

Optimization of NO_x Storage Performance through Modifying Catalyst Composition and Alumina Support

Xiaoyin Chen¹ and Johannes Schwank¹

John Li², William F. Schneider², Christian T. Goralski, Jr.² and Peter J. Schmitz²

¹*Department of Chemical Engineering, University of Michigan, 2300 Hayward, Ann Arbor, MI 48109-2136;* ²*Research and Advanced Engineering, Ford Motor Company, Dearborn, MI 48124*

Abstract The usage of lean-burn engines is a promising strategy for improving the fuel economy of vehicles and reducing the emission of greenhouse gas CO₂. The most complex challenge for lean-burn engines is the need to find a solution for the increased levels of NO_x emissions. Lean NO_x trap (LNT) or NO_x storage-reduction (NSR) catalysts provide a very effective method for NO_x removal in lean-burn gasoline engine exhaust. In this work, we will be focusing on the optimization of NO_x storage performance through modifying the catalyst composition in Ba-based NO_x storage catalytic materials. We intentionally prepared relevant Al₂O₃-supported BaO with modification of NO₂ storage component by addition of K₂O and MgO to widen the lean NO_x storage operation window. Other additives, such as La₂O₃ and TiO₂ were also added to modify support Al₂O₃ before loading of BaO-based storage component. The NO₂ storage and releasing characteristics for these catalytic materials with and without the presence of Pt were investigated using TG-IR. Other methods such as XRD and BET were used to characterize structural and surface properties. The roles of these materials are discussed in light of LNT performance.

1. Introduction

The usage of lean-burn engines is a promising strategy for improving the fuel economy of vehicles and reducing the emission of greenhouse gas CO₂. The most complex challenge for lean-burn engines is the need to find a solution for the increased levels of NO_x emissions (1). Lean NO_x trap (LNT) or NO_x storage-reduction (NSR) catalysts provide a very effective method for NO_x removal in lean-burn gasoline engine exhaust (2,3). For a typical model LNT containing Pt and Ba on alumina, NO is oxidized to NO₂ on the Pt sites, the NO₂ is then being trapped by the Ba to form barium nitrate under lean cycles. During rich cycles, the nitrate decomposes and the released NO_x is reduced on the Pt sites into N₂.

NO_x storage performance is one of critical steps in LNT lean-rich operation cycles because the storage capacity determines the operation strategy of the engine. It was found that the optimum NO_x storage and conversion on BaO-based catalytic material is about at 350°C (4,5). Many efforts have been made in order to increase NO_x conversion efficiency in the whole engine running temperature range to meet the future strict emission standards. One aim is to widen the operation temperature window through adjusting storage component composition by addition of alkaline element like K (4,6-8). It was also found that the NO_x storage-reduction performance could be improved by the modification of catalyst support (4,8,9). However, the relationship between NO₂ storage capacities and the component or support Al₂O₃ modification is still unclear.

On the other hand, it was found that NO_x storage capacity is strongly limited by the thermal stability of nitrate of the storage component (10,11). In other words, the thermal stability of nitrate influences NO_x conversion efficiency through controlling NO_x storage capacity: both depending on operation temperature. Our previous thermal stability study on γ -Al₂O₃-supported Ba(NO₃)₂ by the characterization of TG-IR showed that Ba(NO₃)₂ supported on γ -Al₂O₃ is in the form of two phases: dispersed and bulk-like. The mole ratio of the maximum dispersed amount of Ba species to alumina reaches 0.1, while the amount of bulk-like Ba species linearly increases with the increase of Ba(NO₃)₂ loading on γ -Al₂O₃. Only dispersed BaO and external surface BaO of bulk-like phase are attributed to NO₂ storage.

The objective of this work is to investigate the influences of BaO-based LNT catalyst on NO₂ storage capacity through composition modification by alkaline K₂O and alkaline earth MgO, and support γ -Al₂O₃ modification by weak basic oxide La₂O₃ and weak acidic oxide TiO₂. The NO₂ storage and releasing characteristics, and structural properties for these catalytic materials with and without the presence of Pt were investigated using TG-IR, XRD, BET, and FTIR. The modification influence was discussed with regard to thermal stability of nitrates of storage components.

2. Experimental

2.1. Material preparation

The support used in this work was γ -Al₂O₃, which was obtained through calcination of pseudo-boehmite G-450 (Alcoa World Chemical) at 600°C. For un-modified γ -Al₂O₃ samples, all nitrate precursors were loaded by direct wet impregnation onto γ -Al₂O₃ followed by drying at 120°C. The impregnation sequence is in the order of Ba(NO₃)₂, then KNO₃, and finally Mg(NO₃)₂ if applicable. A single impregnation was used for storage component oxide loading of 5-10% (w/w), and one additional impregnation and drying step was performed for each additional 10% (w/w) increase in loading.

For modified γ -Al₂O₃ sample preparation, γ -Al₂O₃ was modified at first by La₂O₃ with atomic ratio of La to Al of 0.01 or by TiO₂ with TiO₂ weight loading of 1.0%, respectively, before the impregnation of nitrate precursor. La₂O₃ modification on γ -Al₂O₃ was performed by impregnating La(NO₃)₃ solution followed by drying at 120°C and then calcination at 500°C. TiO₂ modification was done by impregnating iso-propanol solution containing iso-Ti(OC₃H₇)₄, followed by drying at 120°C and then calcination at 500°C.

For pure γ -Al₂O₃ or modified γ -Al₂O₃ with the presence of Pt (1%,w/w), Pt loading was performed by impregnation of H₂PtCl₄ solution onto γ -Al₂O₃ or modified γ -Al₂O₃ if applicable, followed by drying at 120°C and reduction by a 5%H₂/N₂ flow at 400°C for 2hr. Then 1%Pt/ γ -Al₂O₃ or 1%Pt/modified γ -Al₂O₃ was used to impregnate nitrates of storage components. All samples are listed in Table 1.

2.2 NO₂ storage

NO₂ storage was carried out in a continuous reaction system. Nitrate-loaded sample was heated at a heating rate of 10 °C/min under a He flow to 800°C for 0.1 hr to form M_xO (M_xO denotes either BaO, K₂O or MgO). Then the system was cooled down to 350°C, a mixing flow consisting of 1.00% (v/v) NO₂-2.80% O₂ with balance N₂ was fed into system for NO₂ stored on the storage component for 15min. After the NO₂ flow, a He flow was again fed through the bed to purge the sample for 10 min.

2.3 Release and measurement of stored NO₂ on M_xO/ γ Al₂O₃

Release of stored NO₂ on M_xO/Al₂O₃ was performed on a TG-IR system (Perkin-Elmer TGA-7 and Spectrum 2000) in the temperature range of 20-900°C under N₂ atmosphere. TG was used to record weight loss and weight loss rate (derivative weight loss) during TG heating due to thermal decomposition of nitrate, which was formed by NO₂ reacting with M_xO in the period of NO₂ storage at 350°C. Quantitative analysis of weight loss for NO₂ storage capacity (efficiency) can be expressed as the ratio of N₂O₅ to M_xO because M(NO₃)_{2/x} decomposes following the stoichiometry $xM(NO_3)_{2/x} \rightarrow M_xO + N_2O_5$ (x=1 for Ba and Mg, x=2 for K) where N₂O₅ denotes either 2NO₂+1/2O₂ or 2NO + 3/2O₂. TGA-7 was coupled, by means of a transfer line, to a gas cell that was located inside the TG-IR interface. Therefore, the concentration of involved gases, which were flushed into IR gas cell by purged N₂, was synchronal measured by IR.

2.4 Other characterizations of samples

The BET surface area and pore volume for γ -Al₂O₃ and modified γ -Al₂O₃ were performed on Micromeritics ASAP 2400 for N₂ isotherm adsorption at liquid N₂ temperature. XRD patterns for storage component loaded or unloaded samples were collected by Rotaflex RU-200B Series powder X-ray diffraction of Rigaku Roating Anode. Vibrational IR spectra for nitrate loaded and NO₂ stored sample were obtained in a Perkin-Elmer FT-IR Spectrum 2000 with KBr discs.

3. Results and Discussion

3.1 NO₂ storage capacity on BaO/ γ -Al₂O₃ with different BaO loadings

In our previous study, TG-IR experiment on thermal decomposition of Ba(NO₃)₂/ γ -Al₂O₃ showed that there were two distinctly separate decomposition peaks for dispersed and bulk-like Ba(NO₃)₂ phases on γ -Al₂O₃. The dispersed Ba(NO₃)₂ presented a decomposition 150°C lower than pure bulk Ba(NO₃)₂. And dispersed Ba(NO₃)₂ produces mainly NO₂ for the thermal decomposition, while bulk-like Ba(NO₃)₂ on γ -Al₂O₃ gives mainly NO gas product. Thermodynamic analysis suggested the difference between thermal decomposition temperature of dispersed and bulk-like Ba(NO₃)₂ on γ -Al₂O₃ is attributed to the induced solid interaction of support γ -Al₂O₃ and BaO, which results from dispersed Ba(NO₃)₂ decomposition. Further TG analysis was obtained through calculation of weight loss due to thermal decomposition. It was found through analysis of TG weight loss, as shown in

Figure 1, that the dispersion amount of Ba(NO₃)₂ on γ -Al₂O₃ reaches a maximum of a ratio of Ba species to γ -Al₂O₃ of close to 0.10 (mol/mol) with the loading increase of Ba(NO₃)₂. NO₂ storage capacity measurement at room temperature showed that only dispersed BaO and external surface BaO of bulk-like phase are responsible for NO₂ storage.

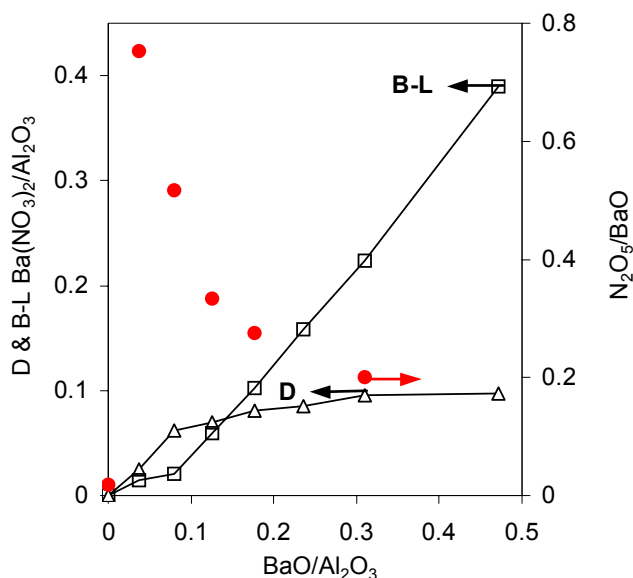


Figure 1. The relationship between dispersed (D, Δ) and bulk-like (B-L, \square) Ba(NO₃)₂ amount on γ -Al₂O₃, and NO₂ storage capacity (\bullet) at 350°C on these samples functioned with the mole ratio of BaO to Al₂O₃.

Table 1: Sample note for storage component and alumina modification.

Storage component	Without Pt			With Pt (Pt/Al ₂ O ₃ =1.0 wt-%)		
Basic sample	Ba	K	Mg	BaPt	KPt	MgPt
Component modification	Ba	BaK	BaKMg	BaPt	BaKPt	BaKMgPt
Alumina modification by La (La/Al=0.1, atomic ratio)	BaLa	BaKLa	BaKMgLa	BaLaPt	BaKLaPt	BaKMgLaPt
by Ti (TiO ₂ /Al ₂ O ₃ =1.0 wt-%)	BaTi	BaKTi	BaKMgTi	BaTiPt	BaKTiPt	BaKMgTiPt
Sample composition (M _x O/Al ₂ O ₃ , mole ratio)	BaO/Al ₂ O ₃ =0.11, K ₂ O/Al ₂ O ₃ =0.11, MgO/Al ₂ O ₃ =0.15 in single component, BaO/Al ₂ O ₃ =0.11, K ₂ O/Al ₂ O ₃ =0.06, MgO/Al ₂ O ₃ =0.15 in bi- and tri- component.					

Figure 1 also shows the release amount (NO₂ storage capacity, denotes as mole ratio of N₂O₅ to BaO) for NO₂ storage performed in this work at 350°C for 15min over these samples. The NO₂ storage capacity decreases with the increase of BaO loading on γ -Al₂O₃ and has a similar tendency to

reach saturation as dispersed $\text{Ba}(\text{NO}_3)_2$ goes in the range of $\text{BaO}/\gamma\text{-Al}_2\text{O}_3$ below 0.31. The storage capacity is 0.75, 0.52, 0.33, 0.28, and 0.2 responding to $\text{BaO}/\gamma\text{-Al}_2\text{O}_3$ mole ratio of 0.04, 0.08, 0.13, 0.18 and 0.31, respectively. The NO_2 storage efficiency goes down with the increase of mole ratio of BaO to Al_2O_3 and tends to be constant in the range of $\text{BaO}/\text{Al}_2\text{O}_3$ between 0.05-0.31. Because the fraction of dispersed Ba amount decreases with the increase of Ba loading, this suggests the dispersed BaO contributes to main storage capacity.

3.2 Influence of modification of storage component

A series of BaO -based modified samples with storage component and alumina modification, which are listed in Table 1, were prepared for NO_2 storage capacity comparison. The M_xO loading on $\gamma\text{-Al}_2\text{O}_3$ ($\text{M}_x\text{O}/\text{Al}_2\text{O}_3$, mole/mole) is 0.11 for BaO , 0.06 for K_2O and 0.15 for MgO , respectively.

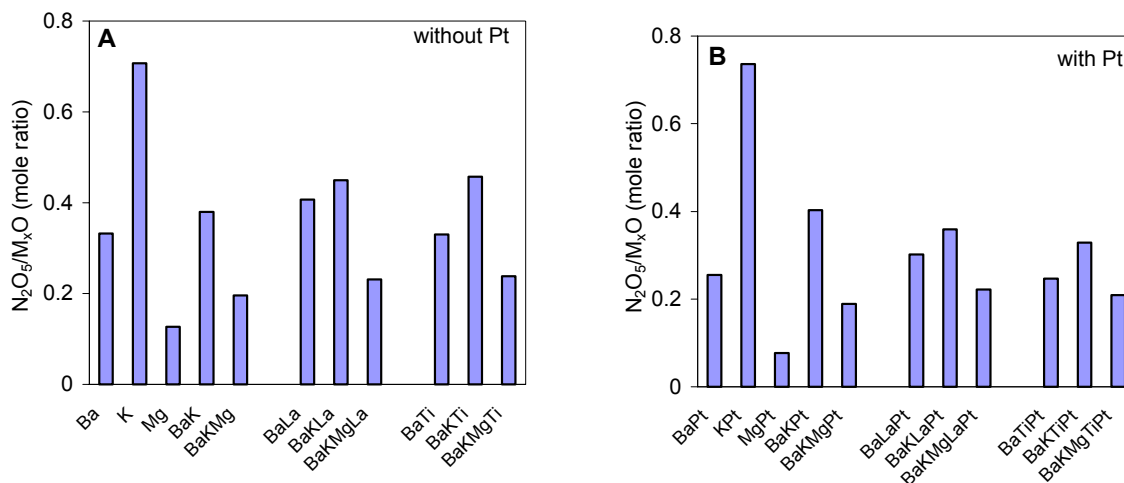


Figure 2. NO_2 storage capacity comparison after storage component modification.

Figure 2 compares the influence of BaO storage component modified by K and Mg elements on NO_2 storage efficiency ($\text{N}_2\text{O}_5/\text{M}_x\text{O}$) for storage components supported on un-modified $\gamma\text{-Al}_2\text{O}_3$ with or without loading Pt .

For samples with pure $\gamma\text{-Al}_2\text{O}_3$ as support and in the absence of Pt , the NO_2 storage efficiency for BaO only as storage component is observed to be 0.33. This means only 1/3 BaO participating in NO_2 storage. When K is added into Ba (sample KBa), the M_xO loading reaches 0.17. The storage capacity is 0.38, which is 36% higher than 0.28 mole N_2O_5 per mole BaO for single Ba used as storage component at similar $\text{BaO}/\text{Al}_2\text{O}_3$ ratio of 0.18 shown in Figure 1. It is even 14% higher storage capacity than single Ba with $\text{BaO}/\text{Al}_2\text{O}_3$ of 0.11, shown in Figure 2A. When both K and Mg are combined with Ba , the NO_2 storage capacity decreases to 0.20, but it is still the same as that of single Ba as storage component with similar BaO loading (0.31) shown in Figure 1, showing the NO_2 storage efficiency of tri-component catalyst can reach the level of single Ba as storage component with the same M_xO loading on $\gamma\text{-Al}_2\text{O}_3$. In the case of alumina modified by La and Ti , respectively, the influence tendency of the addition of new storage component on NO_2 storage capacity is consistent with that on pure $\gamma\text{-Al}_2\text{O}_3$.

Figure 2A also shows that if single K ($\text{K}_2\text{O}/\text{Al}_2\text{O}_3=0.11$) is used as NO_2 storage component, the storage capacity is 113% higher than that of single Ba with the same loading on $\gamma\text{-Al}_2\text{O}_3$ ($\text{BaO}/\text{Al}_2\text{O}_3=0.11$). However, when single Mg ($\text{K}_2\text{O}/\text{Al}_2\text{O}_3=0.11$) is used as storage component, its storage capacity is obviously lower than that of Ba with the similar storage component loading.

For samples in the presence of Pt, the NO₂ storage capacity measurement results, as shown in Fig. 2B, shows the influence tendency of storage component modification on un-modified and on La or Ti modified γ -Al₂O₃ is consistent with that of samples in the absence of Pt.

3.3 Influence of alumina modification

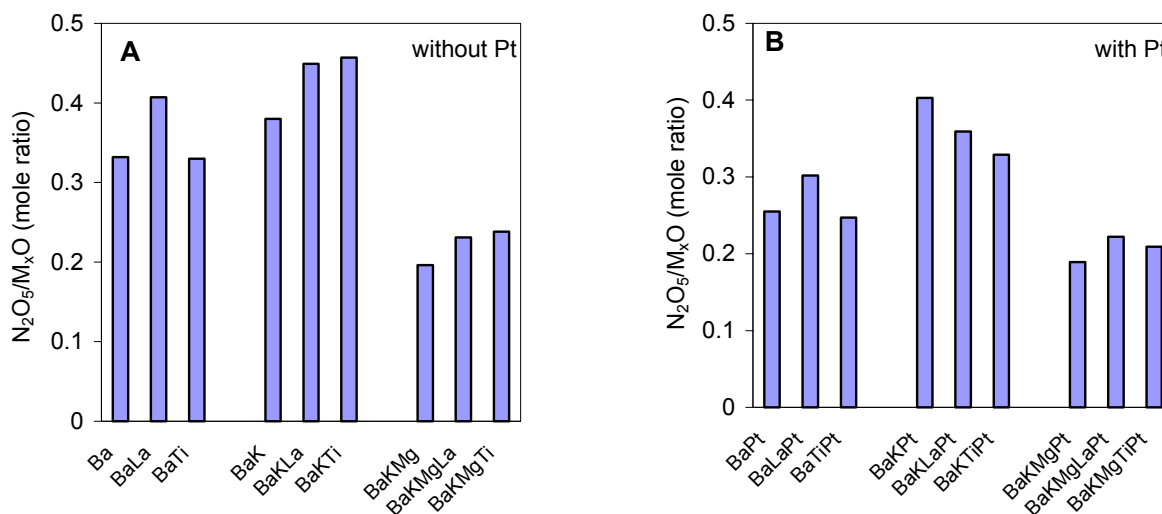


Figure 3. NO₂ storage capacity comparison after support alumina modification.

Table 2: BET surface area and pore volume of different aluminas.

	Sample			
	Al ₂ O ₃	Pt-Al ₂ O ₃	La ₂ O ₃ -Al ₂ O ₃	TiO ₂ -Al ₂ O ₃
BET (m ² ·g)	229	231	236	223
Pore volume (ml·g)	0.76	0.76	0.75	0.75

Because La₂O₃ is a weak base and TiO₂ is a weak acid, the aim of this work is to adjust the surface properties of alumina by La₂O₃ or TiO₂ modification. Table 2 lists BET surface area and pore volume before and after alumina surface modified by La₂O₃ and TiO₂. It is obvious that the modification by small amount of La₂O₃ or TiO₂ does not change the pore structure of alumina.

Figure 3 compares the influence of alumina surface modification by La₂O₃ or TiO₂ on NO₂ storage efficiency (N₂O₅/M_xO) for the same storage components loaded on alumina with or without loading Pt. In the absence of Pt, the alumina modification does not decrease NO₂ storage capacity because the modification does not influence pore structure of γ -Al₂O₃. On the contrary, it can improve the NO₂ storage efficiency for samples except single Ba loaded on Ti-modified alumina. All single Ba, Ba-K bi-component, and Ba-K-Mg tri-component loaded on La or Ti modified alumina show about 20% higher storage capacity than those loaded on un-modified alumina.

In the case of Pt samples, alumina modification does not influence the NO₂ storage efficiency for single Ba and even does have an increase for Ba-K-Mg tri-component system. However, it is observed that La₂O₃ or TiO₂ modification causes a storage capacity decrease of 11% and 18%, respectively for Ba-K bi-component storage system.

3.4 Comparison of Pt influence

Precious Pt is catalytic active component of NO_x trap catalyst for oxidation of NO to NO₂ and reduction of NO_x during lean and rich cycles. Very recently, James *et. al* obtained from the decomposition of Pt-loaded Ba(NO₃)₂ that the presence of Pt decreases greatly the thermal stability

of $\text{Ba}(\text{NO}_3)_2$ and induces a catalytic decomposition to take place at much lower temperature ($< 477^\circ\text{C}$) compared to bulk $\text{Ba}(\text{NO}_3)_2$ (12).

It is observed from comparing the NO_2 storage capacity between Fig. 2A and Fig. 2B that the presence of Pt leads $\sim 25\%$ storage capacity decrease for single Ba component loaded on both pure $\gamma\text{-Al}_2\text{O}_3$ and La_2O_3 or TiO_2 modified $\gamma\text{-Al}_2\text{O}_3$ support. For Ba-K bi-component loaded on pure $\gamma\text{-Al}_2\text{O}_3$ support, the presence of Pt leads to a little increase of NO_2 storage. In the case of La_2O_3 - or TiO_2 modified alumina, the presence of Pt leads to about 20% decrease of storage capacity for Ba-K bi-component system. For Ba-K-Mg tri-component, however, the presence of Pt almost does not change NO_2 storage capacity for storage component supported on modified or un-modified $\gamma\text{-Al}_2\text{O}_3$.

3.5 Characterization of nitrate thermal stability

Figure 4 shows the derivative weight loss curves of $\text{Mg}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$, $\text{Ba}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{KNO}_3/\gamma\text{-Al}_2\text{O}_3$. All samples show two decomposition peaks, suggesting that both dispersed and bulk-like nitrate are present on surface of $\gamma\text{-Al}_2\text{O}_3$. Both $\text{Ba}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{KNO}_3/\gamma\text{-Al}_2\text{O}_3$ give decomposition peaks higher than 350°C . Actually the weight loss due to nitrate decomposition for both $\text{Ba}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{KNO}_3/\gamma\text{-Al}_2\text{O}_3$ start at temperature high than 350°C . This shows that during NO_2 storage at 350°C , NO_2 can completely react with BaO or K_2O storage component to form corresponding nitrate. The controlling step for influencing NO_2 storage efficiency is from NO_2 diffusion or product nitrate immigration into inner part of component particle. However, For MgO used as storage component, dispersed $\text{Mg}(\text{NO}_3)_2$ on $\gamma\text{-Al}_2\text{O}_3$ decomposes at a temperature below 350°C . Thus, at NO_2 storage temperature of 350°C , only bulk-like MgO stores NO_2 . This explains why the NO_2 storage capacity of single Mg as storage component is much lower than single Ba, while that of Ba-K-Mg tri-component has the same storage capacity level as compared to single Ba. The reason is that the supporting of Mg is done after loading of Ba and K on $\gamma\text{-Al}_2\text{O}_3$. So most $\text{Mg}(\text{NO}_3)_2$ presents as bulk-like phase in Ba-K-Mg tri-component catalyst.

Figure 5 shows the concentration change of involved gas NO_2 and NO as function of thermal temperature for $\text{Mg}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$, $\text{Ba}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{KNO}_3/\gamma\text{-Al}_2\text{O}_3$. It verifies that the dispersed nitrate decomposes mainly NO_2 and the bulk-like nitrate decomposes mainly NO . It also demonstrates that the decomposition temperature for dispersed $\text{Ba}(\text{NO}_3)_2$ and KNO_3 supported on $\gamma\text{-Al}_2\text{O}_3$ is 100°C higher than that for NO_2 storage in our experiment, while dispersed $\text{Mg}(\text{NO}_3)_2$ gives decomposition peak for producing NO_2 at 320°C , which is lower than NO_2 storage temperature of 350°C .

4. Summary

(1) The NO_2 storage efficiency decrease with increasing of BaO loading on alumina. Single Ba shows equal NO_2 storage capacity to single K, while single Mg shows lower storage NO_2 efficiency due to thermal stability at storage temperature.

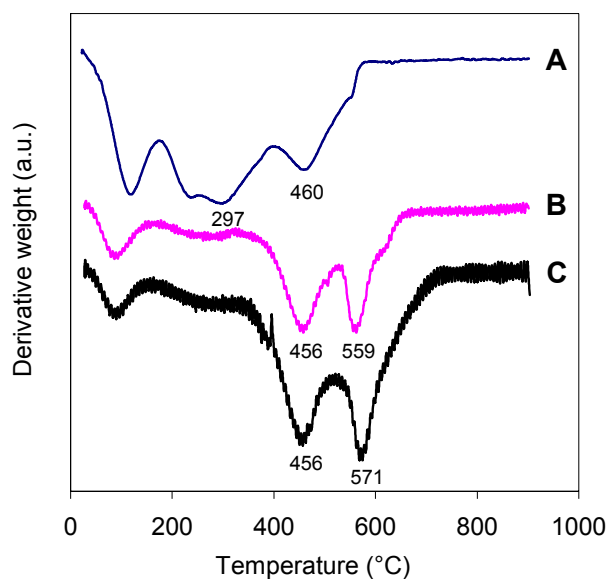


Figure 4: Derivative weight curves of samples at heating rate of $10^\circ\text{C}/\text{min}$. (A) $\text{Mg}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$; (B) $\text{Ba}(\text{NO}_3)_2/\gamma\text{-Al}_2\text{O}_3$; (C) $\text{KNO}_3/\gamma\text{-Al}_2\text{O}_3$.

(2) Compared to the same loading, the added K increases greatly NO₂ storage efficiency, while the addition of Mg does not influence the NO₂ storage efficiency.

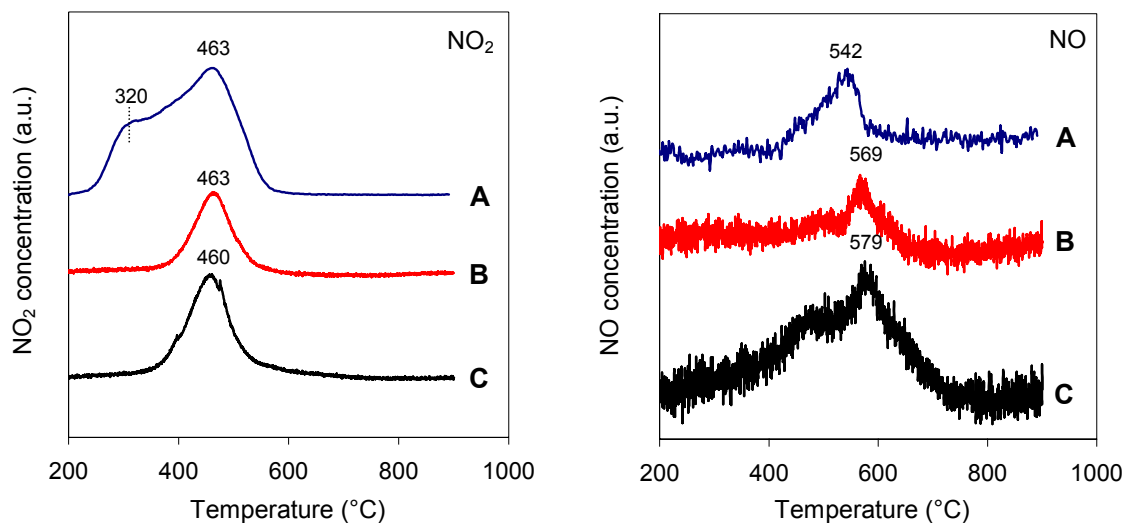


Figure 5: Concentration of evolved gas NO₂ and NO as a function of temperature for γ -Al₂O₃-supported nitrates decomposition. (A) Mg(NO₃)₂/ γ -Al₂O₃; (B) Ba(NO₃)₂/ γ -Al₂O₃; (C) KNO₃/ γ -Al₂O₃.

(3) The modification of alumina by La and Ti improves the storage capacity for all investigated single Ba, bi-component Ba-K and tri-component Ba-K-Mg systems in the absence of Pt. In the presence of Pt, the modification of alumina by La or Ti samples favors NO₂ storage for single Ba and tri-component Ba-K-Mg systems.

(4) The presence of Pt improves NO₂ storage for La or Ti modified Ba-K bi-component system. It does not influence the storage on Ba-K-Mg tri-component system. However, it leads a 25% storage capacity decrease for the single Ba system.

Acknowledgement

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