro platinumic acid (H<sub>2</sub>PtCl<sub>6</sub> × H<sub>2</sub>O) (0.5 g) was added to the above catalyst (20 g) and it was dried in air at room temperature and then at 100 °C. The catalyst was reduced in hydrogen at 350 °C for 5 h. Similarly for the preparation of NSR-5 instead of barium hydroxide, 6.81 g Ba(NO<sub>3</sub>)<sub>2</sub> was used.

### 2.2. Catalyst characterization

The X-ray diffraction analysis was carried out using Rigaku X-ray diffractometer (Model DMAX IIIVC) with Cu K $\alpha$  (1.542 Å) radiation. BET surface area was determined using NOVA 1200 Quanta chrome. FTIR was carried out in Shimadzu 8000 series FTIR spectrometer arranged for DRIFT technique. The in situ FTIR characterization was carried out using DRIFT accessory with environment chamber for high temperature studies. The finely ground catalyst was placed in a sample cup. The sample was heated to 400 °C for 2 h under flow of helium to remove adsorbed moisture. The catalyst was cooled to 350 °C. The spectrum of neat catalyst at 350 °C was recorded. Initially 0.2% NO in He was passed over the catalyst. Air was injected using syringe. The formation of nitrate peaks was monitored in the range of 1000–1600 cm<sup>-1</sup> with time. When no further increase in the intensity of nitrate peak was observed, flow of NO/He and air was stopped and system was flushed with He to remove free NO. After flushing the system, hydrocarbon mixture (2000 ppm propylene + 2% O<sub>2</sub> + 20% CO<sub>2</sub> balance He) was passed over the catalyst at same temperature and reduction of the nitrate was monitored with time.

The spectrum of neat catalyst at 350 °C was subtracted from all the spectra after passing the gases to see the spectrum of adsorbed species.

### 3. Catalytic activity

Evaluation of catalytic activity for NO<sub>x</sub> storage and reduction, at different temperature was studied using a fixed bed reactor with an online mass spectrometer (Hiden analytical, HPR 20) for gas analysis. Catalyst (400–500 mg) in the form of small granules (20–30 mesh size) was placed in the fixed bed U shaped quartz tubular reactor (reactor dimensions: inner diameter 4 mm, outer diameter 6 mm, length 170 mm). The catalyst was activated at 500 °C for 3 h in the helium (He) flow. For NO<sub>x</sub> storage cycle, the mixture of 2000 ppm NO and balance He along with 10% oxygen was passed over the catalyst at the desired temperature and the outlet gases were analyzed using online mass spectrometer. Helium is used as diluent gas as it is inert. In order to analyze the input gas composition the reactant gases were analyzed directly using the gas analyzer by bypassing the catalyst bed. The GHSV used was 10,000 h<sup>-1</sup>. To check the NO<sub>x</sub> storage capacity, NO was passed till the catalyst was saturated with NO and there was no further decrease in NO concentration. The analysis was carried out by monitoring the masses 30 (NO), 28 (N<sub>2</sub>), 44 (CO<sub>2</sub>), 42 (HC, propylene) and 46 (NO<sub>2</sub>) as function of time using an online mass spectrometer. For studying the reduction of stored NO<sub>x</sub>, initially NO<sub>x</sub> storage capacity was determined and before saturation level is attained, a mixture of 2000 ppm propylene + 2% O<sub>2</sub> + 20% CO<sub>2</sub> and balance He was passed and the outlet gases were analyzed using the gas analyzer.

### 4. Results and discussion

X-ray diffraction pattern of NSR catalysts is given in Fig. 1. In the case of catalyst NSR-1 and NSR-2 the XRD shows the formation of  $\gamma$ -alumina and it is clear that

the crystallinity of both the alumina catalysts is the same even though the alumina precursors used are different. These catalysts show the formation of ceria in the cubic form, zirconia in the monoclinic form and alumina in the  $\gamma$ -form ( $2\theta = 66.86^\circ$ ). The support exhibits considerable thermal stability (upto 550 °C), as there is no indication of further transformation of the  $\gamma$  phase to  $\alpha$  or  $\delta$ -Al<sub>2</sub>O<sub>3</sub>. In NSR-3 higher crystallinity is observed and it is clear that zirconia is present in the monoclinic phase ( $2\theta = 24.34^\circ$  and  $34.16^\circ$ ). Ceria is present in the cubic phase as a major phase giving peaks at  $2\theta = 30.20, 46.88$  and  $56.38^\circ$  and minor monoclinic phase giving peaks at  $2\theta = 28.38$  and  $31.52^\circ$  indicating the incorporation of barium into the ceria/zirconium oxide lattice site. In NSR-4 zirconia is in the cubic form with monoclinic phase as impurity. NSR-5 is highly crystalline with cubic zirconia as major phase with minor monoclinic phase indicating the incorporation of barium into the zirconium oxide lattice site stabilizing the zirconia into cubic form. It is well known that barium is incorporated into zirconia lattice position and zirconium oxide is stabilized in cubic form. Since zirconium is replaced by barium into the lattice point, the oxygen vacancies are created for the charge compensation and the final cubic zirconia thus obtained is well known oxide ion conductor and is used as solid electrolyte [7].

The surface area of the catalysts is given in Table 1. As expected the catalysts with alumina supports shows higher surface area (NSR-1, 121 and NSR-2, 146 m<sup>2</sup> g<sup>-1</sup>) compared to the catalysts with ceria and zirconia support.

The FTIR results of the NO<sub>x</sub> storage and reduction studied for catalyst NSR-1 are given in Fig. 2. From the figure, nitrates formation is evident [8]. Oxidation of NO with oxygen under lean burn condition in presence of Pt gives NO<sub>2</sub>, which gets stored as nitrate species [9]. In the storage cycle (Fig. 2a) bands appeared at 1260, 1303 and 1320 cm<sup>-1</sup>, which can be assigned to barium nitrate formation. The bands also appeared at 1587 and 1303 cm<sup>-1</sup> can be assigned to the formation of aluminum nitrate (chelating and bridging bidentate nitrate, respectively) [10]. However the barium nitrate peaks are more intense than aluminum nitrate peaks, which is indicative of predominant formation of barium nitrate compared to aluminum nitrate in storage cycle. Negative band in the region of 1400–1500 cm<sup>-1</sup> is due to the barium carbonate, which forms nitrate in contact with NO and oxygen. This interferes with the detection of other chemisorbed NO<sub>x</sub> species. In reduction cycle when hydrocarbon was passed over the catalyst the intensity of peaks in the range of 1260–1320 cm<sup>-1</sup> decreased drastically indicating incomplete reduction of stored NO<sub>x</sub>. This is in good agreement with experimental results, which shows highly oxidizing nature of these catalysts leading to incomplete reduction of the stored NO<sub>x</sub> and more direct hydrocarbon oxidation. In the reduction cycle, the intensity of aluminum nitrate peaks is much higher than barium nitrate peaks indicating less reducibility of aluminum nitrate compared to barium nitrate.

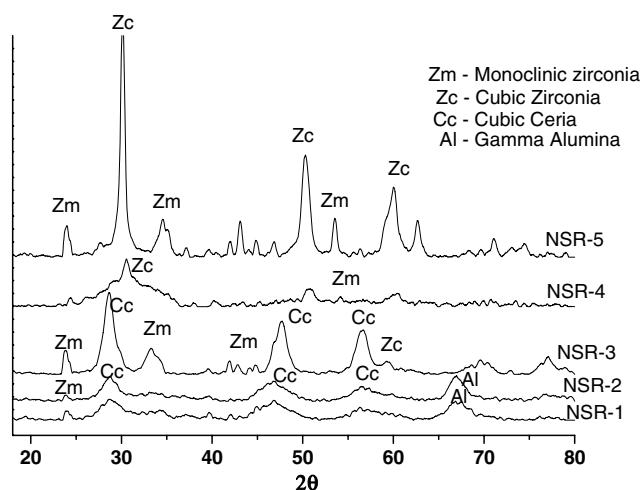


Fig. 1. XRD pattern of NSR catalysts.

Table 1  
Catalyst preparation and surface area

| Catalyst | Catalyst composition                                                                                 | Precursor                         | Surface area, m <sup>2</sup> g <sup>-1</sup> |
|----------|------------------------------------------------------------------------------------------------------|-----------------------------------|----------------------------------------------|
| NSR-1    | 1%Pt–[Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub> ]/[Al <sub>2</sub> O <sub>3</sub> ]/[BaO] | Al-isopropoxide                   | 121                                          |
| NSR-2    | 1%Pt–[Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub> ]/[Al <sub>2</sub> O <sub>3</sub> ]/[BaO] | Boehmite                          | 146                                          |
| NSR-3    | 1%Pt–[Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub> ]/[BaO]                                   |                                   | 46                                           |
| NSR-4    | 1%Pt–BaO/ZrO <sub>2</sub>                                                                            | Ba(OH) <sub>2</sub>               | 35                                           |
| NSR-5    | 1%Pt–BaO/ZrO <sub>2</sub>                                                                            | Ba(NO <sub>3</sub> ) <sub>2</sub> | 38                                           |

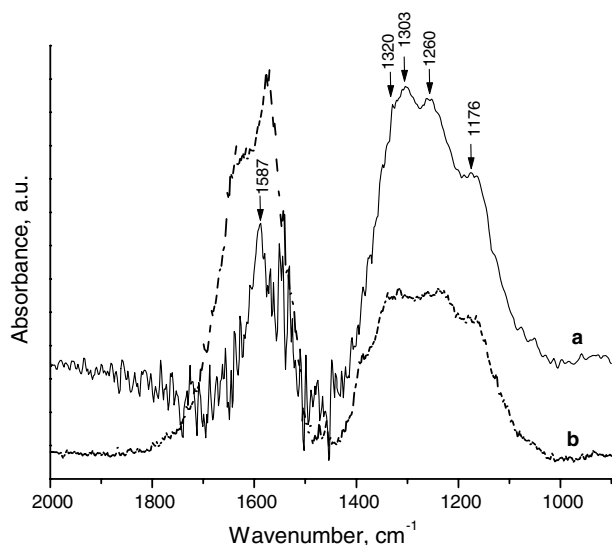
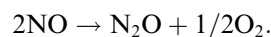
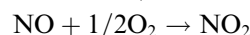
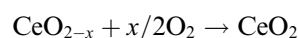
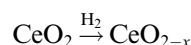


Fig. 2. NO<sub>x</sub> storage-reduction on NSR-1 catalyst at 350 °C. (a) Storage NSR-1 + NO + air. (b) Reduction NSR-1 + (propylene + O<sub>2</sub> + CO<sub>2</sub> + He).

The NO<sub>x</sub> storage behavior of NSR-1 and NSR-2 is given in Fig. 3. Both the catalysts store NO<sub>x</sub> for about 30 min before saturation. Initially for few minutes there was an indication of direct NO<sub>x</sub> decomposition to N<sub>2</sub> on these catalysts. However there was no formation of equivalent amount of oxygen observed in the mass spectrum.

Initial direct NO decomposition may be due to the abstraction of oxygen by the partially reduced cerium in the catalyst. During the synthesis of the catalyst, impreg-

nated Pt salt is reduced in hydrogen to get Pt(0) on the catalyst surface. In this process along with Pt some amount of Ce(IV) also gets reduced to Ce(III). Ceria is known to have oxygen storage property [11], hence there is a competition for oxygen uptake by Ce(III) and NO (for getting oxidized to NO<sub>2</sub>). However ceria has much higher oxygen affinity, hence less oxygen is available for oxidation of NO to NO<sub>2</sub> due to which along with NO<sub>2</sub> certain amount of N<sub>2</sub>O is formed, which does not get stored on the catalyst surface.



The initial NO<sub>x</sub> decomposition may be attributed to the presence of reduced ceria, which gets oxidized by abstracting oxygen from NO<sub>x</sub> liberating N<sub>2</sub>. It is seen that the NO<sub>x</sub> storage capacity of both the alumina based catalyst is similar. In case of NSR-2 catalyst, the effect of support precursor is not considerable. The overall NO<sub>x</sub> storage was about 80–85% of barium content suggesting the availability of most of the barium oxide for the reaction with NO<sub>x</sub> to form barium nitrate (calculations based on the barium oxide used in the catalyst and amount of NO passed before saturation).

The NO<sub>x</sub> storage behavior of non alumina based catalyst NSR-3 is shown in Fig. 4. Interestingly a considerable amount of N<sub>2</sub> formation has been observed on this catalyst

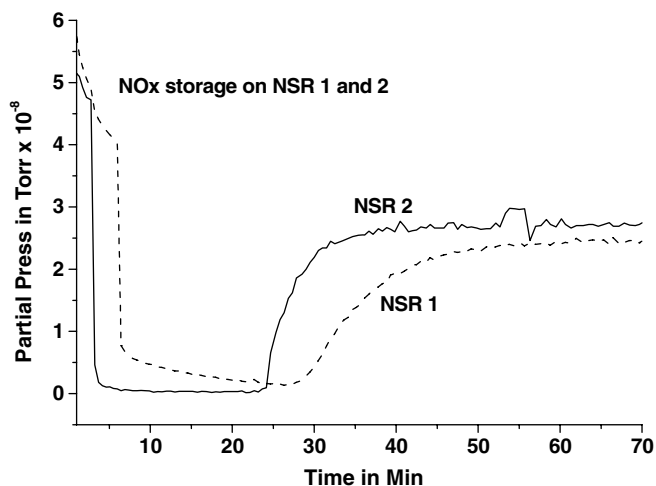


Fig. 3. NO adsorption on NSR-1 and 2 at 300 °C. Reaction conditions: Temp. 300 °C, 0.2% NO + 10% O<sub>2</sub> in He, GHSV 10,000 h<sup>-1</sup>.

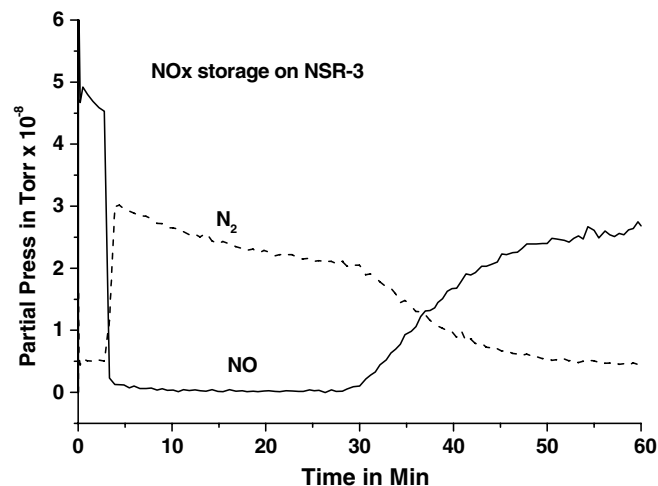


Fig. 4. NO adsorption on NSR-3 at 300 °C. Reaction conditions: Temp. 300 °C, 0.2% NO + 10% O<sub>2</sub> in He, GHSV 10,000 h<sup>-1</sup>.

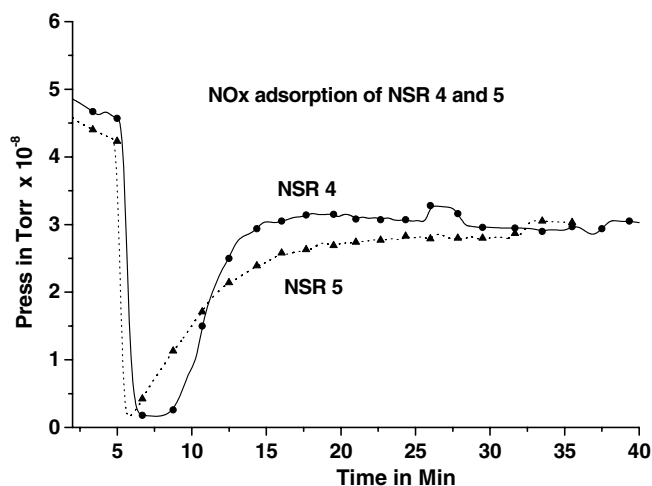


Fig. 5. NO adsorption on NSR-4 and NSR-5 at 300 °C. Reaction conditions: Temp. 300 °C, 0.2% NO + 10% O<sub>2</sub> in He, GHSV 10,000 h<sup>-1</sup>.

compared to NSR-1 and NSR-2. This catalyst also showed less amount of NO<sub>x</sub> storage compared to NSR-1 and NSR-2. The higher decomposition of NO<sub>x</sub> may be due to large quantity of reduced ceria present in this catalyst. Even though the barium oxide content is same in this catalyst the NO<sub>x</sub> storage capacity is very low compared to NSR-1 and 2. The XRD of NSR-3 showed the formation cubic ceria and the barium oxide might be incorporated at the lattice point of cubic ceria structure. The low NO<sub>x</sub> storage capacity of NSR-3 catalyst indicates that the barium oxide on ceria zirconia support occupies the lattice position, which is not active for NO<sub>x</sub> storage.

The NO<sub>x</sub> storage behavior of NSR-4 and NSR-5 is given in Fig. 5. It is clearly seen that both the catalysts show very poor NO<sub>x</sub> storage capacity. The barium oxide on zirconia catalyst prepared using barium nitrate and barium hydroxide precursor showed low NO<sub>x</sub> storage, which may be due to the incorporation barium oxide into zirconia lattice points stabilizing zirconia in the cubic form. There was no indication of direct decomposition of NO to N<sub>2</sub> because of absence of ceria in this catalyst support.

From these results it is seen that the BaO supported on high surface area alumina/ceria/zirconia prepared either by impregnation or sol–gel technique behaves more or less similarly for NO<sub>x</sub> storage. Whereas BaO supported on non alumina support such as ceria/zirconia is not as active as alumina support which may be due to the incorporation of part of BaO into the ceria zirconia lattice points and

hence not available for the reaction and thus is not as active as dispersed BaO on the surface. When reduction of stored NO<sub>x</sub> in the form of nitrate was attempted using rich conditions (2000 ppm propylene + 2% O<sub>2</sub> + 20% CO<sub>2</sub> balance He), considerable amount of stored NO<sub>x</sub> was reduced to N<sub>2</sub>. However due to oxidative nature of the catalysts, direct oxidation of hydrocarbon to CO<sub>2</sub> was observed as a simultaneous reaction and hence there was not enough hydrocarbon available for complete reduction of stored NO<sub>x</sub>.

## 5. Conclusion

Barium oxide supported on high surface area alumina/ceria/zirconia support prepared either by impregnation or by sol–gel synthesis behaves similarly for NO<sub>x</sub> storage in NSR catalyst. Barium oxide supported on non alumina support such as ceria/zirconia and pure zirconia showed very low NO<sub>x</sub> storage capacity even though the barium oxide content was same. The lower NO<sub>x</sub> storage capacity supported on non alumina support may be due to the incorporation of barium oxide into the support structural site, which is inactive for storage.

## Acknowledgement

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## References

- [1] L.F. Liotta, A. Macaluso, G.E. Arena, M. Livi, G. Centi, G. Deganello, *Catal. Today* 75 (2002) 439.
- [2] S. Matsumoto, *Cat. Tech.* 4 (2000) 102.
- [3] S. Matsumoto, *Catal. Today* 29 (1996) 43.
- [4] N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura, K. Kasahara, *SAE Paper* 950809, 1995.
- [5] K. Katoh, T. Kihara, T. Asanuma, M. Gotoh, N. Shibagaki, *Toyota Technol. Rev.* 44 (1995) 27.
- [6] F. Rodrigues, L. Juste, C. Potvin, J.F. Tempère, G. Blanchard, G. Djéga-Mariadassou, *Catal. Lett.* 72 (2001) 59.
- [7] H. Takashi, T. Akihiro, S. Hiroshi, S. Kyoichi, *Trans. Mater. Res. Soc. Jpn.* 25 (2000) 1131.
- [8] K.I. Hadjiivanov, *Catal. Rev. Sci. Eng.* 42 (2000) 71.
- [9] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, *Catal. Today* 27 (1996) 63.
- [10] T.J. Toops, D.B. Smith, W.S. Epling, J.E. Parks, W.P. Patridge, *Appl. Catal. B* 58 (2005) 255.
- [11] A. Trovarelli, C. de Leitenburg, G. Dolcetti, *Chemtech* 27 (1997) 32.