Development of Synergic Mixed Metal Oxides for the Combined Catalytic-Absorptive Removal of Nitric Oxide from Diesel Exhaust

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ABSTRACT: *The NO removal over oxide sorbents (K_2O/Al_2O_3, CaO/Al_2O_3 and BaO/Al_2O_3) at a loading of up to 25 wt.% was investigated using a synthetic diesel exhaust gas containing 1,000 ppm NO, 1000 ppm iso-butane (i-C_4H_{10}), 8% O_2 and N_2 balance. The reactor was operated at 250 ^oC to 450 ^oC for the activity study. NO was effectively stored (removal efficiencies between 30-60 %) as nitrate under experimental conditions after surface oxidation to NO_2; and the maximum removal efficiency decreased in the order of K_2O/Al_2O_3 (55.4 %) > BaO/Al_2O_3 (39.0 %) > CaO/Al_2O_3 (37.0 %). K_2O/Al_2O_3 had higher mobility; but loadings higher than 15 wt.% were detrimental to the morphological properties. Despite higher basicity, CaO/Al_2O_3 showed lower removal efficiency of NO compared to $BaO(10)/Al_2O_3$ due to low catalytic NO_2 formation activity. Unlike $K_2O(10)/Al_2O_3$, $BaO(10)/Al_2O_3$ showed increasing NO removal between 350 ^oC and 450 ^oC. $K_2O(5)BaO(5)/Al_2O_3$ resulted in better surface area and volume leading to about 65 % of NO removal. This was attributed to synergic effects between physicochemical, catalytic and NO removal properties of the components. The high performance of $K_2O(5)BaO(5)/Al_2O_3$ was successfully elucidated based on the characteristics of the sorbent.*

KEY WORDS: *Diesel exhaust, Nitric oxide removal, Sorbent, Mixed oxides, Synergy.*

INTRODUCTION

Diesel-powered engines have better fuel economy than stoichiometric gasoline engines. However, they have many adverse environmental effects, particularly on the excessive nitrogen oxides (NOx) exhaust emission.

Due to the lean burn combustion in the engine, the exhaust gas also contains an excessive amount 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 [1].

NOx Storage and Reduction (NSR), which is sometimes referred to NOx catalytic adsorption and lean NOx trap, have been developed as a promising alternative method to remove NOx from diesel engine emission [2, 3]. These catalytic systems operate in a cyclic manner in which during the operation period of lean reductant (conventionally NH_3, CO or hydrocarbons), the NOx is trapped in the dual-function catalyst-sorbent and stored as 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 in the meantime, the sorbent is regenerated [3]. The NOx trapping materials can be found among the alkali (K, Mg, Ca) and alkaline earth metal (Ba, Li) oxides, in which BaO has been most extensively studied [4-7]. The reaction is generally a non-catalytic acid-base neutralization process to form nitrates but the presence of nitric oxide (NO) will necessitate its catalytic conversion to nitrogen dioxide (NO_2) prior to the storage as nitrates. With this respect, most literature reports focus on single metal oxide sorbents. However, due to different catalytic and storage behaviors of various oxides, the use of mixed metal oxides could offer some interesting advantages.

In general, metal oxides show different efficiencies in storing NOx as nitrates that eventually have different stabilities in the sorbents. As a result, the sorbents generally possess different operation windows (generally occur in a very narrow range) for high NOx removal efficiency. Therefore, the efforts to determine the right type and loading of oxides, or possible combination of oxides in the sorbent should be intensified. The sorbent composition with the right metal oxide composition that results in high NOx removal efficiency is to be sustained over a wider temperature range and other operating conditions. Furthermore, most literature reports focus on NO_2 removal while data on NO removal are still very scarce. The oxidation of NO to NO_2 prior to storage as metal nitrate in the sorbent could result in significant difference in the behavior of the deNOx system.

The objective of this work is to investigate the performance of oxides of K, Ba and Ca supported on Al_2O_3 as the sorbent for the removal of NO in diesel engine exhaust. The efficiency of the process was studied using single and combined oxide sorbent systems with the main objectives of identifying the right combination as well as the right composition of the mixed metal oxide sorbents. The sorbents were characterized to elucidate its specific physicochemical properties leading to differences in their observed catalytic behavior. The behavior of the NO removal process was also elaborated to identify the most active and efficient mixed metal oxides to store NO from diesel engine exhaust gas successfully.

EXPERIMENTAL SECTION
Sorbent preparation

Several metal oxides i.e. oxides of barium (Ba), calcium (Ca) and potassium (K) were studied for their effectiveness in the removing of NOx as nitrates during the lean reductant stage of the deNOx process. Alumina (Al_2O_3) was used as the support in this study. The introduction of active metals was carried out through a wet impregnation method using respective metal nitrates as the precursors and stirred for 2 h at room temperature. After evaporating the solvent at 100 ^{o}C, the sample was dried at 110 ^{o}C overnight and finally calcined in air at 500 ^{o}C for 2 h. For the preparation of mixed metal oxide sorbents, co-solutions of metal nitrates at suitable concentrations were used. A fraction with particle sizes between 425 and 600 µm was obtained by pressing, crushing and then sieving. The sorbents synthesized are denoted $M_1(m)M_2(n)/Al_2O_3$ where m and n represent the weight composition of the metal oxides (M_1 and M_2, respectively) in the sorbent.

Experimental set up

The experimental set up used for activity study consisted of N_2, O_2 and NO (5,000 ppm of NO in N_2), the flow rates of which were controlled by means of mass flow controllers (MKS). The reactor was made of 20 mm i.d. stainless steel tube. The pressure drop across the reactor was negligible under the normal operating conditions. A thermocouple type K (Cole-Palmer-88500-10) 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 to 450 $^{\circ}$C) were achieved by means of a horizontal tubular furnace (Linberg-TF-55035C).

The feed gas components were mixed at desired individual flow rates so that the final feed gas to the reactor system comprised of 1,000 ppm NO, 1,000 ppm of iso-butane (i-C_4H_{10}), 8% O_2 and balance N_2. NOx concentrations in diesel exhausts greatly vary depending on type of engine used, engine load, fuel quality, engine maintenance, etc. Typically, they are reported to be in the range between 100 and 2,200 ppm. As such, a concentration of 1,000 ppm, used in this study, was well within the realistic range. The i-C_4H_{10} component that was purposely included in the feed was used as a model hydrocarbon compound that was expected to act as a reductant in the catalytic NOx removal process.

The NO storage activity of the sorbents was evaluated at atmospheric pressure with a total feed flow rate of 50 mL/min. 200 mg of sorbent was placed 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 min to remove excess oxygen. The feed gas mixture was fed into the system at 50 mL/min and the reactor was heated to the desired reaction temperature before the measurement of gases concentration was made. The feed gas mixture was first allowed to react and chemically stored in the sorbent component for about 20 min before the concentration of gas at the reactor outlet was measured.

The deNOx system was actually operated in an unsteady state condition which was similar to a continuous adsorption process. However, the outlet gas composition was virtually constant between 10 and 40 min on stream as stable gas flow pattern in the reactor was already reached but the breakthrough was yet to occur. Thus, 20 min was set before the concentration measurement was made. These experimental conditions would give a NO removal efficiency of between 30 and 70 % so that the comparison of performance between various sorbent compositions could be made. Therefore, the performance of the sorbent could be rapidly evaluated without the need to actually complete the breakthrough curve (or the outlet NO concentration was equal to that in the inlet gas), a process that could take few hours with the experimental conditions used in the present study.

Focus in this work is mainly dedicated to sorbent development. As such, the experimental conditions for the NO removal process were purposely selected to give NO removals between 30-70 %. In this case, difference in the removals by various materials tested, could be easily seen. In actual operation, higher removals can be easily achieved by using more sorbent in the system, smaller particle size sorbent, lower NO concentration in the feed, lower flow rate (or gas hourly space velocity), etc.

An on-line Gas Chromatography (GC) (Shimadzu GC 8A) was used for the analysis of the feed and product gases. The GC unit was operated in an isothermal condition (80 $^{\circ}$C) with helium as the carrier gas. The GC used was equipped with a thermal conductivity detector, two separating columns and an integrator. A Molecular Sieve 5A (MS 5A) column (Supelco) was used for separating N_2, O_2 and i-C_4H_{10} while Porapak Q column (Supelco) was used for the analysis of NO and CO_2. The presence of NO_2 in the product gas was detected using an Enerac 2000 gas analyzing system.

Characterization of sorbents

Pore volume, surface area and average pore diameter of synthesized sorbents were measured using a Micromeritics (ASAP 2000) surface analyzer. The samples were first dried overnight at temperature of 105°C and degassed for 12h under vacuum at temperature of 300°C before performing the measurement. SEM studies were performed using Leica Cambridge Stereoscan 360 and UK and Polaron was used for the coating system (sputter coating). Before scanning, the powder samples were spread onto a double-side carbon tape, and coated with gold (20-30 nm thickness) in order to increase the conductivity and therefore improving the quality of the results. The fresh and aged sorbent samples obtained in this study were also characterized for the composition analysis using a Perkin Elmer 2400 elemental analyzer. This measurement was made on the used sorbent after 1h on stream at the desired reaction temperatures.

RESULTS AND DISCUSSION
Development of mixed metal oxides sorbents

Table 1 compares the activity of three different types of metal oxide trap sorbents in the NOx removal process. The adsorption of NO on the alumina support at such high temperature was negligible as it was expected to desorb completely at above 220°C as revealed

Table 1: NO removal efficiency by different sorbents and their elemental compositions after 1h on stream.

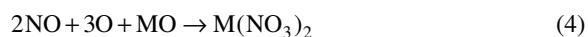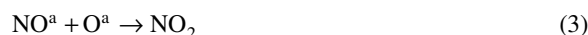| Sorbent	NO removal (%)[a]	Elemental composition of used sorbent (wt. %)[b]		
		Nitrogen	Carbon	Hydrogen
$BaO(10)/Al_2O_3$	39.0	1.88	0.78	0.50
$K_2O(10)/Al_2O_3$	55.4	1.83[c] 2.08	0.54[c] 0.50	0.66[c] 0.57
$CaO(10)/Al_2O_3$	37.1	0.79	1.34	0.98

a) Measured after 20 min on stream at 350 °C.

b) Measured after 1 h on stream at 350 °C, unless otherwise specified..

c) Measured after 1 h on stream at 250 °C.

by *Piacentini et al.* [8] and *Jimenez et al.* [9]. For each experiment, the measured concentration of NO in the outlet gas was significantly lower than that in the inlet gas, suggesting the removal of the NO in the sorbent. These results indicated that, NO was continuously stored on the sorbent under the lean conditions which meant that the contact time in the bed was sufficiently long to allow interaction between the acidic gas and the metal oxides. In the presence of 8 % O_2, K_2O/Al_2O_3 was the most active metal oxide for the removal of NO while CaO/Al_2O_3 showed the lowest efficiency. The performance was quite similar to that reported by *Lietti et al.* [5] using Pt-Ba/γ-Al_2O_3.

In order to compare the NO removal capability by different metal oxides, the mechanism for the formation of nitrates needs to be fully understood. It is reported in the literature that the formation of NO_2 from the reaction between NO and O_2 is a necessary initial step before NOx removal can take place during lean conditions [10, 11]. However, this simple step includes several uncertainties and it could be as a sum of several elementary reaction steps [11]. NOx removal process for lean conditions can be assumed to comprise the following steps with MO as active component in the sorbent:

$$NO^g \rightarrow NO^a \tag{1}$$

$$O_2{}^g \rightarrow 2O^a \tag{2}$$

$$NO^a + O^a \rightarrow NO_2 \tag{3}$$

$$2NO + 3O + MO \rightarrow M(NO_3)_2 \tag{4}$$

$$2NO_2 + O + MO \rightarrow M(NO_3)_2 \tag{5}$$
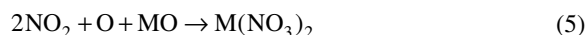
The superscript 'g' refers to gas form while superscript 'a' refers to chemisorbed form of the

chemical compound. This is somewhat a simplified reaction scheme. For example, NO_2 adsorption and desorption are not included [11]. A key role of the sorbent surface was found to be the oxidation of NO to NO_2 [12]. In this study, no NO_2 was detected in the product stream to indicate that the adsorbed species were extremely reactive and short-lived.

The order of basicity strength is $K_2O>CaO>BaO$ [6]. Therefore, the result in Table 1 generally suggests that the stronger the basicity of the NO storage component, the higher the affinity towards interaction with NO to result in higher amount of NO stored. This observation complemented the findings by *Takahashi et al.* [4] when they comparatively analyzed CoO and BaO. The behavior was attributed to the higher stability of nitrates formed by oxides of stronger basicity, with condition that the amount stored was greatly influenced by the net reaction between the formation and the decomposition of nitrates at high temperatures. Despite having higher basicity, potassium was also reported to favor the adsorption of NO [8] and it possessed the surface mobility to facilitate the oxidation of NO to NO_2 prior to the formation of nitrate [6]. The KNO_3 has a melting point of 334 °C and therefore it is presented in a liquid state at a reaction temperature of 350 °C, while the decomposition of this nitrate generally occurs at above 400 °C. However, it could be inferred that CaO was not so efficient in catalyzing the oxidation process compared to BaO. This conclusion was based on the lower removal efficiency by CaO despite having higher basicity than BaO. The difference between NO removal capability of CaO and BaO was quite minimal as the higher catalytic activity of BaO could have been offset by its inefficiency in the subsequent formation of nitrate [5].

The elemental analysis was conducted on the spent sorbents and the composition of carbon, hydrogen and nitrogen content is also shown in Table 1. The results for the aged $K_2O(10)/Al_2O_3$ sorbent marked with superscript 'c' were obtained at a reaction temperature of 250 ^{o}C while the others were obtained at 100 ^{o}C and higher tempratures. The higher reaction temperature was found to increase the nitrogen content of $K_2O(10)/Al_2O_3$ to provide the indication of more nitrate formation at 350 ^{o}C. Thus, 250 ^{o}C was deemed to be insufficiently high to cause optimum chemisorption of NO to initiate the reaction leading to the formation of nitrate. Almost similar observation was reported by *Lietti et al.* [5] in their study by incorporating active component for the oxidation (Pt) in Pt-BaO/Al$_2$O$_3$. Some differences in their study could be due to the improved oxidation of NO by Pt prior to nitrate formation. The order of nitrogen content in these three aged sorbents was also found to be consistent with the result on NO removal efficiency as shown in Table 1.

The existence of the carbon and hydrogen in the aged sorbents was caused by the oxidation of the hydrocarbon (i-C$_4$H$_{10}$) in the feed gas by high temperatures (> 250 ^{o}C) leading to the formation of some carbonaceous materials [13]. Extra hydrogen content was deemed to be caused by the hydrated water in the metal nitrates and it was greatly influenced by the amount of nitrates formed. CaO(10)/Al$_2$O$_3$ was found to accumulate the highest amount of carbon which showed it was the most active sorbent in promoting the formation of polyaromatic carbonaceous materials during the oxidation of i-C$_4$H$_{10}$.

As K$_2$O was identified to be the most active oxide among the three tested, a series of K$_2$O/Al$_2$O$_3$ sorbents containing different K$_2$O loadings (0-25 wt. %) were prepared and tested for NO removal. The objective was to investigate the effect of metal loading on the NO removal process. Accordingly, the role of the K$_2$O loading on the removal of NO could be analyzed. Fig. 1 shows the NO removal performance of the sorbent as a function of K$_2$O loading.

The incorporation of 5-10 wt. % of K$_2$O onto Al$_2$O$_3$ was found to improve the lean NO removal activity of Al$_2$O$_3$, but further increase to 15 wt. % K$_2$O did not bring about the desired effect with respect to the NO removal activity. A drop in activity was experienced with K$_2$O loadings beyond 15 wt. %. This observation was attributed to the progressive blockage of the pore system
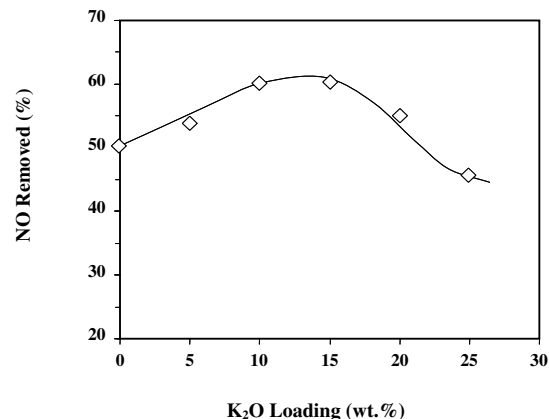

Fig. 1: NO removal efficiency for different K$_2$O loadings in K$_2$O/Al$_2$O$_3$ sorbent.

of support surface by K$_2$O phases causing significant drop in the available surface area. The same observation was also noted at about 16.7 wt. % of BaO supported on CeO$_2$ [8]. In addition, larger K$_2$O crystallites could readily be formed at higher metal loading. *Westerberg et al.* [14] proposed that K$_2$O could play an important role as a NO trapping site only at temperatures below 300 ^{o}C. Thus, the behavior specifically to K$_2$O and BaO on Al$_2$O$_3$ was investigated next since Al$_2$O$_3$ support usually gives better NOx removal compared to SiO$_2$ and ZrO$_2$ [8], attributed to higher surface area and lower macroporosity.

Consistent with a report by *Milt et al.* [6], as the loading of the sorbents was increased, the NO removal activity was also found to be increased. The highest NO removal by K$_2$O/Al$_2$O$_3$ occurred when K$_2$O contents were between 10-15 wt. %. However, beyond that, the percentage of NO removal started to decrease, apparently due to the diffusion limitations and the packing of metal oxides crystals at the pore mouth at higher loading. As the interconnected pores in Al$_2$O$_3$ were quite limited [15], the blockage of pore mouth would result in drastic change in the catalytic activity. This data was in close agreement with literature reports utilizing BaO [14], K$_2$O [12] and CoO [6]. However, the optimum level of metal oxide occurred at different loadings, depending on the preparation method, types of support and type of oxide used.

The decrease in the activity of higher loading of sorbent samples was also attributed to the size of the metal oxide crystals in which smaller crystals, usually achieved at lower metal loading, were generally preferred [15, 16].

Reaction between metal oxide and NO_2 to form metal nitrates would occupy more volume, which could be the detriment of subsequent reaction that led to nitrate formation. As no significant improvement was achieved by increasing the K_2O loading beyond 10 wt. %, this loading was considered the optimum for further investigation.

As noted previously, K_2O was found to be the most active for NO removal followed by BaO. Thus, it is of great interest to investigate the difference in the behavior of these two oxides. In the next study, the dependence of the reaction on the temperature was investigated. For this purpose, sorbent $BaO(10)/Al_2O_3$ and $K_2O(10)/Al_2O_3$ were evaluated on a catalytic reactor rig to reveal their behavior as a function of temperature in the range of 200-450 $^{\circ}$C. Both metal oxide sorbents were prepared and tested under the same reaction conditions.

Fig. 2 shows the results of the temperature dependence of the catalytic activity under lean conditions. The maximum NO removal catalyzed by $K_2O(10)/Al_2O_3$ of circa 58 % occurred at 250 $^{\circ}$C. However, it was observed that NO removal reaction decreased with temperature increment up to 450 $^{\circ}$C. As reported by *Fridell et al.* [11], the decrease in NO removal at higher temperature was associated to instability of metal nitrate at high temperature. In contrast to the $K_2O(10)/Al_2O_3$ sorbent, $BaO(10)/Al_2O_3$ sorbent demonstrated increasing NO removal at higher temperature and the lean feed showed peak steady-state NOx removal of approximately 48 % at 450 $^{\circ}$C. This behavior was claimed to be contributed by the formation of $BaCO_3$ through the reaction between BaO and CO_2 which was increasingly generated from the oxidation of i-C_4H_{10}. $BaCO_3$ is able to store NO through the following reaction [8].

$$BaCO_3 + 2\,NO + 3/2\,O_2 \rightarrow Ba(NO_3)_2 + CO_2 \qquad (6)$$
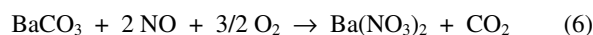
This reaction generally occurs significantly at a reaction temperature higher than 350 $^{\circ}$C.

$BaO(10)/Al_2O_3$ sorbent showed higher NO removal activity than $K_2O(10)/Al_2O_3$ sorbent at higher temperatures, particularly above 400 $^{\circ}$C. In another study, *Xiao et al.* [17] reported the optimum NOx conversion of about 30 % with $Mn/Ba/Al_2O_3$. These suggested the ionic bonding character of the $Ba(NO_3)_2$ that generally increases with increasing temperatures [18].
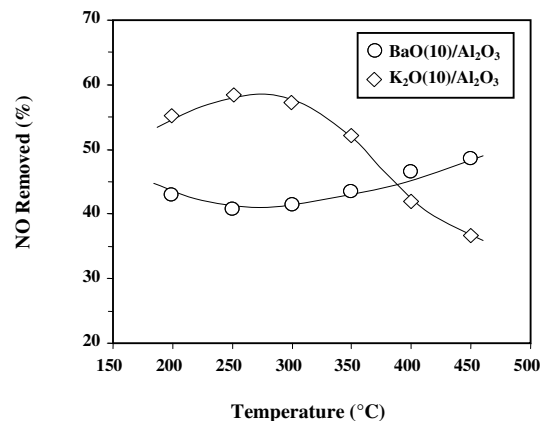
Results in Fig. 2 indicate that a combination of

Fig. 2: NO removal efficiency by $BaO(10)/Al_2O_3$ and $K_2O(10)/Al_2O_3$ as a function of reaction temperature.

K_2O and BaO could result in a sorbent that has better NO removal efficiency over a wider operating temperature window. Therefore, the effect of the addition of BaO to $K_2O(x)/Al_2O_3$ sorbent was then studied. Considering that BaO has better NO oxidation efficiency than K_2O especially at higher temperatures, while K_2O has good NO_2 storing capacity, the synergic effects of these mixed metal oxides were investigated. Activity studies were performed with $K_2O(3)BaO(7)/Al_2O_3$, $K_2O(5)BaO(5)/Al_2O_3$ and $K_2O(7)BaO(3)/Al_2O_3$ i.e. by maintaining the total metal oxide loading at 10 wt.% and the performances were compared with the data obtained with $K_2O(10)/Al_2O_3$ and BaO/Al_2O_3.

The amounts of NO stored by different sorbents are summarized in Table 2. It was noted that the presence of 3 wt. % and 5 wt. % of BaO in $K_2O(m)BaO(n)/Al_2O_3$ led to an improvement in NO removal by about 3 % and 10 %, respectively. The highest NO removal occurred when the loadings of both metals were equal (i.e. $K_2O(5)BaO(5)/Al_2O_3$). It should be highlighted that this efficiency was even higher than that catalyzed by $K_2O(10)/Al_2O_3$ or $BaO(10)/Al_2O_3$ alone. This result gave an indication of synergic effects occurrence between K_2O and BaO components of the sorbents. Further increase in BaO content beyond 5 wt. % resulted in a detrimental effect to the NO removal efficiency. However, the presence of 3 wt. % of K_2O at high BaO content of 7wt.% in $K_2O(3)BaO(7)/Al_2O_3$ significantly improved the NO removal activity as compared to single oxide BaO sorbent. It should be noted that the improvement by

3 wt.% of BaO to the K_2O sorbent was more pronounced compared to that of 3 wt. % K_2O to the BaO sorbent.

The synergic effects between K_2O and BaO components of the sorbents could be explained based on the understanding of the mechanism in the NO removal. The two steps involved are the oxidation of NO to NO_2 and the acid-base neutralization reaction between the NO_2 and the metal oxide [11]. BaO was a better sorbent to promote the NO oxidation while the absorption of NO_2 to form nitrate was better on K_2O. Thus, in the presence of BaO, more surface NO_2 formed to subsequently react in the second stage reaction to form nitrate. However, it should be considered that the melting points of KNO_3 is at 334 °C and its decomposition occurred relatively lower at temperature above 400 °C against 592 °C for $Ba(NO_3)_2$ decomposition [5]. Since KNO_3 is more mobile on the surface than a relatively denser $Ba(NO_3)_2$ (the density of $Ba(NO_3)_2$ is 3.24 g/mL against 2.11 g/mL for KNO_3), KNO_3 formation would not block the subsequent reaction between the K_2O or BaO with NO_2 at reaction temperature of 350 °C.

The increment of BaO composition in the sorbent up to 5 wt. % resulted in higher NO removal. This was attributed to the more stable nitrate formation with BaO. Moreover, the BaO was relatively denser and hence, occupying less volume on the surface. As a consequence, the pore mouth blockage could be minimized. However, beyond the optimum composition of 5 wt. % of K_2O and BaO, a decrease in the NO removal efficiency was observed due to less basicity of BaO to react with NO_2 despite forming a more stable nitrate. The higher activity of $K_2O(3)BaO(7)/Al_2O_3$ compared to $BaO(10)/Al_2O_3$ simply proved the advantage of having surface mobility species in capturing NO_2.

Characterization of K-Ba sorbents

As $K_2O(5)BaO(5)/Al_2O_3$ was found to be most active metal oxides for NO removal, it was further characterized to understand its physicochemical characteristics leading to its high activity. For comparison, the most active single metal oxide i.e. $K_2O(10)/Al_2O_3$, was also tested for comparison while Al_2O_3 was used as the control. Fig. 3 shows nitrogen adsorption-desorption isotherm of those materials. $K_2O(10)/Al_2O_3$ showed type III isotherm while Al_2O_3 and $K_2O(5)BaO(5)/Al_2O_3$ showed isotherms approaching type II which were typical for mesoporous

Table 2: NO removal efficiency over different storage compositions of the sorbent in lean phase

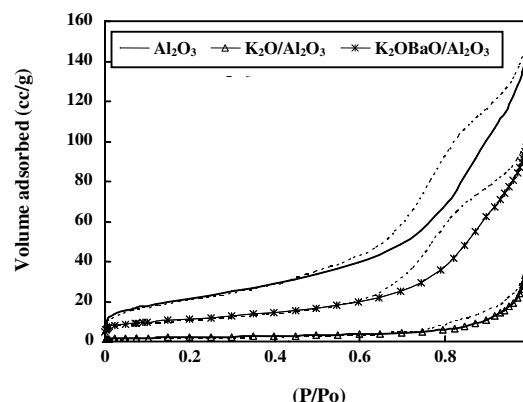| Sorbent	NO Removal (%)
$K_2O(10)/Al_2O_3$	55.4
$K_2O(7)BaO(3)/Al_2O_3$	58.2
$K_2O(5)BaO(5)/Al_2O_3$	65.9
$K_2O(3)BaO(7)/Al_2O_3$	48.0
$BaO(10)/Al_2O_3$	39.0

Fig. 3: Nitrogen adsorption (solid line) and desorption (dotted line) isotherm of alumina-based sorbents.

solids [19]. The isotherms were characterized by a rather rapid nitrogen uptake (a 'shoulder') at low pressure ($P/P_o<0.1$) followed by a slow uptake at medium pressure while rapid uptake was observed at high pressure. As the relative pressure increased to above 0.7, 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. $K_2O(10)/Al_2O_3$ showed smaller hysteresis loop and it occurred at relatively higher P/P_o as compared to the other two materials. Significant reduction in the amount of nitrogen adsorbed by the two oxide sorbents compared to the control was also noted. However, it was interesting to note that the adsorbed amount in $K_2O(10)/Al_2O_3$ was relatively lower than that of $K_2O(5)BaO(5)(10)/Al_2O_3$.

The surface characteristics and porosity in terms of BET surface area, pore volume and average pore diameter of the sorbents are given in Table 3.

Table 3: BET surface area, pore volume, average pore diameter of alumina-based sorbents.

Sample	Surface area (m^2/g)	Mesoporous area (%)	Microporous area (%)	Pore volume (ml/g)	Average pore size (nm)
Al_2O_3	77.3	95	0	0.28	10.8
$K_2O(10)/Al_2O_3$	17.5	78.1	1.8	0.04	21.6
$K_2O(5)BaO(5)/Al_2O_3$	39.5	89.2	10.8	0.14	13.9

$K_2O(10)/Al_2O_3$ and $K_2O(5)BaO(5)/Al_2O_3$ showed lower surface area and pore volume compared to unloaded Al_2O_3 support. This was indeed an expected finding as both impregnated metals filled up and plugged some of pores, resulting in less surface area available for nitrogen adsorption. These oxides also contributed to the weight of the sorbent, thus, lowering the surface area and pore volume measured on a weight basis. Impregnation with 10 wt. % K_2O resulted in 77 % decrease in the BET surface area while that of $K_2O(5)BaO(5)/Al_2O_3$ dropped by about 49 %.

Mesoporous pores constituted about 90% of the pores presented in the Al_2O_3 while the rest were made up by macropores. Its high fraction of mesoporous resulted in high pore volume (0.28 ml/g) compared to the other two materials. Impregnation of metal oxides resulted in marked drop in the mesopores, especially in $K_2O(10)/Al_2O_3$. The presence of micropores in these materials was attributed to the interparticle pores in the metal oxide matrix. It was noted that mixed combination of BaO and K_2O improved the microporosity, as those metal oxides had different crystal sizes of different densities which was proved by the higher pore volume of $K_2O(5)BaO(5)/Al_2O_3$ compared to that of $K_2O(10)/Al_2O_3$. The impregnation process also resulted in an increase in the average pore size which indicated that the loss of mesopores was accompanied by an increase in the macroporosity. This observation was attributed to the macrostructure of the metal oxides presented in the sorbents [14]. The pore size distributions (within micropore to mesopore ranges) of sorbents as illustrated in Fig. 4 also showed good agreement with results in Table 3. To support the agreement of these figures, all sorbents exhibited pore size peaks occurred within 5-10 nm which were actually in micro size range. However, mesopores of wide range of sizes could have shifted the average pore diameters to meso size range.
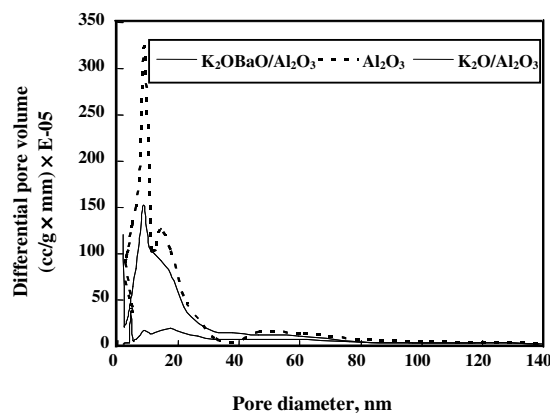
Fig. 4: Pore size distribution of alumina-based sorbents.

In the reaction between NO and the metal oxides, some differences in terms of the physical characteristics of the sorbents were expected. Therefore, the topological information of the aged $K_2O(10)/Al_2O_3$ and $(K_2O(5)BaO(5)/Al_2O_3$ sorbents was studied to investigate the physical changes of the sorbent that occurred with the formation of nitrates as well as to observe the effect of various operating temperature and possible coke compounds. These used sorbent samples were obtained by subjecting them to NO removal condition for 1h under a reaction temperature of 350 °C.

The topological information such as crystal structure and morphology of a fresh and spent $K_2O(10)/Al_2O_3$ and $K_2O(5)BaO(5)/Al_2O_3$ sorbents were studied using a Scanning Electron Microscope (SEM). Fig. 5(a) shows a SEM micrograph of fresh $K_2O(10)/Al_2O_3$ sorbent while Fig. 5(b) shows the SEM micrograph of the fresh $K_2O(5)BaO(5)/Al_2O_3$ sorbent. As noted in these figures, $K_2O(5)BaO(5)/Al_2O_3$ had a relatively clear crystalline shape compared to $K_2O(10)/Al_2O_3$. The sharp and fine spikes were therefore attributed to the crystal structure of the BaO component of the sorbent that played active roles in NO removal [11]. One could observe that the surface
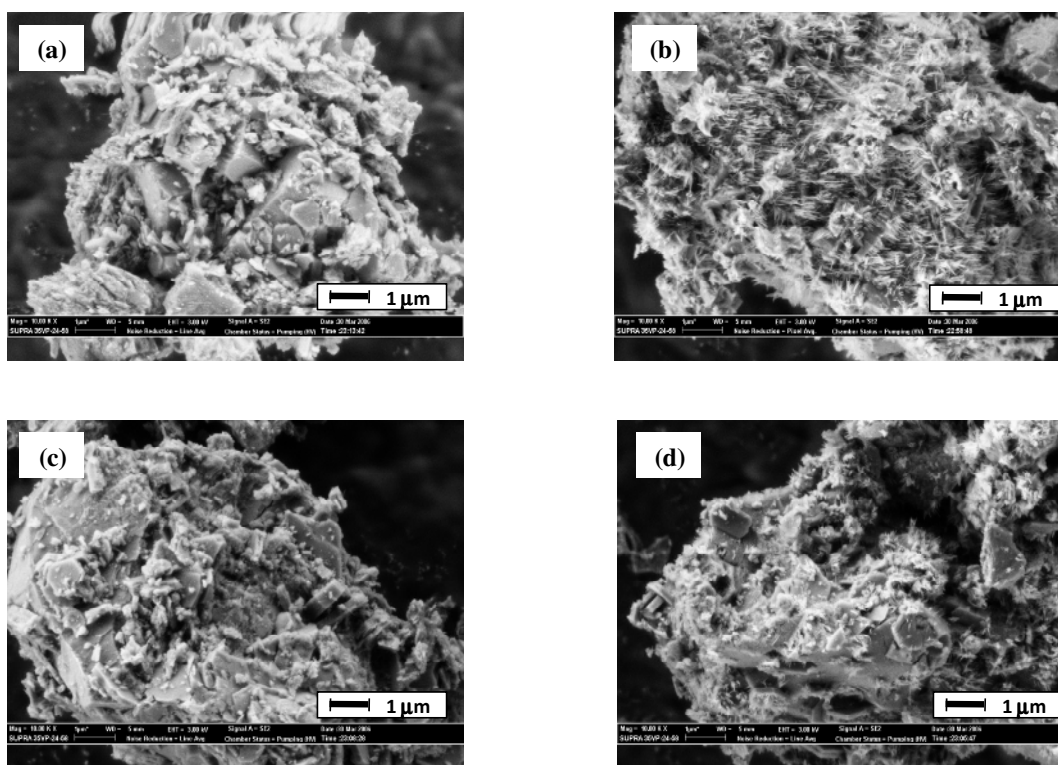
Fig. 5: SEM micrograph of fresh sorbents: (a) Fresh $K_2O(10)/Al_2O_3$, (b) Fresh $K_2O(5)Ba(5)/Al_2O_3$, (c) aged $K_2O(10)/Al_2O_3$ and (d) aged $K_2O(5)Ba(5)/Al_2O_3$.

of alumina in sample $K_2O(5)BaO(5)/Al_2O_3$ was more evenly covered by metal oxides as compared to sample $K_2O(10)/Al_2O_3$. With this special property, the shape of BaO crystals allowed the K_2O crystals to be dispersed over the surface area, which gave benefits to the materials acting as heterogeneous sorbent. The crystal structure of the metal oxide component in $K_2O(5)BaO(5)/Al_2O_3$ was resulted from the creation of secondary porosity as suggested by data in Table 3 and Fig. 4. This interesting observation on physical synergism between K_2O and BaO was hardly reported in the literature and was hypothesized to be partly responsible for the highly efficient performance in NO removal.

Figs. 5(c) and (d) show the SEM micrograph of aged sample of $K_2O(10)/Al_2O_3$ and $K_2O(5)BaO(5)/Al_2O_3$, respectively. As shown in the micrograph, there were some structural changes in different extents in both samples after being subjected to the NOx removal process. A minimal change was detected in aged $K_2O(10)/Al_2O_3$ which suggested

that KNO_3 crystal structure was almost similar to that of K_2O. No significant change was therefore expected in terms of the porosity of the material with respect to the reaction time. In contrast, the storage of NO as nitrate in $K_2O(5)BaO(5)/Al_2O_3$ led to the disappearance of sharp spikes on the surface. As the spikes were associated to the presence of BaO in the material, the disappearance of sharp spikes concluded that the BaO component was also actively involved in the removal of NO. The remaining BaO crystals presented in the sample also suggested that the reaction leading to nitrate formation was actually a non-selective reaction.

CONCLUSIONS

The NO removal efficiency was found to be dependent on the basicity of the trapping component. K_2O/Al_2O_3 sorbent with 10 wt. % metal loading was the most active for the NO removal with the performance decrease in the order of K_2O/Al_2O_3 (55.4 %) > BaO/Al_2O_3 (39.0 %) > CaO/Al_2O_3 (37.1 %). The NO

removal efficiency was optimum at around 250 ^{o}C for $K_2O(10)/Al_2O_3$ and significantly decreased at temperatures above 300 ^{o}C. On the other hand, the NO removal efficiency of $BaO(10)/Al_2O_3$ increased at temperatures above 250°C. The addition of K_2O negatively affected the morphological properties of the trap sorbent system at loadings above 15 wt. %. Despite higher basicity, CaO/Al_2O_3 showed lower NO removal efficiency compared to $BaO(10)/Al_2O_3$ due to low catalytic NO_2 formation activity. Unlike $K_2O(10)/Al_2O_3$, $BaO(10)/Al_2O_3$ showed increasing NO removal efficiency between 350 ^{o}C and 450 ^{o}C. $K_2O(5)BaO(5)/Al_2O_3$ resulted in better surface area and volume leading to about 65 % of NO removal. This was attributed to synergic effects between physicochemical, catalytic and NO removal properties of the components. Characterization of the $K_2O(5)BaO(5)/Al_2O_3$ revealed its suitable physicochemical properties that were associated with the high NO removal efficiency of the trap material.

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