Storage of Nitrous Oxide (NOx) in Diesel Engine Exhaust Gas using Alumina-Based Catalysts: Preparation, Characterization, and Testing

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Abstract: This work investigated the nitrous oxide (NOx) storage process using alumina-based catalysts (K_2O/Al_2O_3, CaO/Al_2O_3, and BaO/Al_2O_3). The feed was a synthetic exhaust gas containing 1,000 ppm of nitrogen monoxide (NO), 1,000 ppm i-C_4H_{10}, and an 8% O_2 and N_2 balance. The catalyst was carried out at temperatures between 250–450°C and a contact time of 20 minutes. It was found that NOx was effectively adsorbed in the presence of oxygen. The NOx storage capacity of K_2O/Al_2O_3 was higher than that of BaO/Al_2O_3. The NOx storage capacity for K_2O/Al_2O_3 decreased with increasing temperature and achieved a maximum at 250°C. Potassium loading higher than 15% in the catalyst negatively affected the morphological properties. The combination of Ba and K loading in the catalyst led to an improvement in the catalytic activity compared to its single metal catalysts. As a conclusion, mixed metal oxide was a potential catalyst for de-NOx process in meeting the stringent diesel engine exhaust emissions regulations. The catalysts were characterized by a number of techniques and measurements, such as X-ray diffraction (XRD), electron affinity (EA), a scanning electron microscope (SEM), Brunner-Emmett-Teller (BET) to measure surface area, and pore volume and pore size distribution assessments.

Keywords: NOx storage, Lean de-NOx, Exhaust catalyst, Diesel exhaust, Mixed metal oxide.

تخزين NOx لغاز عوادم محركات الديزل باستخدام محفزات أساسات الألومينا: التحضير، الخصائص والاختبار

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الملخص: هذا البحث يفحص طريقة تخزين NOx علي محفزات أساسات الألومينا (K2O، Al2O3، CaO/Al2O3 وBaO/Al2O3). التغذية كانت تحتوي علي غاز عادم اصطناعي ١٠٠٠ جزء في المليون من NO، ١٠٠٠ جزء في المليون من i- C4H10، ٨ ٪ من O2 وتوازن N2 . تم إجراء نشاط الحافز بين درجة حرارة ٢٥٠ درجة مئوية إلى ٤٥٠ درجة مئوية وزمن اتصال ٢٠ دقيقة. وجد أن NOx تم امتصاصه بفعالية في وجود الأكسجين. سعة NOx التخزينية لـ K2O/Al2O3 كانت أكثر علواً من <BaO/Al2O3 وتقل مع زيادة درجة الحرارة وتحقق القيمة العظمي عند درجة ٢٥٠ مئوية. زيادة تحميل البوتاسيوم بنسبة أعلي من ١٥ ٪ في الحافز تؤثر سلباً علي الخصائص الشكلية. المزج بين تحميل كل من Ba و K يؤدي إلى تحسين نشاط الحافز بالمقارنة إلى الحوافز ذات الفلز الواحد. وخلاصة؛ أكسيد المعدن المختلط كان حافز كامن لعملية de-NOx في مواجهة انبعاثات عادم محركات الديزل. الحافز يتميز بعدد من التقنيات والقياسات مثل XRD، EA، SEM، مساحة السطح BET، حجم المسام وتوزيع مقاس المسام.

الكلمات المفتاحية: تخزين NOx، ميل de-NOx، حافز العادم، عادم الديزل، أكسيد المعدن المختلط.

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1. Introduction

Diesel engines are caught in an area of conflict between a wide variety of requirements ranging from maximum customer benefit to minimum fuel consumption and emissions (Michael *et al*. 2014). However, they have many adverse environmental effects, particularly due to the emission of excessive nitrogen oxide (NOx) in its emissions. Due to the lean burn combustion in the engine, the exhaust gas also contains an excess of oxygen that complicates conventional approaches to chemically reduce NOx to environmentally benign nitrogen gas. Therefore, there is an urgent need to develop diesel emission control technology to take full advantage of the fuel efficiency and durability of diesel vehicles (Athanasios *et al*. 2015; Kabin *et al*. 2004).

NOx storage and reduction (NSR) catalysts, which are also sometimes referred to as NOx adsorption catalysts and lean NOx traps, have been developed as a promising alternative method to remove NOx from diesel engine emission (Athanasios *et al*. 2015; Centi *et al*. 2003; Epling *et al*. 2004; Michael *et al*. 2014). These catalysts operate in a cyclic manner where during the lean reductant (conventionally ammonia [NH$_3$], carbon monoxide [CO], or hydrocarbons) period of operation, the catalyst stores or traps NOx as a nitrate species. A periodic and short rich pulse of reductant is then introduced so that the trapped NOx is released and reduced to N$_2$ and the catalyst is regenerated (Epling *et al*. 2004). The NOx trapping materials can be found among the alkali (potassium [K], magnesium [Mg], calcium [Ca]) and alkaline earth metal (barium [Ba], lihium [Li]) oxides, with barium oxide (BaO) having been most extensively studied experimentally (Bethke *et al*. 1995; Fridell *et al*. 1999; Josh *et al*. 2013; Michael *et al*. 2014; Milt *et al*. 2003a; Milt *et al*. 2003b; Sedlmair *et al*. 2003; Su and Amiridis 2004; Takahashi *et al* 1996; Westerberg and Fridell 2001). In general, these metals show different efficiencies in storing NOx as nitrates that eventually have different stabilities in the catalysts. Therefore, efforts to determine the right types and content of oxides, or possibly a combination of oxides in the catalyst, should be explored.

The main aim of this work was to investigate the performance of oxides of K and Ba supported on an aluminum oxide (Al$_2$O$_3$) catalyst for storage of NOx in diesel engine exhaust gas. The efficiency of the process was studied with single and combined oxide systems. The behavior of the process was characterized and elucidated with the final aims of identifying the active and efficient mixed metal oxides to store NOx from diesel engine exhaust gas.

2. Materials and Methods

2.1 Catalyst Preparation

Oxides of Ba and K supported on Al$_2$O$_3$ were tested for their effectiveness in the storage of NOx during the lean reductant stage of the deNOx process. The introduction of active metals was carried out through a wet impregnation method using respective metal nitrates as the precursors. In a typical procedure, for the preparation of BaO/Al$_2$O$_3$ (10 wt. %), 3.5 ml of deionized water was added while stirring to 4.5 g of the supporting oxide. After that, 10 ml of an aqueous solution containing 0.96 g of barium nitrate [Ba(NO$_3$)$_2$] was mixed with the paste and stirred for two hours at room temperature. After evaporating the solvent at ≈ 100°C, the sample was dried at 110°C overnight and finally calcined in the air at 500°C for two hours. A fraction with particle sizes between 425–600 μm was obtained by pressing, crushing, and then sieving. The catalysts synthesized are denoted as MO(x)/Al$_2$O$_3$, where x represent the weight composition of the metal oxide in the catalyst.

2.2 Experimental Setup

The feed used in this study consisted of nitrogen (N$_2$), oxygen (O$_2$), 5,000 ppm of NO in N$_2$ and 5,000 ppm of isobutene (*i*-C$_4$H$_{10}$) in N$_2$ gases. The flow rate was controlled by means of mass flow controllers. The reactor was made of 20 mm i.d. stainless steel tubing and was designed as a cross sectional detachable type with a center joint, where the catalyst packing could be mounted and removed easily from the reactor. The pressure drop across the reactor was negligible under the normal operating conditions. A thermocouple type K 88500-10 (Cole-Parmer, Vernon Hills, Illinois, USA) connected to a multi-channel digital temperature scanner (Cole-Palmer-92000-05) was used to measure the temperature inside the reactor. The reaction temperatures (200–450 °C) were achieved by means of a horizontal tubular furnace (Lindberg-TF-55035C, Thermo Fisher Scientific, Inc., Waltham, Massachusetts, USA). The feed gas components comprised of

1,000 ppm of NO, 1,000 ppm of butane (C_4H_{10}), 8% O_2, and balanced N_2 were mixed to give the feed gas.

The NO storage activity of the catalysts was evaluated at atmospheric pressure with a total feed flow rate of 50 ml/minute. Lean NO that presented in feed was reacted and chemically stored in the catalyst storage component for 20 minutes. The packing of 200 mg of catalyst was mounted at the center of the catalytic reactor. The furnace was allowed to cool down and the tubing system was flushed with nitrogen for about 30 minutes to remove excess oxygen. The feed gas mixture was fed into the system at 50 ml/minute, and the reactor was heated to the desired reaction temperature before measuring the concentration of gases. The feed gas mixture was allowed to run for about 10 minutes to ensure a steady state and a uniform mixture before measuring the outlet concentration of the gases.

An in-line gas chromatography (GC 8A) (SHIMADZU Corp., Kyoto, Japan) was used for the analysis of the feed and product gases. The GC unit was operated in an isothermal condition (80°C) with helium as the carrier gas. The GC used was equipped with a thermal conductivity detector, two separating columns, and an integrator. A Supelco molecular sieve 5A column (Sigma Aldrich, St. Louis, Missouri, USA) was used for separating N_2, O_2, and *i*-C_4H_{10} while a Porapak Q column (Supelco) was used for the analysis of CO_2 and NO.

2.3. Characterization of Catalysts

The surface area pore volume and average pore diameter of the synthesized catalysts were measured using the Accelerated Surface Area and Porosimetry System (ASAP 2000) supplied by Micromeritics Instruments Corporation, Norcross, Georgia, USA. The samples were dried overnight at 105°C and degassed for 12 hours under vacuum at a temperature of 300°C using the ASAP2000 instrument before measurements were performed (Alsobaai *et al.* 2007a). Powder X-ray diffraction (XRD) patterns of prepared materials were obtained using a D5000 X-ray diffractometer (Siemens, Munich, Germany) with CuKα radiation (λ = 1.54056 Å) at 40 kV and 30 mA and a scanning speed of 2 degrees per minute (Alsobaai et al., 2007b). Scanning electron microscope (SEM) studies were performed using a Cambridge stereo scan 360 (Wetzlar, Germany) and polaron for the sputter coating. Before

scanning, the powder samples were spread onto the double-side carbon tape and coated with gold (20–30 nm thickness) in order to increase the conductivity and therefore the quality of the results (Alsobaai *et al.* 2007c). An elemental analyzer (EA) was also used to analyze the composition of fresh and aged catalyst samples.

3. Results and Discussion

3.1 Characterization of Catalysts

The porosity and surface characteristics in terms of Brunner-Emmett-Teller (BET) surface area, pore volume, and average pore diameter of the catalysts are given in Table 1. The catalysts loaded with K_2O and K_2OBaO showed lower surface area and pore volume compared to the unloaded Al_2O_3 support. This finding is reasonable as the impregnated metals both fill up and plug some pores, making less area available for nitrogen adsorption and contributing to the weight of the catalyst, lowering the surface area and pore volume measured on a weight basis. Figure 1(a) shows nitrogen adsorption-desorption isotherms of alumina and alumina-based catalysts. The isotherms were type IV, corresponding to mesoporous solids (Halachev *et al.* 1996)**.** As the relative pressure increased (P/Po >0.2), the isotherms exhibited sharp inflections characteristic of capillary condensation within mesopores. In any case, the sharpness of this step suggested a uniform size pore system and provided evidence of the high quality of the catalysts. The pore size distributions of catalysts are illustrated in Fig. 1(b). As shown in this figure, all catalysts exhibit mesopores with size peaks centered at 5–10 nm.

Figure 2 presents XRD traces of the catalysts. For Al_2O_3, only diffraction peaks due to the alumina support material were observed, and no K or Ba-related phases were evident. For K_2O/Al_2O_3 and K_2OBaO/Al_2O_3, new peaks at 2θ values of 22, 36, and 42 in addition of the Al_2O_3 pattern which did not change from the original pattern. The presence of these new peaks confirmed that the K and Ba species were present in the prepared materials. These results are in good agreement with those reported by Kim *et al.* (2007).

The structure and morphology of the fresh and spent catalysts were also investigated. Topological information such as crystal structure and morphology of the fresh and

Table 1. BET surface area, pore volume, average pore diameter of alumina-based catalysts.

Sample	Surface area, m^2/g	Mesoporous area, %	Microporous area, %	Pore volume, cm^3/g	Average pore size (APS), nm
Al_2O_3	77.285	100	0	0.208	10.773
K_2OBaO/Al_2O_3	39.516	89.239	10.761	0.138	13.99
K_2O/Al_2O_3	7.457	98.155	1.845	0.0403	21.598

(a)

(b)
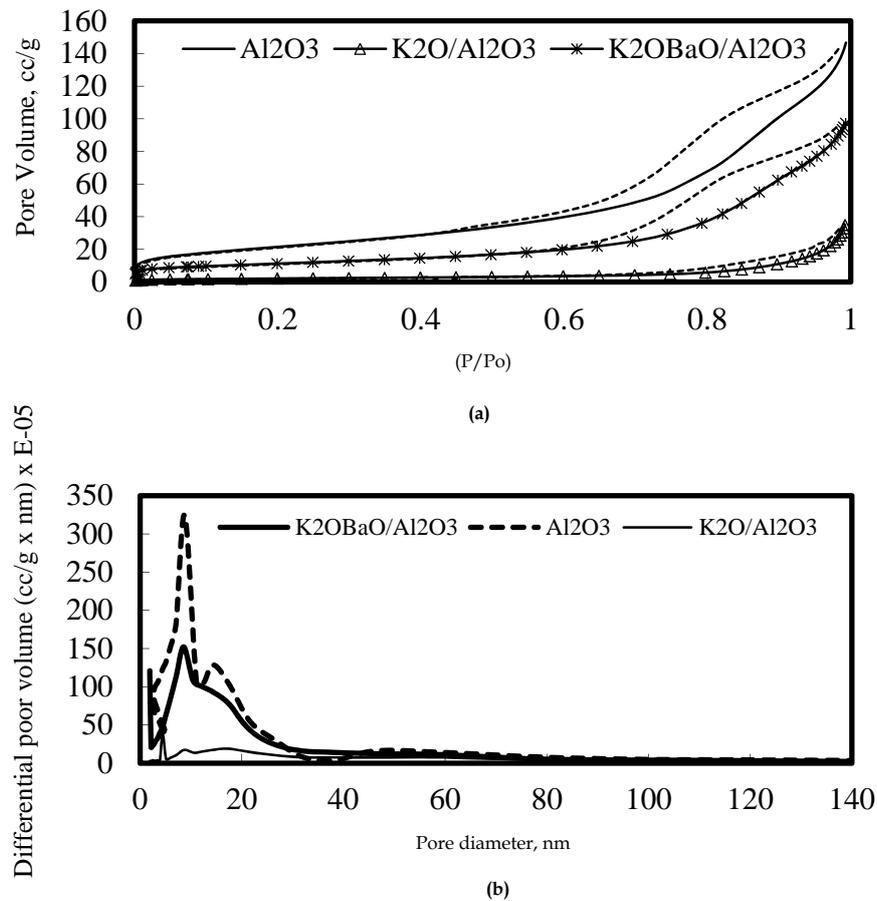
Figure. 1 Porosity measurements of alumina-based catalysts (a) adsorption (solid line) and desorption (dotted line) isotherm, and (b) pore size distribution.

spent $K_2O(10)/Al_2O_3$ and $K_2O(5)BaO(5)/Al_2O_3$ catalysts were studied using an SEM. Figure 3(a) shows a SEM micrograph of fresh $K_2O(10)/Al_2O_3$ catalyst while Fig. 3(b) shows the SEM micrograph of the fresh $K_2O(5)BaO(5)/Al_2O_3$ catalyst. As shown in these figures, the sample $K_2O(5)BaO(5)/Al_2O_3$ had a clear crystalline shape compared to

$K_2O(10)/Al_2O_3$. The micrograph of both samples suggested that the surface of alumina in the sample of $K_2O(5)BaO(5)/Al_2O_3$ was homogenously covered by metal as compared to the sample of $K_2O(10)/Al_2O_3$.

Analytical techniques were also carried out to characterize the structure of the aged catalyst. The information about the structure
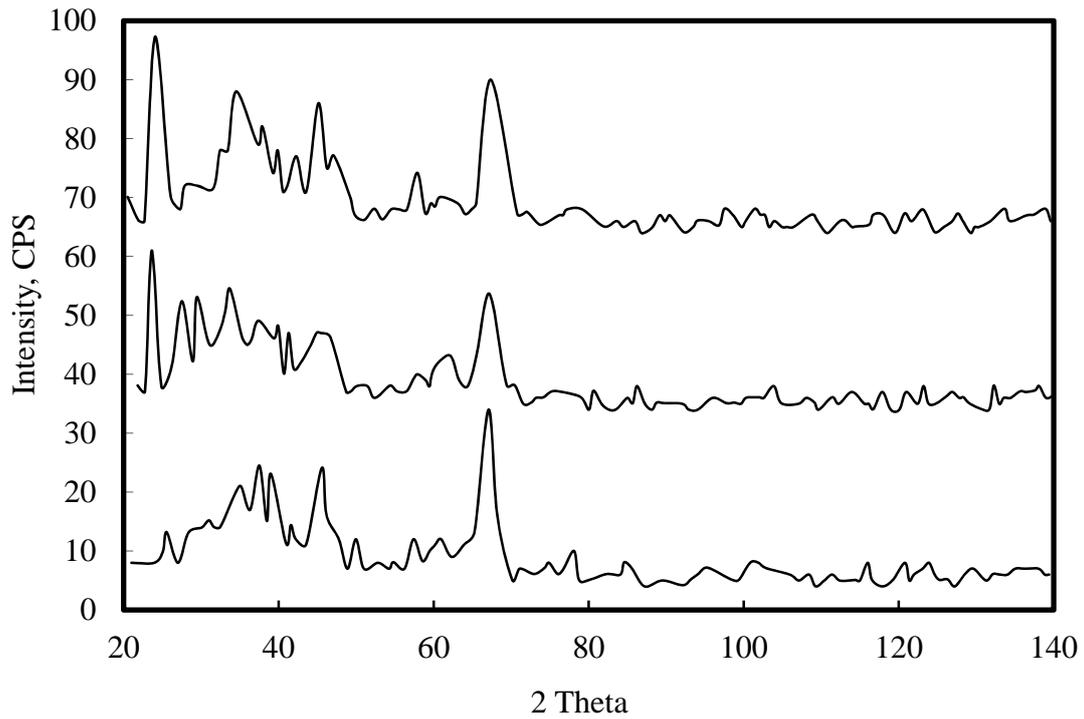
Figure 2. XRD pattern for alumina-based catalysts.

(a)

(b)

(c)

(d)
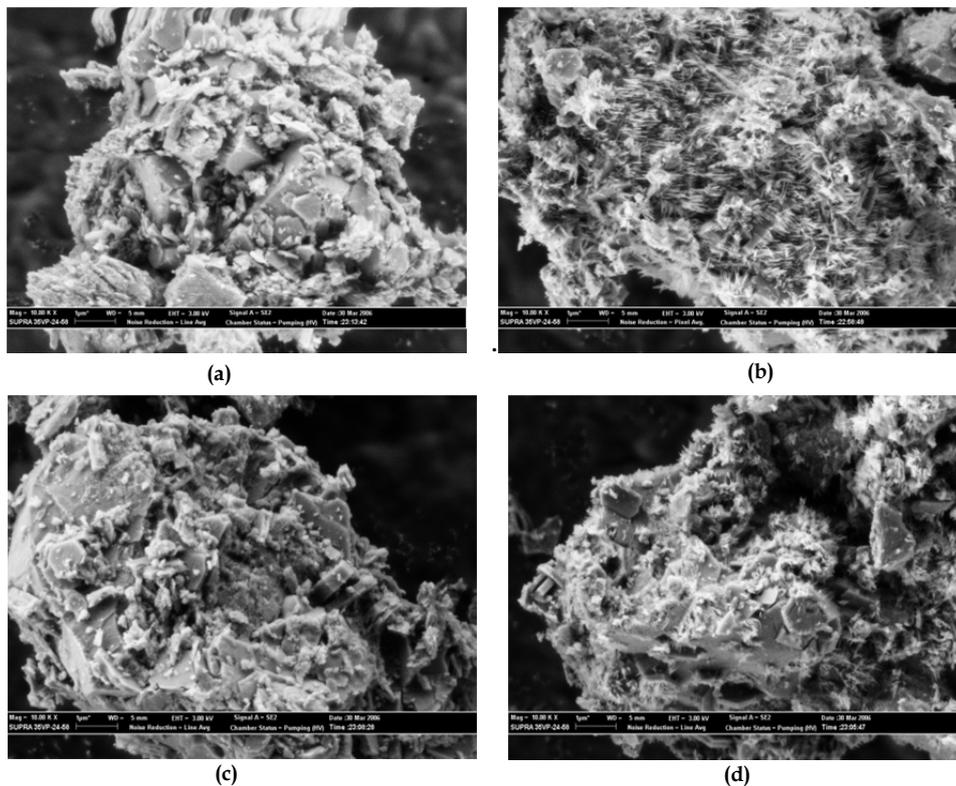
Figure 3. SEM micrograph of fresh and aged catalysts: (a) fresh K_2O (10)/Al_2O_3, (b) fresh $K_2O(5)Ba(5)$/Al_2O_3 (c) aged $K_2O(10)$/Al_2O_3, (d) aged $K_2O(5)BaO(5)$/Al_2O_3.

and morphology of aged catalyst was investigated. The topological information of the aged $K_2O(10)$/Al_2O_3 and $(K_2O(5)BaO(5)$/Al_2O_3 catalysts were studied. The used sample was the catalyst that was previously subjected to the NO storage condition for a duration of 1600

seconds under a reaction temperature of 350°C. Figures 3(c) and (d) show the SEM micrograph of the $K_2O(10)/Al_2O_3$ and $K_2O(5)/Al_2O_3$ aged samples, respectively. As shown in the micrograph, there was no structured change to either sample after being subjected to the NOx storage process if compared to the micrographs shown in Figs. 3(a) and (b). As compared the fresh and aged samples, it could be concluded that as the coverage of metal in the surface increased, the capacity of storage also increased. Similar observation were reported by Fanson *et al*. (2003). However, the researchers were unable to unambiguously identify the species of the surface compound that resulted and were unsure of their exact origin.

Elemental analysis was also conducted on the spent catalysts. The composition of C, hydrogen (H), and N content is shown in Table 2. The $K_2O(10)/Al_2O_3$ catalyst with notation (a) was tested under a reaction temperature of 250°C, while the catalyst with notation (b) was tested under a reaction temperature of 350°C. The percentages of C, H, and N were found to increase from those of the fresh catalyst. The existence of C and H was caused by the oxidation of the hydrocarbon (C_4H_{10}) in the feed gas by high temperatures (>250°C) (Despres *et al*. 2003). The clear evidence of N chemisorption could be observed when N content varied between 0.35–0.45 in the fresh sample. The decomposition process of NO to N_2 and O_2 inside the catalyst contributed to the growing N content (Bethke *et al*. 1995). On the other hand, it was found that BaO/Al_2O_3 was not efficient to catalyze the oxidation of NO to NO_2 and then to N_2 if compared to K_2O/Al_2O_3 and CaO/Al_2O_3. It has been reported that BaO/Al_2O_3 did not store NO to a great extent. A similar observation was reported by Lietti *et al*. (2001).

Table 2. Composition of carbon, hydrogen, nitrogen and sulfur content in aged catalyst.

Element	$K_2O(10)$ /Al_2O_3[a]	$K_2O(10)$ /Al_2O_3[b]	$BaO(10)$ /Al_2O_3
Carbon (wt %)	0.54	0.50	0.78
Hydrogen (wt %)	0.66	0.57	0.50
Nitrogen (wt %)	1.83	2.08	0.79

[a]Tested at 250°C; [b]Tested at 350°C

3.2 Process Studies

The experimental results obtained from a series of catalytic tests on NO storage by single and mixed metal oxide catalysts were presented and discussed. Experiments were carried out to determine the effect of the important independent process variables (*i.e.* storage compounds, reaction temperature, percentage of metal loading, and metal composition) at fixed amounts of catalyst, and a fixed reaction duration and feed composition. The experiments were performed at a temperature of 350°C with a reaction duration of 20 minutes. In order to examine the performance of different storage components, 20 mg of different catalysts (*i.e.* $BaO(10)/Al_2O_3$ and $K_2O(10)/Al_2O_3$) were investigated. Table 3 compares the activities of these catalysts in NOx storage at 350°C.

For each experiment, the concentration of NO in the outlet gas measured was lower than that of the inlet gas. These results indicate that NO was stored on the catalyst under the lean conditions. In the presence of 8% O_2, K_2O/Al_2O_3 was more active for the storage of NO than BaO/Al_2O_3. The sequence of basicity strength is K>Ba. Therefore, the result suggested that the stronger the basicity of the NOx storage compound, the larger the quantity of the NO stored. A similar observation was reported by Takahashi *et al.* (1996). It was attributed to the higher stability of nitrates formed by oxides of stronger basicity (Takahashi *et al.* 1996). Potassium also favored surface mobility, and had a higher surface basicity (Milt *et al*. 2003a). On the other hand, it was found that BaO/Al_2O_3 was not efficient in catalyzing the oxidation of NO to NO_2; therefore, it could not efficiently store NO to a significant extent, even in the presence of oxygen (Lietti *et al.* 2001). Also the ionic size and charges of K+ is less than Ba+, and this may be considered in explaining ion-supported interactions and a loss of porosity in these samples. The larger ionic size can cause more loss in porosity and less activity.

It is generally reported in the literature that the formation of NO_2 from NO and O_2 is a necessary initial step before NOx storage can take place during lean conditions (Bethke *et al.* 1995; Fridell *et al.* 1999). However, this simple step already includes several uncertainties and, further, may be the sum of several elementary reaction steps (Fridell *et al.* 1999). The NOx storage process for lean conditions can be

Table 3. Amount of NO storage by different catalysts at a temperature of 350°C and reaction time of 20 min

Catalyst	NO Concentration (ppm)		Amount of NO stored (%)
	$(C_{NO})_{in}$	$(C_{NO})_{out}$	
$BaO(10)/Al_2O_3$	1014	638.3	39.0
$K_2O(10)/Al_2O_3$	1009	450.4	55.4

assumed to comprise the following steps with M as a storage component in the catalyst:

$$NO^g \rightarrow NO^a \qquad (1)$$

$$O_2^g \rightarrow 2O^a \qquad (2)$$

$$NO^a + O^a \rightarrow NO_2 \qquad (3)$$

$$2NO + 3O + MO \rightarrow M(NO_3)_2 \qquad (4)$$

$$2NO_2 + O + MO \rightarrow M(NO_3)_2 \qquad (5)$$
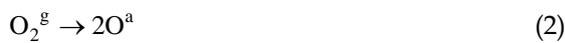
The superscript (g) refers to gas form while superscript (a) refers to the absorbed form of the chemical compound. This is a somewhat simplified reaction scheme. For example, NO_2 adsorption and desorption are not included (Fridell *et al*. 1999). A key role of the catalyst surface was found to be the oxidation of NO to NO_2 (Milt *et al*. 2003b).

In order to determine the parameters for the NOx storage process, the temperature dependence of the reaction at constant feed gas composition was investigated. For this purpose, catalysts $BaO(10) / Al_2O_3$ and $K_2O(10)/Al_2O_3$ were evaluated on a catalytic reactor rig to determine their properties as a function of temperature at 200–450°C. Both metal oxide catalysts were tested under the same reaction conditions. Figure 4 shows the result of the temperature dependence of the catalytic activity under lean conditions. The difference between inlet and outlet NO concentrations indicated the NOx storage.
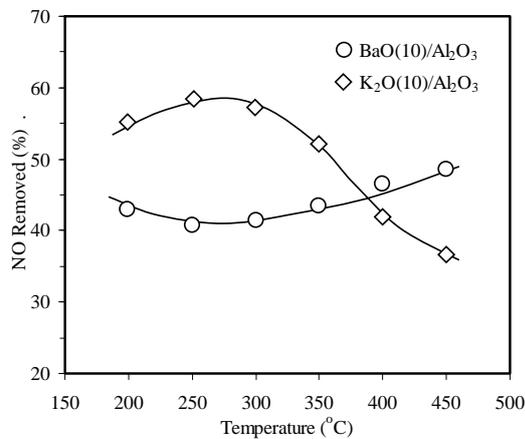
The maximum NO storage for $K_2O(10)/Al_2O_3$ of around 58% occurred at 250 °C. After this, the NO storage reaction decreased with increasing temperature. As reported by Fridell *et al*. (1999), the decrease in NO storage at higher temperatures was associated with the stability of metal nitrate. In contrast to the $K_2O(10)/Al_2O_3$ catalyst, the $BaO(10)/Al_2O_3$ catalyst showed higher conversions at higher temperatures. For $BaO(10)/Al_2O_3$, the lean feed shows a peak steady-state NOx storage of approximately 47% at 450°C. The $BaO(10)/Al_2O_3$ catalyst had higher NO storage activity than the $K_2O(10)/Al_2O_3$ catalyst at higher temperatures, particularly above 400°C. This suggested that the ionic bonding character of Ba nitrates increased with increasing temperatures (Sedlmair *et al*. 2003). The NO storage for both catalysts exceeded 40% at 200°C. It was because of the Al_2O_3 catalysts that they were capable of playing an important role as the storage site at temperatures below 300°C (Westerberg and Fridell 2001). Contrary to the literature, maximum NOx storage was not seen at around 380°C for either case. Similar behavior was also reported by Fridell *et al*. (1999).

A series of K_2O/Al_2O_3 catalysts containing different K loadings (in the range 0–25 wt. %) was prepared and tested for NO storage. The objective was to investigate the effect of metal loading on the storage process. Accordingly, the role of the K loading on the storage of NOx could be analyzed. Figure 5 shows the NO storage performance of the catalyst as a function of K_2O loading. Supporting 5–10 wt %

Figure 4. Percentage of NO storage onto $BaO(10)/Al_2O_3$ and $K_2O(10)/Al_2O_3$ as a function of reaction temperature.
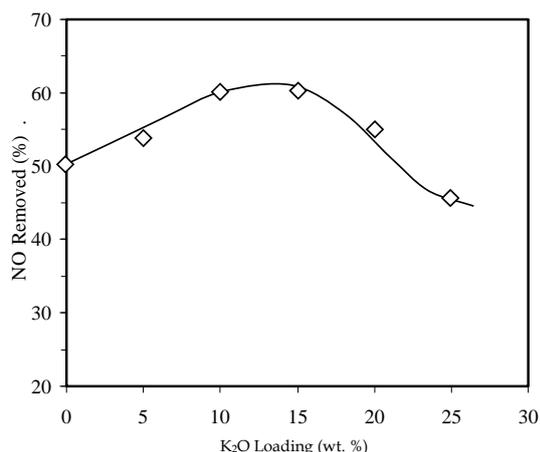
Figure 5. Amount of NO storage for different K$_2$O loadings in K$_2$O/Al$_2$O$_3$ catalyst.

of K$_2$O on Al$_2$O$_3$ was found to improve the lean NO storage activity of Al$_2$O$_3$, but the incorporation of 15 wt % K showed no significant improvement in the storage activity. The further addition of K$_2$O proved to be detrimental to the performance of the catalyst. Westerberg and Fridell (2001) proposed that K$_2$O could play an important role as a storage site at temperatures below 300°C.

As the loading of the catalysts increased, the activity increased as indicated by the percentage of NO storage. The highest NO storage over K$_2$O/Al$_2$O$_3$ occurred when K contents were between 10–15 wt %. However, beyond that, the percentage of NO storage started to decreased, probably due to the diffusion limitations at higher loading. These data were in agreement with some of the literature (Bethke *et al.* 1995; Castoldi *et al.* 2004; Milt *et al.* 2003a). The decrease in activity for the higher loading samples was also attributed to the dissolution of some amount of K(NO$_3$) during the impregnation process and caused higher K coverage of the Al$_2$O$_3$ surface (Castoldi *et al.* 2004; Dawody *et al.* 2004). Both K and Al$_2$O$_3$ were able to react with NO$_2$-forming nitrates species. Both K$_2$O(5)/Al$_2$O$_3$ and K$_2$O (20)/Al$_2$O$_3$ produced NO retentions lower than, or similar to, pure Al$_2$O$_3$. In this way, K$_2$O (10)/Al$_2$O$_3$ showed the highest stability for nitrate species among the K(x)/Al$_2$O$_3$ formulations studied.

The effect of the addition of BaO to the K$_2$O(x)/Al$_2$O$_3$ system was studied with the objective of improving the interaction with NO molecules and improving the catalytic activity for the NO storage reaction by increasing the formation of surface NO intermediates.

Activity studies were performed on K$_2$O(3)BaO(7)/Al$_2$O$_3$, K$_2$O(5)BaO(5)/Al$_2$O$_3$ and 1K$_2$O(7)BaO(3)/Al$_2$O$_3$. The amounts of NO stored are shown in Table 4.

First, the presence of Ba led to lower NO storage activity for K$_2$O(3)BaO(7)/Al$_2$O$_3$. By increasing the loading of potassium into these catalysts, an increase in the activity could be observed. The highest NO storage over Ba,K/Al$_2$O$_3$ occurred when the loading of both metals was equal (i.e. K$_2$O (5)BaO(5)/Al$_2$O$_3$). The K$_2$O(7)BaO(3)/Al$_2$O$_3$ catalyst presented an activity similar to K$_2$O (10)/Al$_2$O$_3$, which was in agreement with results reported by Matsumoto, 2004. The combination of the Ba and K loading resulted in a catalyst capable of showing improvement in the catalytic activity compared to single metal loading, and may be attributed to some synergistical effects between these two metal oxides. The catalyst behavior was influenced by three factors: ion size, alkalinity of the element, and preservation of the original surface area and porosity of the Al$_2$O$_3$. The heavy element Ba produces fewer Ba++ ions than the lighter element K+. The presence of more K+ ions can give K/Al2O3 better reactivity for NOx storage.

4. Conclusion

The NO storage amount in a lean exhaust stream was dependent on the basicity of the storage compounds. K$_2$O/Al$_2$O$_3$ catalyst was found to be the more active for the NO storage process than BaO/Al$_2$O$_3$. The NO storage capacity for K$_2$O(10)/Al$_2$O$_3$ also decreased with increasing temperature, especially at above 300°C. The NO storage process achieved its maximum at an intermediate temperature (250°C) for K$_2$O(10)/Al$_2$O$_3$. As for BaO(10)/Al$_2$O$_3$, the NO storage capacity increased with increase in operating temperature. The effect of K loading 0-25 % (w/w) in the storage over K$_2$O/Al$_2$O$_3$ samples was investigated and the results indicated that the addition of K$_2$O negatively affected the morphological properties of the catalyst system at loading higher than 15 %. Nevertheless, the increase in the K$_2$O loading resulted in a strong increase of the NO adsorption at breakthrough. Under these conditions, a maximum value of NO storage of around 60% was observed for the K(15)/Al$_2$O$_3$ sample. Significant amounts of NO were found to be stored in the catalysts

Table 4. Amount of NO storage over different storage composition in lean phase at a temperature of 350°C and reaction time of 20 min.

Catalyst	NO Concentration (ppm)		Amount of NO stored (%)
	$(C_{NO})_{in}$	$(C_{NO})_{out}$	
$K_2O(3)BaO(7)/Al_2O_3$	988	514.1	48.0
$K_2O(5)BaO(5)/Al_2O_3$	996	339.2	65.9
$K_2O(7)BaO(3)/Al_2O_3$	1012	422.6	58.2

containing $K(5)-Ba(5)/Al_2O_3$. The combination of Ba and K loading in catalyst led to an improvement in the catalytic activity compared to single metal catalyst.

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