STRUCTURE AND NO_x UPTAKE PROPERTIES OF Fe-Ba/Al₂O₃ AS A MODEL NO_x STORAGE MATERIAL

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MASTER OF SCIENCE

by

EMİNE KAYHAN

JUNE 2009

To My Husband Mehmet

and

My Parents Elif & Adil

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Assistant Prof. Dr. Emrah ÖZENSOY (Supervisor)

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Prof. Dr. Ömer DAĞ

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Prof. Dr. Şefik SÜZER

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Assoc. Prof. Dr. Margarita KANTCHEVA

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Prof. Dr. Gürkan KARAKAŞ

Approved for the Institute of Engineering and Sciences

Prof. Dr. Mehmet BARAY

Director of Institute of Engineering and Sciences

ABSTRACT

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EMİNE KAYHAN

M.S. in Chemistry Supervisor: Assistant Prof. Dr. Emrah ÖZENSOY June 2009

The composition-effect of iron (5 and 10 wt. % Fe) on the nature of the NO_x species and NO_x storage properties of (8 and 20 wt. %) BaO/ γ -Al₂O₃ was investigated. Nitrate-loaded samples, which were synthesized by incipient-wetness impregnation with nitrate precursors, were further treated at elevated temperatures (323 K-1273 K) in order to monitor the thermally induced structural changes. In the first part of this study, diffraction (X-ray Diffraction, XRD), BET (Brunauer, Emmett, and Teller) surface area measurement, spectroscopy (Raman and X-Ray Photoelectron Spectroscopy, XPS) and microscopy (Transmission Electron Microscopy, TEM and Electron Energy Loss Spectroscopy, EELS) techniques were used for investigating the thermally induced structural changes on the sample surfaces. In the second part of the text, NO₂ (g) adsorption experiments were performed on the NO_x-free samples. FTIR (Fourier Transform Infrared) spectroscopy technique was used to monitor the NO_x species stored on the sample, Temperature Programmed Desorption (TPD) technique was also exploited.

For the as prepared (nitrated) samples, the surface distribution and the thermal stability of the deposited Ba-nitrates were found to depend strongly on the interaction with the Fe-containing domains and the γ -Al₂O₃ support material. It was observed that deposited nitrates have a different thermal stability on the Fe/Ba/Al samples in comparison to the Fe-free Ba/Al samples. Besides, XRD data revealed that BaAl₂O₄ formation at elevated temperatures was diminished to a certain extent in the presence of Fe. Moreover, the presence of Fe in the form of α - Fe₂O₃ in the Fe/Al and Ba-Fe/Al systems depressed the γ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃ phase transformation temperature and favored the corundum formation above 1073 K. Relative surface dispersions of the Fe- and Ba-species on the 10Fe/20Ba/Al sample were also analyzed via TEM and EELS where the dispersion of barium species were found to be relatively higher than that of iron.

FTIR experiments revealed that NO₂ (g) adsorption at 323 K leads to the formation of nitrites for all of the samples at the initial introduction of NO₂ (g). In addition, iron containing samples indicate nitrosyl formation as well. With further doses of NO₂ (g), nitrite bands were converted into nitrate signals. NO₂ (g) adsorption on 5(10)Fe/8(20)Ba/Al system resulted in the accentuation of the surface/bidentate nitrates. Temperature dependent FTIR experiments showed that ionic (bulk) nitrates were thermally more stable than the surface nitrates in 8(20)Ba/Al and 5(10)Fe/8(20)Ba/Al systems. TPD profile for the 8Ba/Al sample was also found to be in line with the FTIR results, indicating that the high-temperature decomposition of bulk nitrates were in the form of NO (g) and O₂ (g). In the presence of Fe (5 and 10 wt %) thermal stability of the nitrates were found to decrease.

Keywords: NSR, NO_x storage materials; Ba/Fe, Fe/Al, Fe/Ba/Al; γ -Al₂O₃; α -Fe₂O₃; NO₂; FTIR spectroscopy; TPD; XRD; Raman; XPS; BET; TEM and EELS.

ÖZET

MODEL NO_x DEPOLAMA MALZEMESİ OLAN Fe-Ba/Al₂O₃ MALZEMESİNİN YAPISAL VE NO_x ALIM ÖZELLİKLERİ

EMİNE KAYHAN

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Bu çalışmada, kütlece % 8 ve % 20 BaO içeren, BaO/ γ -Al₂O₃ malzemelerinin, kütlece % 5 ve % 10 oranında Fe içeren bileşiklerinin yapıları ve NO_x depoloma davranışları incelenmiştir. Bu çalışmanın ilk kısmında, malzemelerin sıcaklığa bağlı yapısal değişiliklerinin detaylı olarak incelenmesi için, kırınım (X-Işını Difraksiyonu, XRD), BET (Brunauer, Emmett, ve Teller) yüzey alanı ölçümleri, spektroskopik (Raman ve X-Işını Fotoelektron Spektroskopisi, XPS) ve mikroskopik (Geçişli Elektron Mikroskopu, TEM ve Elektron Enerji Kaybı Spektroskopisi, EELS) teknikler kullanılmıştır. Çalışmanın ikinci kısmında, NO_x-içermeyen numunelere yapılan NO₂(g) adsorpsiyon deneyleri yer almaktadır. FTIR (Fourier Dönüşüm Infrared Spektroskopisi) tekniği, malzemelerde depolanan NO_x türlerinin analizinde kullanılmıştır. Ayrıca, NO_x yapılarının yüzeyden geri salınım davranışını açıklayabilmek için, sıcaklık programlı desorpsiyon (TPD) tekniği de kullanılmıştır. Islak emdirme yöntemiyle sentezlenmiş nitratlanmış numunelerde, depolanan Ba-nitrat birimlerinin yüzey dağılımının ve ısıl kararlığının, bu birimlerin Fe-içeren alanlarla ve γ -Al₂O₃ destek malzemesiyle olan etkileşimine bağlı olduğu saptanmıştır. Fe-içermeyen Ba/Al numunelerine kıyasla, Fe/Ba/Al malzemelerinde depolonan nitratların farklı ısıl kararlılıkları olduğu gözlemlenmiştir. Bunun yanısıra, XRD verisi, yüksek sıcaklıklardaki BaAl₂O₄ oluşumunun Fe varlığında azaldığını ortaya çıkarmıştır. Ayrıca, Fe/Al ve Fe-Ba/Al sistemlerindeki Fe varlığının, γ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃ faz dönüşüm sıcaklığını 1073 K'e düşürdüğü gözlemlenmiştir. 10Fe/20Ba/Al numunesinin TEM ve EELS teknikleriyle analizi sonucunda, yüzeydeki Ba-birimlerinin, Fe-içeren birimlere nazaran daha yüksek bir yüzey dağılımına sahip olduğu görülmüştür.

323 K'de yapılan FTIR NO₂ (g) adsorpsiyon deneyleri, başlangıçta yüzeye gönderilen NO₂ (g) sonucunda, tüm numunelerde nitrit oluşumunu göstermiştir. Buna ek olarak, Fe-içeren yüzeylerde nitrosil oluşumu da gözlemlenmiştir. Daha sonraki NO₂ (g) dozları, nitrit kaynaklı bandı nitrata dönüştürmüştür. 5(10)Fe/8(20)Ba/Al sistemi için yapılan NO₂ (g) adsorpsiyon deneyleri yüzey/bidentate nitratlarındaki artışla sonuçlanmıştır. 8(20)Ba/Al ve 5(10)Fe/8(20)Ba/Al sistemleri için yapılan sıcaklığa bağlı FTIR deneyleri iyonik (yığın/bulk) nitratların yüzey nitratlarına kıyasla ısıl olarak daha kararlı olduğunu göstermiştir. 8Ba/Al sistemine ait TPD profili, numunenin FTIR sonucuyla tutarlı bulunmuş ve kısmi olarak daha yüksek sıcaklıklara kadar kararlı olan iyonik nitratların NO (g) and O₂ (g) şekilinde parçalandığını, diğer taraftan yüzey nitratlarının ise NO₂(g) salınımı yoluyla parçalandığını göstermiştir.

Anahtar Kelimeler: NSR, NO_x depoloma malzemeleri; Ba/Fe, Fe/Al, Fe/Ba/Al; γ -Al₂O₃; α -Fe₂O₃; NO₂; FTIR spektroskopisi; TPD; XRD; Raman; XPS; BET; TEM ve EELS.

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1 INTRODUCTION

The concentration of carbon dioxide (CO₂) in the atmosphere has increased from 315 ppm in the year 1960 to 365 ppm in 2000 [1]. The increase in the anthropogenic CO₂ due to combustion processes in power-plants, industry and transportation systems has a significant contribution to the green-house effect. As a result, most of the industrialized countries agreed to take action by signing the Kyoto protocol [2, 3]. Moreover, due to the decline of the oil reserves and increasing fossil fuel costs, there is an increasing demand for minimizing the fuel consumption in the automobile sector. These environmental and economic concerns have led to the development of the fuel efficient lean-burn engine technology in 1984 [4, 5]. Fuel-efficient lean-burn engines operate at air-fuel (A/F) ratios of 25:1 rather than the conventional gasoline engines that operate at A/F ratios of 14.5:1 [4, 5].

In a typical internal combustion engine, CO (g), unburned hydrocarbons and NO_x are the main hazardous post-combustion products that have to be catalytically converted into harmless chemicals. These species are converted via the following general chemical pathways [6]:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{1.1}$$

 $Hydrocarbons + O_2 \rightarrow H_2O + CO_2 \tag{1.2}$

$$NO_x + CO + H_2 + Hydrocarbons \rightarrow N_2 + CO_2 + H_2O$$
 (1.3)

Besides CO₂, increasing emissions of pollutants such as hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) have become a worldwide environmental problem. NO_x in diesel exhaust is mainly composed of nitric oxide (NO) (>90%) [6]. It is formed during the reaction between nitrogen and oxygen and oxidation of fuel-derived nitrogen-containing compounds at high temperatures and pressures as shown below [6]:

$$N_2 + O \rightarrow NO + O \tag{2.1}$$

$$N + O_2 \rightarrow NO + O$$
 (2.2)

$$N + OH \rightarrow NO + H$$
 (2.3)

 NO_x concentration in exhaust gas (which may vary with the engine combustion conditions such as temperature and air/fuel ratio) is around 1000 ppm. Table 1 shows average concentrations of exhaust gas constituents.

Table 1. Typical concentrations of Exhaust Gas Constituents (average emissions over a Federal Test Procedure (FTP) test) [6].

HC NO _x CO H ₂	750 ppm 1050 ppm 0.68 vol% 0.23 vol%	$\begin{array}{c} \mathrm{CO}_2\\ \mathrm{O}_2\\ \mathrm{H}_2\mathrm{O} \end{array}$	13.5 vol% 0.51 vol% 12.5 vol%
_			

There are regulations limiting the amount of NO_x emissions due to health, ecological and environmental concerns. Furthermore, these NO_x exhaust emission limits have been reduced constantly every few years. Table 2 illustrates some example limits accepted by the United States and the European Union [7, 8].

Table 2. Limitations on emission of NO_x in the United States and the European Union.

USA ^{a,b}			
YEAR	NO _x	NMHC ^c	CO
1991 2004 2007 2008 2009 2010	1.00 0.20 0.15 0.10 0.05 0.00	0.410 0.125 0.094 0.063 0.031 0.000	3.4 1.7 1.3 0.8 0.4 0.0

EU ^{a,b}				
YEAR	NO _x	NMHC ^c	CO	
2000 2005	0.24 0.13	0.320 0.158	3.71 1.61	

^a unit for emission:g/mile

^bReferences [7,8]

^c NHMC:non-methane hydrocarbon

In Europe by the end of 2014, NO_x emissions from diesel engines are required to go through a three-fold decrease from 0,25 g.km⁻¹ to 0,08 g.km⁻¹ as mentioned in the EURO 6 AECC regulations named as the "Emission Control Technologies and the Euro 5/6 Emission Legislation" [9]. Thus, in order to meet these strict regulations, automotive catalyst makers are forced to develop novel catalysts that could be alternative to the traditional automotive catalysts. Three-waycatalysts (TWCs) are the most common catalysts for gasoline after-treatment applications. They have three main functions as presented in reactions 1.1 - 1.3, above. These reactions consist of the oxidation of CO to CO₂, oxidation of HC to CO_2 and H_2O and the reduction of harmful NO_x to harmless N_2 gas. Typically, TWCs have a general formulation containing precious metals and a support oxide such as: Pt/Rh $(90/10)/\gamma$ -Al₂O₃ or Pd/ γ -Al₂O₃ [8]. In addition to these, numerous other alkaline/alkaline earth/transition metals or their oxides are also added to the formulation as performance enhancers. TWCs are very successful in gasoline-engine vehicles in terms of removing NO_x in the exhaust. However they do not efficiently operate under lean-burn conditions. The inherent problem in catalytic reduction of NO_x is the need to reduce NO_x to N_2 in the presence of a large surplus of oxygen [10-23]. As can be readily seen in Figure 3, TWCs perform very efficiently at an A/F ratio of 14.5:1. However, under oxidizing (lean) conditions ((A/F) ratio of 25:1), TWCs become ineffective for NO_x removal.



Figure 1 Fuel consumption and 3-way performance of a gasoline engine as a function of air–fuel (A/F) ratio [5].

As a result, new catalysts are needed to meet the future emission standards for lean-burn engines. There are two major catalytic technologies proposed and used for the removal of NO_x emissions from the lean-burn vehicles. These are the Selective Catalytic Reduction (SCR) and the NO_x Storage and Reduction (NSR) technologies.

SCR catalysts can be made out of zeolitic materials supported with metals (ex. Cu/ZSM-5) or precious metals with high surface area metal oxides (ex.Pt-Pd-Rh/Al₂O₃) or combination of mixed metal oxides (ex.V₂O₅/TiO₂/MoO₃) [23-31]. There are two main types of SCR catalysts; ammonia/urea selective catalytic reduction catalysts (NH₃-SCR) and hydrocarbon selective catalytic reduction catalysts (HC-SCR) [4].

In NH₃-SCR system, ammonia is used as a selective reductant and the general reaction between ammonia and nitric oxide is [32]:

$$NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{3.1}$$

Although SCR is a well-developed and a proven technique in industrial stationary applications since 1970s [33], U.S. clean air authorities (US

Environmental Protection Agency; EPA) have voiced concerns regarding the use of NH_3 in mobile applications, as NH_3 is a both toxic and a corrosive gas [34]. Moreover, an extra NH_3 (or urea solution) storage tank is also needed for the supply of ammonia to the exhaust system. As a result of the reaction between NO_2 and NH_3 , formation of the explosive ammonium nitrate is also observed which has a potential to lead temporary deactivation of the catalyst by being deposited in the pores of the support material [35].

Besides NH₃-SCR, HC-SCR catalysts are also able to reduce NO_x in the presence of oxygen. However, the use of zeolite-based HC-SCR exhibits crucial drawbacks such as almost no low-temperature activity due to the reduction of NO_x at temperatures below 300°C and also deactivation by water and SO₂ [4]. Therefore, instead of using zeolitic materials, non-zeolite oxide-based catalysts were suggested [36, 37, 38].

Besides HC-SCR method, another possible solution to the conversion of NO_x under the oxygen-rich regime is the so-called NO_x storage reduction (NSR) catalysts (also known as lean NO_x traps (LNT) or NO_x adsorption catalysts) that are firstly put into the market by Toyota in 1994 [5]. NSR catalysts consist of supported precious metals such as Pt, Pd and Rh, and a storage component such as an alkaline-earth oxide (e.g. BaO). Hence a typical NSR catalyst has the formulation: Pt/BaO/Al₂O₃ [39-64] where alumina is the underlying support material.

NSR catalysts operate in a cyclic manner in two dissimilar regimes. A longer (lean) regime with a duration of ca. 60 sec and the short (rich) regime with a duration of c.a. 8 sec. [4]. As it is shown in Figure 2, during the lean (oxygen-rich) storage period, NO is oxidized into NO₂ and then stored as nitrites or nitrates on the storage material. Next, during the rich (oxygen deficient) period, stored NO_x is released from the solid storage units and reduced to N₂ with the help of hydrocarbons, while Ba(NO₃)₂ storage units are converted into BaO [39-64].



Figure 2. A possible mechanism of the NO_x storage-reduction on the NSR catalyst [12].

A commonly accepted view of the operation of the NSR catalysts is given below [5]:

NO
$$\xrightarrow{O_2}$$
 NO₂ $\xrightarrow{O_2}$ Ba(NO₃)₂ (4.1)

$$Ba(NO_3)_2 \xrightarrow{HC, H_2, CO} BaO + NO_2 \xrightarrow{HC, H_2, CO} N_2 + CO_2 + H_2O$$
(4.2)

Currently, there exist two different theoretically proposed mechanisms for the formation of nitrates on the surface. Broqvist et al. investigated NO₂ adsorption on BaO and found a cooperative effect in a mechanism where the initial adsorption occurred on a surface anion of oxygen [65]. In this study, it is explained that the adsorbed nitrite would subsequently transfer to the cation in order to leave room for a second NO₂ on the same BaO unit. These two adsorbed nitrite species disproportionate into a nitrate and NO which combined with a third adsorbed NO₂ to form a second nitrate. This theoretical explanation provides a plausible interpretation of previous study of Fridell et al. who experimentally observed stoichiometry of one NO molecule released per two formed surface NO₃⁻ [45].

The disproportionation mechanism mentioned above can be summarized as follows [66]:

$$2 \operatorname{NO}_2 \to \operatorname{NO}^+ \operatorname{NO}_3^- \tag{5.1}$$

$$Al^{3+}O^{2-} + NO^{+}NO_{3}^{-} \leftrightarrow NO_{3}^{-} \dots Al^{3+}O^{2-} \dots NO^{+}$$
(5.2)

$$NO_2^- + NO_2 \leftrightarrow \dots NO_3^- + NO$$
 (5.3)

Later, Hess and Lunsford provided additional support for the disproportionation mechanism where they observed formation of nitrites on BaO which were transformed into nitrates upon further exposure of NO_2 in the absence of oxygen, [50]. However, at 400 °C after 20% O_2 was included in the gas flow; direct nitrate formation was observed without the preceding nitrite step. Hence, besides the disproportionation mechanism, in the absence of O_2 , Hess et al. proposed a second mechanism that involves the direct reaction of NO_2 with the surface peroxide observed in the initial phase of the reaction [50]. In the presence of O_2 , direct nitrate formation was also observed as follows [50].

$$BaO \xrightarrow{+ NO_2/He}_{Ba} Ba^{2+} \xrightarrow{+ NO_2/He}_{Ba(NO_2^*)]^+} + [Ba(NO_3^*)]^+$$

$$\downarrow + O_2/He \xrightarrow{- NO_2/He}_{He} \xrightarrow{+ NO_2/He}_{- NO}$$

$$BaO_2 \xrightarrow{+ NO_2/He}_{Ba(NO_3)_2}$$
(5.4)

Alkali or alkaline-earth metals are important for the storage of NO_2 as they provide a basic surface character for the catalyst. Thermodynamic evaluation and the reaction kinetics data show that the basicity of the component is important for the NO_x trapping performance [67, 25, 68]. It was also suggested that the adsorption properties of NO_x can be correlated with the basicity of the substrate. The lattice constant of the alkaline-earth metal oxides increases strongly in the sequence MgO to BaO. The electrostatic stabilization of the ionic charge separation decreases whereas the electron-donating property (or the basicity) increases with the increasing lattice parameter [69-72]. Thus the alkaline-earth basicity increases in the following order: MgO < CaO < SrO < BaO. The stability of the adsorbates on alkaline-earth oxide surfaces are also associated with the substrate basicity, which in turn is closely related to the lattice parameter.

Alkali or alkaline earth components are commonly used as promoters for precious metals during redox reactions. It was reported that Ba or K can enhance the high-temperature catalytic activity [12]. Moreover, the presence of Na or Ba was found to increase the NO adsorption strength while weakening the N-O bond strength [12]. Thus, Na or Ba promotion enhances the reduction of NO to N₂ and increases the selectivity of the reaction towards N₂ [12]. Among alkali and alkaline-earth elements, Ba is the most commonly used storage component in the NSR catalysts. It is typically abbreviated as Ba in the NSR formulation, however it is found as BaO, BaO₂, Ba(OH)₂ or BaCO₃ on the catalyst surface due to its high affinity towards CO₂, H₂O and O₂.

Barium loading in the catalyst composition has a direct influence on the amount of trapped NO_x . On the other hand, increasing the Ba content of the catalyst beyond 20 wt. % was found to have no positive effect on the amount of trapped NO_x species. The reason behind this is unclear however it is plausible that increasing the amount of Ba above 20 wt% may result in blocking of the available Pt sites and/or a decrease in the Pt dispersion on the surface [12].

Numerous theoretical and experimental studies on the realistic and model NSR catalysts focused on the characterization of the alumina supported barium oxide (BaO/ γ -Al₂O₃). These studies mostly exploited vibrational spectroscopic (IR and Raman) and/or mass spectroscopic (temperature-programmed desorption, TPD) techniques in order to elucidate the chemical nature of the NO_x species formed on the surface of BaO/ γ -Al₂O₃[73-81].

Although, the majority of the former studies in the literature focused on the NO_x storage properties of the realistic high surface area materials, relatively detailed surface science studies on the NO_x storage capacity and the thermal aging of model NO_x storage materials in the form of BaO/θ -Al₂O₃/ NiAl(100) [76] have also been

reported recently. Deposition, oxidation and growth of the Ba phase on an atomically ordered θ -Al₂O₃ ultra thin film grown on a NiAl(100) bimetallic alloy substrate, mimicking the high surface area alumina counterpart, have been studied via different preparation and characterization protocols [77, 78]. The spectroscopic characterization of the alumina support material [79], and its interactions with H₂O [79], NO₂ [80], and H₂O + NO₂ [81] in the absence of the active Ba-containing phase were studied as well. More recently, a similar surface science approach was also extended to the BaO/ θ -Al₂O₃/NiAl(110) model system [82-85].

Pt, Pd and Rh are among the most common precious metal components used in NSR formulations [86-88]. Rh and Pd are much more active for NO_x reduction but much less active for NO oxidation [86-88]. On the other hand, Pt was also found to enhance the adsorption of NO_2 by producing stable nitrates on the catalyst surface [22]. Besides the type of the precious metal, amount and the dispersion of the metal sites and their interaction with the underlying support material significantly influence the kinetics of catalytic NO oxidation [12]. 1 wt% Pt was experimentally found to be an efficient composition for redox reactions in NSR applications [12].

NO adsorption experiments for Pt-BaO/Al₂O₃ showed that NO decomposed on Pt and NO was also oxidized to NO₂ via oxygen adatoms by the following possible reactions [89, 90]:

$$NO + Pt \rightarrow Pt-NO$$
 (6.1)

$$Pt-NO + Pt \rightarrow Pt-N + Pt-O \tag{6.2}$$

$$Pt-NO + Pt-O \rightarrow NO_2 + 2Pt \tag{6.3}$$

It was also proposed in the literature that during the NO doses, Pt sites could lose their activity for NO decomposition due to the accumulation of atomic oxygen on the Pt sites [89, 90]. However, BaO sites that are in close proximity of the Pt particles was suggested to facilitate the spillover of the oxygen adatoms from Pt to BaO making Pt sites free of NO [89, 90]. This spillover phenomenon may also lead to the formation of BaO₂ species as follows:

$$O-Pt + BaO \rightarrow BaO_2 - Pt \tag{6.4}$$

FTIR investigations demonstrated that NO_x storage in BaO/Al₂O₃ was enhanced in the presence of Pt [91]. It was argued that Pt sites provided atomic oxygen to Ba and Al sites which catalyzed the formation of Ba- and Al- nitrates from nitrite species [91]:

$$Ba(NO_2)_2 + 2 \text{ O-Pt} \rightarrow Ba(NO_3)_2 + 2Pt$$
(6.5)

The noble metals and the storage materials are dispersed over a support which plays a significant role in NSR mechanism. These supports could be simple oxides such as Al₂O₃, ZrO₂, CeO₂, MgO or mixed metal oxides such as MgO-CeO₂, MgO-Al₂O₃ [90].

 γ -Al₂O₃ is the most commonly used oxide support in NSR formulations due to its porous structure with fine particle size, high surface area, high catalytic surface activity, distinctive chemical, mechanical and thermal properties [90, 92, 93]. γ -Al₂O₃ has a defect spinel structure (space group Fd3m) where the aluminum cations are located in the octahedral (O_h) and tetrahedral (T_d) interstitial sites identified by the face-centered-cubic (fcc) oxygen anion sublattice [110]. γ - Al₂O₃ is usually formed by thermal dehydration of aluminum hydroxide (boehmite; γ -AlOOH) precursor [93]. Further thermal dehydration steps yield various polymorphs of Al₂O₃

$$\gamma \text{-}\text{AlOOH} \rightarrow \gamma \text{-}\text{Al}_2\text{O}_3 \rightarrow \delta \text{-}\text{Al}_2\text{O}_3 \rightarrow \theta \text{-}\text{Al}_2\text{O}_3 \rightarrow \alpha \text{-}\text{Al}_2\text{O}_3 \tag{7.1}$$

Each thermal treatment step leads to a notable decrease in the surface area of the alumina polymorphs. Commonly γ - Al₂O₃ polymorphs are used in the NSR applications have a surface area of ca. 200 m²/g and posses a good thermal stability within the operational temperature window of the NSR catalysts (i.e. 250 - 400 °C) [12]. Due to its high surface area, γ - Al₂O₃ is also an important NO_x storage

compound at low temperatures (i.e T < 250 °C) that forms surface nitrites and nitrates due to the efficient adsorption of NO_x species on γ -Al₂O₃[13].

Interaction of BaO and γ - Al₂O₃ phases in NSR systems can also yield a BaAl₂O₄ spinel structure on the support surface [94-97]. Szailer et al. reported that although no BaAl₂O₄ formation was observed at T < 1000°C for 8 wt% Ba loading BaAl₂O₄ formation was readily visible at 800°C for in the BaO/ γ - Al₂O₃ system containing 20wt% Ba [96]. It was also suggested in various former studies that BaAl₂O₄ could be responsible for lowering the NO_x storage performance [94-96]. On the other hand, there also exist contradictory results indicating that BaAl₂O₄ can be used as an effective NO_x storage material [98-101]. Hodjati et al. showed the storage of nitrates on bulk BaO and BaAl₂O₄ by performing NO_x adsorption experiments probed by FTIR [101]. It is also concluded that BaCO₃ or BaSO₄ formation, which decrease the NO_x storage capacity, was hindered on BaAl₂O₄ [100, 101]. Hence, the actual role of the BaAl₂O₄ phase in NSR systems is still controversial in the literature.

A major issue regarding the NSR catalysts is the deactivation problem which results from the deterioration of the material integrity due to thermal phenomena and sulfur poisoning [53]. The thermal deterioration is mainly associated with the precious metal particle size growth and other solid state reactions between oxide domains (examples for such reactions will be presented in the next chapters of the current text). Sulfur poisoning seems to be the most challenging problem associated with NSR catalysts. Sulfur poisoning typically leads to the formation of alkaline earth metal and precious metal sulfate or sulfide complexes that are thermodynamically more stable than nitrates. For, a large numbers of oxide substrates the stability of the surface species increases in the following order: $NO_2^- \sim CO_3^{2-} < NO_3^{-} < SO_4^{2-}$ [72].

Misono [102], and Fritz [103] and others [104-110] reported detail studies on the improvement of the durability of NSR catalysts. It should be noted that the commercially formulated NSR catalysts were originally used in Japan where the sulfur content of the diesel fuel is relatively low (10 ppm) [111]. However, it cannot be used in the U.S. or in Europe where the sulfur content is relatively higher (500 ppm and 50 ppm respectively) in diesel fuel [111]. Matsumoto et al. found out that the sulfate particle size has a crucial role in controlling the sulfate decomposition/desorption temperature [24]. It was shown that the smaller the sulfate particle size, the easier the decomposition [24]. This approach became the basis for attacking the deactivation problem in NSR system [52]. Yamazaki et al. found that addition of Fe promoters to the Pt/Ba/Al₂O₃ NSR system is a promising way for improving the S tolerance [52]. It was reported that the introduction of Fe to the NSR system lowered desorption temperature of the adsorbed sulfates by inhibiting the growth of BaSO₄ particles under oxidizing conditions in the presence of SO₂ [52]. However, Fanson et al. reported that the promotion with iron improved the durability of NSR catalyst not by decrease in the sulfate decomposition temperature but by forming a previously unobserved bulk nitrate species which are sulfur resistant [54]. It is also found that these iron sites could also store NO_x in the NSR system [54]. However, Hendershot et al. reported a detrimental effect of Fe on NO_x storage capacity of Pt/Ba/Al₂O₃ NSR system [112]. It was found that Fe-introduced NSR system stored much lower amount of NO_x at temperatures above 250°C by comparing the system without Fe and also concluded that the performance of the catalyst was related to the catalyst preparation techniques that were used [112]. On the contrary, Li et al. noticed that the complex Ba-Fe oxide catalysts annealed at 750 ^oC possessed a high NO_x storage capacity and a high sulfur resistance [113]. Later, Yamazaki et al. showed that the addition of an Fe-compound is also effective in the improvement of TWC performance after thermal aging [53]. It was reported that Fecompound on the aged Pt/Ba/(Al₂O₃-CeO₂-Fe₂O₃) catalyst plays two important roles, (a) acting as oxygen storage sites more effectively than CeO_2 , and (b) diminishing the CO self-poisoning for the CO-O₂ reaction and the CO-NO reaction under reducing conditions [53]. Hendershot et al. stated that the Fe improved the sulfur resistance by decreasing the bond strength between Ba and SO₂ [108]. However, reports demonstrating NSR catalytic performance over a wide range of operating conditions for catalysts of varying conditions indicated that the Fe did not significantly affect the poisoning of the Pt sites or the overall saturation NO_x storage capacity [108]. Vijay et al. suggested that the addition of iron to $1Pt/15Ba/\gamma-Al_2O_3$ improved the NO_x storage by 25-30% [111]. Hendershot et al. found that Fe acts as a

promoter by extending the region of the complete NO_x conversion to lower Pt and Ba weight loadings, and acting as an oxidizing agent in the absence of Pt and storing NO_x in the absence of Ba [112]. However, further studies of Hendershot et al. indicated that the effect of Fe weight loading on the performance of NSR catalysts was a much less significant than the effects of the Pt and Ba loadings [109]. Lastly, Luo et al. reported two different functions for the Fe domains on the Ba/Al₂O₃ and Pt/Al₂O₃ systems. In the former system, Fe was found to slightly decrease the SO_x absorption by enhancing the bulk BaAl₂O₄ formation and suppress the growth of the bulk BaSO₄. In addition Fe was also suggested to increase the NO_x storage performance of the system and formation of bulk Ba(NO₃)₂ by enhancing the mobility of the stored NO_x [110]. In the later system, Fe resulted in a decrease of NO_x storage capacity of the catalyst due to the encapsulation of the Pt in the lattice of Fe/FeOx matrix leading to the weakening of the Pt/Ba interaction. Moreover, it was also argued that Fe in the Pt/Ba/Al₂O₃ could selectively catalyze the reduction of BaSO₄ into BaS and so making sulfur removal of the stored sulfates more difficult [110].

Despite the numerous studies directed to investigations of the effect of Fe given so far, unfortunately many of the results are contradictory and specific spectroscopic details of the effect of Fe on the storage behavior of the Ba/ γ -Al₂O₃ system remain unclear in the open literature. Consequently, in the current STUDY, the interaction between Fe containing surface oxide domains with Ba/ γ -Al₂O₃ NO_x storage material are reported by examining the composition-dependent structural and morphological changes as well as the alterations of thermal stabilities of the nitrates in the Ba/Fe/ γ -Al₂O₃ system [114, 115].

2 EXPERIMENTAL

2.1 Sample preparation

A series of $Ba/\gamma-Al_2O_3$, $Fe/\gamma-Al_2O_3$ and $Ba/Fe/\gamma-Al_2O_3$ samples with different Ba (8 and 20 wt. % BaO) and Fe (5 and 10 wt. % Fe) loadings were synthesized by conventional incipient wetness impregnation [116] of γ -Al₂O₃ (PURALOX, 200 m²/g, SASOL GmbH, Germany). In this synthetic protocol, the support material was impregnated with aqueous solutions of barium nitrate (ACS Reagent, $\geq 99\%$, Riedel – de Haën) (for Ba/ γ -Al₂O₃ samples) or Fe(NO₃)₃. 9H₂O (iron (III) nitrate nonahydrate, ACS reagent, $\geq 98\%$, Sigma - Aldrich) (for Fe/y- Al_2O_3 samples). It is explained in the literature that 8wt% BaO forms < 1 monolayer while 20 wt% BaO > 2 monolayers on γ -Al₂O₃ surface having 200 m²/g. Hence, loadings of the storage unit (BaO) in the system were chosen as 8 wt% and 20 wt% of γ -Al₂O₃ in order to make a comparison between different coverages of BaO on the support. The mixed Ba/Fe/y-Al₂O₃ (8 or 20 wt. % BaO and 5 or 10 wt. % Fe) samples were prepared by simultaneous impregnation of the support with the aqueous solutions of barium and ferric nitrates. In this synthetic approach, both Ba and Fe components were introduced on the alumina support almost exclusively in the form of nitrates. Thus, the state of the freshly prepared materials, in a way, can be viewed as model systems which mimic the NO_x-loaded or nitrate-saturated storage materials. After the impregnation, synthesized materials were dried at 353 K and then annealed in Ar atmosphere for 2 h at different temperatures, ranging from 423 K to 1273 K. Such a thermal treatment also reveals an opportunity to study the thermal decomposition of nitrates. Hence, after each temperature treatment, representative samples from the treated batches were collected for ex-situ analysis.

Compositions of the NO_x storage materials and their acronyms used in the current text are as follows: Al, γ -Al₂O₃, 8Ba/Al and 20Ba/Al samples contained 8 and 20 wt. % BaO, respectively (with balancing amounts of γ -Al₂O₃). 5Fe/Al and 10Fe/Al samples contained 5 and 10 wt. % Fe, respectively (with balancing amounts of γ -Al₂O₃). Mixed-oxide storage materials were synthesized with the following compositions: 5Fe/8 or 20Ba/Al samples contained 5 wt. % Fe, 7.6 or 19 wt. % BaO

and balancing amounts of γ -Al₂O₃, respectively whereas 10Fe/8 or 20Ba/Al samples contained 10 wt. % Fe, 7.2 or 18 wt. % BaO and balancing amounts of γ -Al₂O₃, respectively. In other words, synthetic ratios were chosen such that the mixed Ba/Fe/Al systems had the same BaO to γ -Al₂O₃ weight ratio with that of the Ba/Al samples which do not contain any Fe. Besides, reference NO₂ adsorption experiments were carried out with the commercial BaAl₂O₄ sample (F.W. 255.29/ powder, MATECK GmbH, Germany).

2.2 Experimental set-up

2.2.1 Reactor set-up



Figure 3. Simplified schematic of the custom-designed insitu-FTIR catalytic analysis system coupled to the quadrupole mass spectrometer chamber. Abbreviations used in the scheme are given in the inset above.

The system designed for FTIR, RGA and TPD experiments is shown in Figure 3. The custom-designed catalytic FTIR-TPD analysis system consists of the following main sections: a) sample holder assembly, b) ex-situ sample annealing

and in-situ sample heating units, c) vacuum components, d) Bruker Tensor 27 FTIR Spectrometer coupled to the in-situ catalytic reactor, and e) Mass Spectrometer chamber.



2.2.1.1 Sample Holder Assembly



Electrical vacuum feed-through and the sample holder assembly (made out of high conductivity copper), are shown in Figure 4. Pressure inside the feedthrough was isolated from the atmosphere by a 2.75" Con-flat copper gasket. The powder catalyst sample (typical having a mass of c.a. 0.01 g - 0.04 g), was pressed onto high purity photo-lithographically etched tungsten grid (50-mesh). Then, a small tantalum foil was spot–welded onto the top center of W-grid in order to attach the thermocouple wires firmly on the sample holder. Next, a K-type (alumelchromel) thermocouple was spot-welded on the tantalum piece which allows direct monitoring of the sample temperature. Later, W-grid was attached to the copper sample holder assembly mounted on vacuum feed-through. Finally the thermocouple wires were connected to the sample holder via spot-welding. Heating cables and the thermocouple wires were also isolated by covering the wires with macor and ceramic beads.

2.2.1.2 Thermal Treatment Instrumentation

2.2.1.2.1 Tube furnace operating under controlled Ar (g) flow



Figure 5. Tube furnace operating under controlled Ar (g) flow.

For the pre-treatment of the synthesized catalyst samples, a programmable tube furnace (PROTHERM Inc., Turkey) was employed. In the pre-treatment protocols, catalyst samples were annealed under inert Ar (g) atmosphere (in order to avoid any carbonate formation on the studied samples via the reaction between atmospheric CO₂ and BaO) at the desired temperatures for given durations. Continuity of the Ar (g) flow during the annealing processes is also checked using two gas bubblers that are located at the inlet and outlet connections of the tube furnace. Hence, the synthesized catalyst samples can be treated within 300 K -1473 K using the setup described above. In the current work, the catalyst samples were typically treated within 423 K-1273 K, the annealing durations were equal to 2 hrs.

2.2.1.2.2 Computer-controlled linear heating system



Figure 6. Components of the computer-controlled linear heating system.

Samples that are pressed onto the W-grid were heated by the computercontrolled heating system. Sample temperature was read as a DC voltage (0 -3 mV or 273 K – 1000 K) via the K-type thermocouple. Typical DC voltage and current values provided by the DC-power supply during heating ramps ranged within V= 0 -1.5 V and I = 0 - 60 A, respectively. After having various empirical optimization tests, the most effective PID parameters for our specific system were also determined. Thus the following parameters were used in the PID algorithms during the sample heating ramps: P = 100, I = 5, D = 1. It should be noted that the computer-controlled heating system was designed to work within 273 K – 1273 K. This was due to the choice of the specific PID controlled used in our system, which did not allow processing of temperatures with negative °C values. On the other hand, it should also be mentioned that the sample could be cooled (though in an uncontrolled fashion) to temperatures down to c.a. 100 K as well, by filling the liquid nitrogen (LN₂) reservoir that was designed as an integral part of the sample holder. In order to sustain the mechanical integrity of the W-grid during temperature ramps, particularly at high temperatures, a moderate resistive linear heating rate of 12 K/min was chosen and all of the system parameters were optimized according to this heating rate. During the heating ramp, temperature monitoring software (Vaksis Inc.) also allowed us to monitor the time-dependent deviations between the target and the measured temperature values. In order to achieve an acceptable linear temperature ramp, it was found that special attention needs to be spent on various experimental points such as the proper insulation of the heating cables, quality of spot welded sections on the feed-through, contact area between the copper legs and the W-grid and the pressing quality of the powder sample on the W-grid etc. An example heating ramp recorded in one of our experiments is given in Fig 9 below:



Figure 7. An example heating ramp (temperature, °C vs. time, s) which was recorded in one of our experiments. Red line indicates the set (target) temperature curve while the black curve corresponds to the experimentally measured temperature values. Overlap of the black curve with the red curve shows that the PID algorithm successfully controls the temperature values for heating ramp of 12 K/min.

2.2.1.3 Vacuum Components

The vacuum in the in-situ FTIR-QMS system is obtained by employing two independent turbo pumping systems (each including a separate diaphragm fore line pump) and a dual-stage rotary-vane pump. There are three compartments in the vacuum system: gas manifold system, catalytic reactor and the mass spectrometer chamber.


Figure 8. Different sections of the gas manifold in the in-situ catalytic analysis system.

2.2.1.3.2 Gauges

Three types of pressure gauges were used in the gas fold section to detect pressures at dissimilar pressure regimes. One of these gauges is the WRG (Wide Range Gauge, BOC Edwards) which consists of a combination of a cold cathode gauge which allows pressure reading within $10^{-9}-10^{-3}$ Torr and a piranyi gauge that operates within $10^{-3} - 1000$ Torr. WRG is a gas-type sensitive manometer and factory calibrated for N₂ and is mainly used for measuring low vacuum values in the reactor and the gas manifold system. Thus for absolute and accurate pressure

measurements for moderate pressures (i.e. 0.5 - 100 Torr) a third pressure gauge, namely CM (Capacitance Manometer, MKS Baratron) was used. CM operates within 1.0 - 1000 Torr and provides reproducible pressure readings independent of the type of the gas(es) used. Therefore, CM was absolutely crucial for preparing perfectly reproducible as well as accurate doses of gases in the gas manifold which may include a mixture of different gases with dissimilar thermal conductivities and ionization potentials (whose absolute pressures cannot be accurately measured via cold cathode or piranyi gauges).

2.2.1.3.3 Gas pumping units

Using a combination of diaphragm pumps, turbomolecular pumps as well a rotary vane pump, pressure in the gas manifold and the reactor section could be controlled within 10^{-6} - 1000 Torr. On the other hand the mass spectrometer chamber was pumped only with a turbomolecular pumping station where the pressure varied within $5 \times 10^{-5} - 2 \times 10^{-8}$ Torr.



Figure 9. Gas pumping units of gas manifold/reactor sections and the mass spectrometer chamber.

The ultimate pressure in the gas manifold and the reactor compartments were inherently dictated by the leak rate through the custom-designed IR (KBr or BaF₂) windows that were installed on the vacuum reactor as shown in Figure 10. Accordingly, the minimum attainable pressure in the gas manifold and the reactor sections was c.a. 10^{-6} Torr. However, it should be noted that, if needed, these IR windows can also be differentially pumped (after a slight modification of the window assembly design) so that an ultimate vacuum of 10^{-8} Torr can be obtained in the reactor.



Figure 10. Custom-designed IR (KBr or BaF₂) window assembly and its installation scheme to the vacuum reactor body.

2.2.1.4 Bruker Tensor 27 FTIR Spectrometer coupled to the in-situ catalytic reactor



Figure 11. Custom-designed in-situ catalytic vacuum reactor.

Fourier transform infrared (FTIR) spectroscopic measurements were carried out in transmission mode, using (Bruker Tensor 27) FTIR spectrometer, equipped with a liquid nitrogen cooled Hg-Cd-Te cryodetector (MCT detector) and BaF_2 windows working in the range of 850-5000 cm⁻¹ where each spectrum was acquired with a resolution of 4 cm⁻¹ and by averaging over 128 scans).



Figure 12. Bruker Tensor 27 FTIR Spectrometer coupled to the in-situ catalytic reactor.

2.2.1.5 Mass Spectrometer Chamber

Mass spectrometer chamber was consisted of a four-way ConFlat 2.75" port. This section was pumped with a turbomolecular pumping station (P < $2x10^{-8}$ Torr) where the pressure was measured via a Bayerd-Alpert type nude ionization gauge (Instrutech Inc.). Quadruple Mass Spectrometer (QMS, SRS RGA200) has a mass range of 0-200 amu which was equipped with a Faraday cup as well as an electron multiplier. Operation of the QMS with the electron multiplier provides a higher sensitivity (Multiplier Gain $\leq 1,000,000$, V = 1500 V) and allows low operational pressures (P < $1x10^{-6}$ Torr). By employing the Faraday Cup QMS can be operated at relatively higher pressures (P < $1x10^{-4}$ Torr). Mass spectrometer chamber was connected to the in-situ reactor section via a high-conductance (ConFlat 2.75") pneumatically controlled gate valve so that during the TPD investigations, re-

adsorption of the desorbed molecules on the sample surface was precluded due to the high pumping speed. The gate valve between the reactor and the mass spectrometer was completely open in order to obtain a high pumping rate during the TPD experiments. In the TPD mode, up to 10 different desorption channels could be simultaneously recorded which allowed monitoring the evolution of a large number of species during TPD experiments within 50-750 °C.



Figure 13. Quadruple Mass Spectrometer (TPD/RGA) Chamber.

2.3 Experimental Protocols

2.3.1 FTIR Experiments

Two different types of IR experiments were conducted. The first type of the FTIR experiments focused on the NO_x uptake of the synthesized materials at 323 K under monotonically increasing exposures of NO₂. FTIR experiments of the second type were associated with the thermal stability of the surface species that were generated upon NO_x adsorption. Prior to each NO_x adsorption experiment, the walls of the vacuum system (including also sample) were passivated by flushing 2 Torr of NO₂ (g) for an extended period of time (20 min) followed by evacuation at the same temperature. Next, in order to obtain a surface that is free of adsorbed NO_x and other adsorbates, the sample was annealed in vacuum by giving ramp to the sample temperature to 1023 K in a linear fashion with a heating rate of 12 K min⁻¹. After this annealing/cleaning protocol, the sample was cooled down to 323 K in vacuum. Before the acquisition of each spectral series, a background spectrum of the clean, adsorbate-free sample was obtained in vacuum at 323 K (with a residual reactor pressure <1 x 10⁻⁴ Torr).

 NO_2 (g) used in the experiments were synthesized by mixing NO (g) (99.9% purity, Air Products USA) and O_2 (g) (99% Ersoy Gaz) in a glass-bulb and purified via multiple freeze-thaw-pump treatments. During the NO_2 (g) adsorption experiments, precisely controlled doses of NO_2 (g) (measured by a 1000 Torr MKS Baratron absolute pressure transducer that is insensitive to the gas types) were introduced into the IR cell and a steady gas pressure reading was established.

2.3.1.1 Low temperature (323 K) Stepwise NO₂ (g) adsorption experiments

In a stepwise NO₂ adsorption experiment, for each dosing step, 0.6 Torr of NO₂ was introduced into the IR cell at 323 K. Before introduction of another dose, IR

cell was evacuated (<1 x 10^{-3} Torr). After the initial dose of NO₂, the sample spectrum was acquired at 323 K. By repeating this stepwise protocol, initial adsorption stages of NO_x-surface interactions are readily monitored. Typically, the low-temperature adsorption series was completed with a final dose at 323 K, where this time a high pressure dose of NO₂ (c.a. 8 Torr) was introduced on the sample surface for 20 min to ensure the saturation of the surface sites.

2.3.1.2 Temperature-dependent FTIR experiments

In a typical temperature-dependent adsorption experiment, the sample held at 323 K was exposed to 8 Torr of NO₂ for 20 min, which typically led to the saturation of the surface with NO_x species. Next, the system was evacuated ($<1 \times 10^{-4}$ Torr) and then the sample temperature was linearly ramped to a given temperature in vacuum. Once the target ramp temperature is reached, annealing was stopped, sample was cooled in vacuum to 323 K and the sample spectrum was acquired in vacuum. The same procedure was repeated for different target temperatures within 323 – 923 K in order to map the thermal behavior of the surface species via FTIR.

2.3.2 TPD Experiments

Prior to the each TPD data collection, oxidation-resistant thoria coated iridium filament of mass spectrometer was warmed up for 30 min and outgassed thoroughly. Later, the sample (annealed at 873 K for 2 hrs under inert atmosphere) was purged with 2 Torr NO₂ for 20 min and then the sample surface was cleaned by increasing the temperature from 323 K to 1023 K in a linear fashion. Then the sample was saturated with 8 Torr of NO₂ for 20 min and the IR cell was evacuated to 10^{-4} Torr. Finally, gate valve between IR cell and mass spectrometer was opened and TPD experiment was run while the sample temperature was raised to 1023 K in a linear fashion with a heating rate of 12 K/min.

2.3.3 XRD and BET

The powder XRD patterns were recorded using a Rigaku diffractometer, equipped with a Miniflex goniometer and an X-ray source with CuK α radiation, at λ = 1.54 Å, 30 kV and 15 mA. The powder samples were pressed and affixed to standard-sized glass slides and scanned in the 10–80°, 2 θ range with a scan rate of 0.01° s⁻¹. Diffraction patterns were assigned using Joint Committee on Powder Diffraction Standards (JCPDS) cards supplied by the International Centre for Diffraction Database (ICDD).

Surface area measurements of the samples (which were initially dehydrated at 623 K for 4 hrs) were determined by N_2 adsorption at 77 K via conventional BET (Brunauer, Emmett, and Teller) method by using a BET surface area analyzer (Micromeritics TriStar Surface Area and Porosity Analyzer).

2.3.4 Raman Spectroscopy

Raman spectra were recorded on a HORIBA Jobin Yvon LabRam HR 800 instrument, equipped with a confocal Raman BX41 microscope, spectrograph with an 800 mm focal length and a nitrogen cooled CCD detector. The Raman spectrometer was equipped with a Nd:YAG laser ($\lambda = 532.1$ nm). During the Raman experiments, the laser power was tuned to 20 mW, measured at the sample position, in order to minimize the sample heating effects. Before the Raman measurements, the powder samples were mechanically dispersed onto a single-crystal Si holder. The incident light source was dispersed by holographic grating with a 600 grooves/mm and focused onto the sample by using a 50X objective. The confocal hole and the slit entrance were set at 1100 μ m and 200 μ m, respectively. The spectrometer was regularly calibrated by adjusting the zero-order position of the grating and comparing the measured Si Raman band frequency with the typical reference value of 520.7 cm⁻¹. All Raman spectra were acquired within 100-4000 cm⁻¹ with an acquisition time of 213 s and a spectral resolution of 4 cm⁻¹. Bulk Ba(NO₃)₂, Fe(NO₃)₂.9H₂O and nano

powder Fe_2O_3 (Sigma-Aldrich, part no: 544884-5G) samples were used for the reference Raman spectra.

2.3.5 XPS

XPS measurements were performed using an ion-pumped Perkin-Elmer PHI ESCA 560 system with a PHI 25-270AR double pass cylindrical mirror analyzer (CMA). A Mg K α anode, operated at 15kV and 250 W with a photon energy of hv= 1253.6 eV, was used. The pressure of the chamber did not exceed 5×10^{-8} Torr during scans. Samples were mounted onto a probe with double-sided tape (3M Scotch). The C 1s core level at 284.7 eV, corresponding to adventitious carbon, was used to charge reference the spectra. XPS data was curvefitted using CasaXPS VAMAS processing software version 2.2 (Devon, United Kingdom) with a Shirley background subtraction and 70%-to30% Gaussian-Lorenztian lineshapes. Nitrate peaks (i.e. a discernible N 1s signal) could not be observed in XPS measurements due to the exposure of samples to the soft X-rays during XPS analysis, which are known to decompose nitrates [117]. Furthermore, prolonged scan times (ca. ~3 hours) were required to obtain satisfactory S/N for Ba 3d and Fe 2p orbitals. Although the nitrate structures were not amenable to XPS analysis, we were able to characterize the powder metal oxide structures. No changes in lineshape, denoting decomposition of the Ba, Fe or oxides were observed during data acquisition; hence, these structures examined were not altered during the photoelectron spectroscopy measurements.

2.3.6 TEM

The transmission electron microscopy (TEM) specimens were prepared by dispersing the fine catalyst powder particles in an ethanol suspension and applying this suspension onto a (lacey type) carbon film coated copper TEM grid. TEM analysis was carried out on a FEI Tecnai G2 F30 microscope with a specified point

resolution of 0.17 nm. The operating voltage of the microscope was 300 keV. All images were digitally recorded with a slow scan CCD camera. Elemental analysis and distribution of the species was analyzed at different points of the sample by acquiring electron energy loss spectroscopy (EELS) spectra.

3 RESULTS AND DISCUSSION

In order to understand the structure and NO_x uptake properties of the samples, ex-situ and in-situ instrumentations were used for analysis of the systems. Samples prepared by using incipient-wetness impregnation were examined by using two different NO_x uptake protocols. In the first protocol, the nitrate-loaded samples synthesized using solutions with nitrate precursors were further treated at elevated temperatures in order to monitor the thermally induced structural changes. In the second protocol, NO_2 (g) adsorption experiments were performed on the NO_x free samples so as to monitor NO_x stored species on the samples. Therefore, the results of this section consist of two parts: NO_x from solution precursors and NO_x storage behaviors of the synthesized materials from gas phase. It can be noted that all of the results in this study were performed by repeating of the experiments several times in order to establish reproducibility.

3.1 NO_x from solution precursors

Nitrate-loaded samples due to the impregnation protocol were annealed at the temperatures within 423-1273 K. Later, structural changes and thermal decomposition of the nitrates were examined via XRD and Raman spectroscopy. In order to understand the complex structures of ternary oxide system (Fe/Ba/Al), the simpler structural subunits, Al, Ba/Al and Fe/Al, were also initially analyzed. This analysis approach is given in Scheme 1.

Analysis of samples: from simple to complex structures i) 8(20) Ba/Al ii) 5(10)Fe/Al iii) Target system: 5(10)Fe/8(20)Ba/Al

Scheme 1. The list of the samples with varying structural complexities analyzed via XRD and Raman spectroscopy.

3.1.1 XRD and Raman Spectroscopy studies

3.1.1.1 8(20)Ba/Al

For the XRD and Raman analyses, samples were prepared via the impregnation protocol described in section 2.1, where the materials were synthesized using solutions with nitrate precursors and the nitrate-loaded samples were further treated at elevated temperatures in order to monitor the thermally induced structural changes.



Figure 14. Thermal behavior of the XRD profiles corresponding to the annealed (423 - 1273 K) and dried Ba/Al NO_x-storage materials with different Ba loadings: (a) 8Ba/Al and (b) 20Ba/Al (see text for details).

XRD profiles of the Ba/Al samples with 8 and 20 wt. % BaO loadings are presented in Figures 14a and 14b, respectively. The XRD patterns of the unannealed (i.e. mildly dried at c.a 323 K) 8(20)Ba/Al samples present diffraction maxima that can be assigned to γ -Al₂O₃ (JCPDS 29-0063, marked with filled circles) and crystalline Ba(NO₃)₂ (JCPDS 24-0053, marked with stars). Heat treatment at 423 K and increasing the temperature up to 623 K did not result in any significant changes in the XRD profiles. A further increase in the annealing temperature up to 873 K, leads to the complete disappearance of the diffraction maxima due to the Ba(NO₃)₂ for both samples with different Ba contents. It can be seen in Figure 14a that only very broad diffraction features associated with the γ -alumina support are visible in the XRD profiles of the 8Ba/Al sample annealed in the range of 873-1273 K. In addition to these major broad features, minor diffraction peaks corresponding to BaAl₂O₄ (JCPDS 17-0306) (marked with open circles) also starts to be visible at temperatures above 873 K, particularly for the 20Ba/Al sample (Figure 14b). The intensities of these latter reflections increase with increasing the annealing temperature to 1273 K.



Figure 15. Temperature-dependent ex-situ Raman spectra corresponding to the annealed (423 - 1273 K) and dried Ba/Al NO_x -storage materials with different Ba loadings: (a) 8Ba/Al and (b) 20Ba/Al. The inset presents the reference Raman spectrum of an unsupported (bulk) Ba(NO₃)₂ sample.

Figures 15a and 15b display a series of Raman spectra corresponding to the dried and annealed (423–1273 K) Ba/Al (8 and 20 wt. %) samples. The inset of Figure 15 presents the reference Raman spectrum of unsupported pure (bulk) Ba(NO₃)₂. This reference spectrum can be readily assigned to crystalline Ba(NO₃)₂, as revealed by the positions and sharpness of the Raman bands [118]. In addition, the detection of the lattice phonon band at 134 cm⁻¹ is also an indicator of crystallinity [118]. Barium nitrate crystallizes in the calcite structure [118, 119, 50, 51], and the observed Raman bands of bulk Ba(NO₃)₂ are assigned as follows: the most prominent band at 1043 cm⁻¹ is attributed to the symmetric stretching mode of the

nitrate (NO⁻₃) ion; the weak band at 1634 cm⁻¹ is assigned to the longitudinal optical (LO), and the group of weak bands at about 1357 and 1406 cm⁻¹ to the transverse optical (TO) modes of the antisymmetric stretch, respectively. The observation of the Raman-forbidden antisymmetric stretching modes also confirms that the calcite structure is not perfectly ordered. The peak with medium intensity at 730 cm⁻¹ is assigned to the nitrate bending mode.

The Raman spectra of the dried 8 and 20 wt. % Ba/Al samples (Figure 15a and 15b) are characterized by two major Raman bands at 1053 and 736 cm⁻¹ that are attributed to the symmetric stretching and bending modes of the NO₃⁻ ions that can be mostly associated with Ba sites (probably with some minor contribution from the Al sites on the support). In these spectra, the Ba(NO₃)₂ lattice phonon bands at 138 cm⁻¹ (for 8Ba/Al) and 142 cm⁻¹ (for 20Ba/Al) as well as weakly expressed features at 1356, 1406 and 1634 cm⁻¹ are visible. All these bands are characteristic features of the Ba(NO₃)₂ structure, similar to the ones observed in the reference (bulk) Ba(NO₃)₂ spectrum in the inset of Figure 15. However these major bands in Figure 15 are slightly blue shifted to higher wavenumbers (~10 cm⁻¹) in comparison to the ones given in the reference spectrum. These shifts can be attributed to the presence of surface NO₃⁻ species on the support surface with a lower degree of crystallinity and coordination [118].

Annealing of the samples with different Ba loadings at various temperatures within 423 to 1273 K, results in noticeable spectral changes. It is visible that after the annealing at 423 K and further increasing the temperature to 623 K, the Raman bands of the 8Ba/Al sample (Figure 15a) shift to lower wavenumbers (~9 cm⁻¹) with respect to the dried sample. Similar Raman shifts are also apparent for the 20Ba/Al sample (Figure 15b) after annealing at 873 K. This red shift in the frequencies of the Raman features as well as the attenuation of their intensities suggest the decomposition of the surface Ba(NO₃)₂ species. Therefore the Raman bands observed at 623 K (for the 8Ba/Al sample) and 873 K (for the 20 Ba/Al sample) characterize the presence of mostly crystalline/bulk nitrates left on the surface, which are still not completely decomposed at these temperatures. In addition, the series of spectra in Figures 15a and 15b also allow us to follow the intensity trends of the Raman features originating

from different species on the sample surfaces at various temperatures. It should be noted that the Raman intensities may not be proportional to the concentration of the species being observed [120]. However, repeated series of experiments with the current samples reveal that the observed changes in the Raman intensities are in a good correlation with the results of the XRD experiments performed for identical samples (Figure 14). Another important observation regarding the temperature dependent Raman data presented in Figure 15a is that, the most prominent Raman bands (the symmetric stretching mode of the nitrate ions and the lattice phonon band) in the spectrum of the 8Ba/Al sample at 623 K dramatically lose their intensities. Concomitantly, a new and relatively broad set of bands within 350–500 cm⁻¹ start to appear. In a series of former studies conducted by Mestl et al. [118, 121] these bands were attributed to defect - rich BaO structure. Barium oxide crystallizes in the rock salt structure and the first order Raman scattering is symmetry forbidden. Therefore, the bands developing in the lattice mode regime (350 – 500 cm⁻¹) in the current results are assigned to defect - induced Raman scattering of BaO.

For the 8Ba/Al sample (Figure 15a), a further increase in the annealing temperature to 873 K, leads to the complete disappearance of all nitrate-related Raman bands including the lattice phonon band at 133 cm⁻¹. Under these conditions, only the broad feature related to the BaO species remains visible. This result is indicative of the complete decomposition of Ba(NO₃)₂ to BaO on the 8Ba/Al sample at 873 K. It is also worth mentioning that the BaO feature is visible only as a very weak shoulder in the Raman spectrum corresponding to 873 K. A further increase in the annealing temperature leads to nearly complete disappearance of BaO feature. It is conceivable that this is related to the formation of BaAl₂O₄ and/or a crystallographically well-defined and a relatively more ordered BaO structure in which Raman scattering is symmetry forbidden.

Similar structural changes also take place on the sample with a higher Ba loading (Figure 15b); however the temperature for the completion of nitrate decomposition is about 250 K higher than that of the sample with 8 wt. % BaO. As can be observed from Figure 15b, at 873 K, the intensities of the most prominent nitrate – related Raman bands significantly decrease and the weak BaO related

features become visible. It should be emphasized that the Ba(NO₃)₂ species visible in the Raman spectrum at 873 K in Figure 15b are not quite observable in the corresponding XRD data (Figure 14b). This is most probably due to the low degree of ordering and crystallinity of these Ba(NO₃)₂ domains as well as the dissimilar detection limits of these two different experimental techniques. Increasing the annealing temperature of the 20Ba/Al sample to 1073 K resulted in the complete decomposition of nitrates. The Raman spectra presented in Figure 15b reveal that after annealing at temperatures higher than 1073 K, no Ba-nitrate bands can be observed except the very weak and broad set of bands due to BaO (350 – 500 cm⁻¹). In agreement with the XRD data (Figure 14b), it can be suggested that for the 20Ba/Al sample, decomposition of Ba(NO₃)₂ above 873 K is accompanied by the BaAl₂O₄ formation.

Observations given above reveal that the Ba-nitrate species on the alumina support material exhibit distinctively different thermal stabilities at various temperatures as a function of the Ba loading. In addition, the XRD and Raman data suggest that the temperature required for the complete decomposition of nitrates is about 250 K higher for the 20Ba/Al sample. The observations discussed above are also in good agreement with the former studies focusing on the effects of the Ba loading and the annealing temperature on the Ba/ γ -Al₂O₃ NO_x storage system [15, 60, 96]. Evidence for the presence of two different types of nitrate species with different thermal stabilities (surface nitrates that are associated with a monolayer BaO on the alumina support, and a bulk-like nitrate species that forms on this thin BaO layer) on the NO₂ –saturated BaO/ γ -Al₂O₃ sample has been reported in a previous series of studies [15, 60, 96].

3.1.1.2 5(10)Fe/Al



Figure 16. Thermal behaviour of the XRD profiles corresponding to the annealed (423 – 1273 K) and unannealed Fe/Al samples with different Fe loadings: (a) 5Fe/Al and (b) 10Fe/Al.

Figures 16a and 16b present the XRD data corresponding to the 5Fe/Al and 10Fe/Al samples. It can readily be seen that the unannealed samples as well as the samples annealed within 423 to 1073 K contain very broad diffraction maxima that can mostly be attributed to γ -Al₂O₃. It should be noted that the relatively minor diffraction features (marked with squares) are also visible particularly in Figure 16b. These peaks become discernible especially at high temperatures such as 1073 K - 1273 K. They can be attributed to the presence of α - Fe₂O₃ (hematite) (JCPDS 72-0469). At 1273 K, intensities of the diffraction maxima due to hematite increase which is accompanied by the development of very intense diffraction features associated with α -Al₂O₃ (corundum) (JCPDS 10-0173) which are marked with triangles, in Figures 16a and 16b. These observations indicate that α - Fe₂O₃ to α -Al₂O₃ in the temperature range of 1073 – 1273 K. It should be considered that such

a phase transformation between γ -Al₂O₃ and α -Al₂O₃ polymorphs occurs at relatively higher temperatures on pure alumina surfaces. Therefore it is apparent that the presence of highly dispersed α -Fe₂O₃ particles interacting with the γ - Al₂O₃ surface facilitates this transformation by lowering the phase transition temperature. Numerous studies investigated the influence of Fe³⁺ ions on the transformation from γ -Al₂O₃ to the α -Al₂O₃ phase, (e.g. in the form of ionic admixtures to the respective sol [122, 123] or as Fe₂O₃ [124, 125]). It was suggested that isolated Fe³⁺ ions can initiate local structural changes but have almost no influence on the temperature of corundum formation. On the other hand, the phase transformation temperature was reported to decrease due to the presence of small α - Fe₂O₃ (hematite) particles [126].



Figure 17. Temperature-dependent ex-situ Raman spectra corresponding to the annealed (423 - 1273 K) and dried Fe/Al samples with different Fe loadings: (a) 5Fe/Al and (b) 10Fe/Al. The Raman spectra in the insets present: (i) unsupported (bulk) Fe(NO₃)₃ • 9H₂O and (ii) unsupported (bulk) Fe₂O₃.

Figure 17a and 17b illustrate the Raman spectra corresponding to the Fe/Al samples containing different Fe loadings (5 and 10 wt. % Fe, respectively). The inset of Figure 17 also shows the reference Raman spectra of unsupported (bulk) (i) Fe(NO₃)₃ • 9H₂O and (ii) α - Fe₂O₃ (hematite). The reference Raman spectrum of bulk Fe(NO₃)₃ • 9H₂O is characterized by a set of typical Raman bands [127]. The most prominent band at 1054 cm⁻¹ can be assigned to the symmetric stretching vibration mode of the nitrate (NO₃) ions. The band with a medium intensity at 720 cm⁻¹ can be attributed to the nitrate bending mode. The weak band at 1634 cm⁻¹ can be attributed to the longitudinal optical (LO) mode, and the group of weak bands in the spectral range of 1250–1700 cm⁻¹ to the transverse optical (TO) mode of the nitrate antisymmetric stretch, respectively. In addition to these major features, the

Raman spectrum of $Fe(NO_3)_3 \cdot 9H_2O$ presents additional low frequency Raman bands (< 600 cm⁻¹) which can probably be associated with the formation of a Fe³⁺-NO₃⁻ complex in which water is also coordinated to the Fe³⁺ ion [127]. The weak band at 520 cm⁻¹ and the broad shoulder at ~433 cm⁻¹ characterize the symmetric $A_{1g}(Fe-OH_2)$ stretch mode of the $Fe(H_2O)^{3+}_{6}$ ion, while the low frequency broad bands at ~ 277 and 259 cm⁻¹ are assigned to the lattice mode of the iron nitrate crystal.

The crystalline α - Fe₂O₃ (hematite) (Figure 17, spectrum ii) belongs to the D⁶_{3d} crystal space group, which exhibit the following Raman features: [128-133] seven phonon lines (two A_{1g} modes at 232 and 506 cm⁻¹ and five E_g modes at 252, 293, 299, 417 and 618 cm⁻¹), and two-magnon scattering features at 1323 cm⁻¹ and 1332 cm⁻¹. Furthermore, a number of additional minor bands at 820, 952, 1060 and 1111 cm⁻¹, which are also characteristic of the hematite structure can also be seen in the reference spectrum [128].

The Raman spectra of the dried Fe/Al samples (Figure 17a and 17b), are characterized by the bands at ~1044, 716 cm⁻¹, the weak shoulder at ~ 433 cm⁻¹ and a group of bands at 1332 and 1447 cm⁻¹. Considering the Raman spectrum of the Fe(NO₃)₃ · 9H₂O sample given in the inset (i) of Figure 17, all of these bands can be attributed to Fe(NO₃)₃. It can also be seen in the topmost spectra of Figure 17 that the prominent symmetric stretching and bending bands of the nitrate ions are red shifted to lower wavenumbers in comparison with those in the reference Fe(NO₃)₃ spectrum. These shifts can probably be attributed to the small particle size of the Fe(NO₃)₃ domains, presence of coordinatively unsaturated surface Fe sites and/or the interaction of the NO₃⁻ species with the γ -Al₂O₃ support surface.

When the 5Fe/Al and 10Fe/Al samples (Figures 17a and 17b) were heated at 423 K, the nitrate-related Raman features undergo relatively minor changes, mostly in the form of intensity attenuation. On the other hand, annealing at 423 K results in the generation of additional minor features that are visible at 227, 295, 413 cm⁻¹, a broad band within 600–950 cm⁻¹, as well as a strong broad band at ~1320 cm⁻¹. These additional bands can readily be assigned to the typical Raman modes of α -

Fe₂O₃ (Figure 17, inset ii) which forms due to the partial decomposition of iron nitrates on the surface of the 5(10)Fe/Al samples. Increasing the annealing temperature to 623 K results in almost complete destruction of the nitrate related Raman bands. Despite the small differences in peak positions, the Raman spectra after annealing within 423–1273 K are characterized with strongly expressed bands that correspond to α - Fe₂O₃ structure. These results demonstrate that the decomposition of the supported iron nitrate on the γ -Al₂O₃ surface starts taking place below 423 K and leads to α - Fe₂O₃ formation in both 5(10)Fe/Al samples. Accentuation of the Raman band intensities corresponding to the hematite domains at higher temperatures may suggest enrichment in the surface concentration of α- Fe₂O₃ species, ordering of the hematite crystal structure as well as an increase in the α -Fe₂O₃ particle size (i.e. sintering). Raman spectra of both Fe containing oxide materials corresponding to 1273 K also reveal a readily distinguishable band at 663 cm⁻¹. According to the former Raman spectroscopy studies in the literature on various iron oxides [129, 133], Raman spectrum of Fe₃O₄ (magnetite) is characterized by strongly expressed bands located at 663 cm⁻¹ and weakly intensive bands at 302, 514 and 534 cm⁻¹. Thus, it is apparent that within 623–1273 K, the Raman spectra of the 5(10)Fe/Al samples given in Figures 17a and 17b consist of combinations of bands related to the simultaneous presence of α - Fe₂O₃ (hematite) and Fe₃O₄ (magnetite). It should also be noted that the presence of minority iron oxide domains with dissimilar stoichiometries to the ones discussed above or other crystalline/amorphous iron oxides with very small particle sizes cannot be ruled out, as these structures may be difficult to detect.

3.1.1.3 5(10)Fe/8(20)Ba/Al



Figure 18. Thermal behavior of the XRD profiles corresponding to the annealed (423 - 1273 K) and dried Fe/Ba/Al mixed oxide NO_x-storage materials with 5 wt. % Fe loading and varying Ba loadings: (a) 5Fe/8Ba/Al and (b) 5Fe/20Ba/Al (see text for details).

Figures 18a and 18b present the XRD profiles of 5Fe/8Ba/Al and 5Fe/20Ba/Al mixed oxide NO_x -storage materials with a relatively lower Fe loading while Figures 19a and 19b show the XRD data for the 10Fe/8Ba/Al and 10Fe/20Ba/Al samples with higher Fe loadings. From the Figures 18 and 19, it can be seen that all of the dried samples with different Ba and Fe loadings are characterized by diffraction peaks due to the crystalline Ba(NO₃)₂ (marked with stars in Figures 18 and 19) and very broad features of the γ -Al₂O₃ (marked with dark circles in Figures 18 and 19). The intensity of the characteristic Ba(NO₃)₂-related reflections are practically unchanged in the temperature range of 423-623 K, suggesting that the ordered Ba(NO₃)₂ crystallites are relatively thermally stable on the support surface. It is also seen that the Ba(NO₃)₂-related reflections in the XRD

profiles of the 5Fe/8Ba/Al samples are characterized with relatively higher intensities in comparison with that of the 8Ba/Al sample which do not contain any Fe (Figure 14a). In contrast, such a situation is not valid for the samples containing higher loadings of Ba where bulk-like $Ba(NO_3)_2$ is already formed. This points to the fact that the presence of 5 or 10 wt. % Fe in the samples containing lower Ba content results in the formation of crystallographically more ordered $Ba(NO_3)_2$ domains on the Al₂O₃ material during the impregnation protocol.

Increasing the annealing temperature to 873 K leads to the almost complete disappearance of all of the features due to Ba or Fe associated domains and results in XRD profiles which are similar to the profile of the Al_2O_3 material (Figures 18 and 19). This thermal behavior suggests that at 873 K all of the mixed NO_x -storage materials present a disordered structure or posses crystalline domains with extremely small sizes.

Figure 18 shows that after the annealing at 1073 K, 5Fe/8Ba/Al sample maintains its disordered structure (Figure 18a) while BaAl₂O₄ formation (marked with open circles in Figures 18 and 19) is observed for the 5Fe/20Ba/Al sample at this temperature (Figure 18b). At higher annealing temperatures such as 1273 K, both in the 5Fe/8Ba/Al and 5Fe/20Ba/Al samples, γ -Al₂O₃ support material starts to undergo a phase transformation towards the α -Al₂O₃ (corundum) phase (marked with open triangles in Figures 18 and 19). This is also accompanied by the formation of the BaAl₂O₄ phase for both samples, although this occurs to a smaller extent for the 5Fe/8Ba/Al case. It should be noted that such a phase γ -Al₂O₃ to α -Al₂O₃ transformation take places at relatively higher temperatures on pure alumina surfaces.

It is worth mentioning that at 1273 K, the corundum-related reflections are characterized with drastically lowered intensities for the 5Fe/20Ba/Al sample (Figure 19b) in comparison with that of the 5Fe/8Ba/Al sample. It is evident that the increased Ba content (20 wt. % BaO) suppresses the corundum formation to a certain extent. Such behavior is also observed for the synthesized NO_x storage materials with a higher Fe content (Figures 19a and 19b). Addition of doping elements to alumina,

in order to prevent or thermally delay the polymorphic phase transformations have been extensively studied in the literature [134, 135]. Along these lines, it was reported that, the addition of Ba as a doping element (2.7 wt.% Ba) to the alumina enhances the thermal stability of γ -Al₂O₃ by increasing the polymorphic phase transition temperature up to 1588 K [135].



Figure 19. Thermal behavior of the XRD profiles corresponding to the annealed (423 - 1273 K) and dried Fe/Ba/Al mixed oxide NO_x -storage materials with 10 wt. % Fe loading and varying Ba loadings: (a) 10Fe/8Ba/Al and (b) 10Fe/20Ba/Al (see text for details).

Figure 19 reveals further insight regarding the thermally induced structural changes in the NO_x-storage materials with 10 wt. % Fe loading. XRD profiles corresponding to 1073 K, presents indications of the presence of Fe₂O₃ (marked with dark squares in Figure 19) for both of the 10Fe/8Ba/Al and 10Fe/20Ba/Al samples. Although, some of the Fe₂O₃ remains to exist at 1273 K on the 10Fe/8Ba/Al sample (Figure 19a), hematite domains seem completely to disappear for the 10Fe/20Ba/Al sample at this temperature (Figure 19b). At 1273 K, corundum reflections dominate

in the XRD profiles of both samples. Another important aspect at 1273 K (in Figures 19a and 19b) is that although no $BaAl_2O_4$ is observed for the sample with low Ba content (Figure 19a), $BaAl_2O_4$ starts to form on the sample with high Ba content. This observation is also in line with the data shown in Figure 18 indicating that the presence of Fe suppresses the $BaAl_2O_4$ formation, particularly for high Fe loadings.

XRD data clearly demonstrate that adding a Fe component to a typical $BaO/Al_2O_3 NO_x$ -storage material leads to significant structural changes, alterations in the thermal behavior and the stability of the NO_x -storage units. Further insight regarding these structural changes upon Fe addition to the BaO/Al_2O_3 system can be gained via Raman spectroscopy.



Figure 20. Temperature-dependent ex-situ Raman spectra corresponding to the annealed (423 - 1273 K) and dried Fe/Ba/Al mixed oxide NO_x -storage materials with a 5 wt. % Fe loading and varying Ba loadings: (a) 5Fe/8Ba/Al and (b) 5Fe/20Ba/Al. The insets present (i) the lattice phonon and nitrate stretching bands and (ii) the nitrate bending band.



Figure 21. Temperature-dependent ex-situ Raman spectra corresponding to the annealed (423 - 1273 K) and dried Fe/Ba/Al mixed oxide NO_x -storage materials with a 10 wt. % Fe loading and varying Ba loadings: (a) 10Fe/8Ba/Al and (b) 10Fe/20Ba/Al. The insets present (i) the lattice phonon and nitrate stretching bands and (ii) the nitrate bending band.

The temperature dependent ex-situ Raman spectra of the 5Fe/8Ba/Al and 5Fe/20Ba/Al samples are given in Figures 20a and 20b, respectively. Similarly, Figures 21a and 21b present the Raman data corresponding to the 10Fe/8Ba/Al and 10Fe/20Ba/Al, respectively. The insets of Figures 20 and 21 highlight the Raman

shifts of the most prominent bands in the spectra, where the insets labeled as (i) show the lattice phonon and the symmetric nitrate stretching bands while the insets labeled as (ii) display the nitrate bending band.

The Raman spectra due to the dried samples in Figures 20 and 21 present similar characteristics. These spectra are dominated by the strong Raman bands associated with the symmetric, antisymmetric stretching and bending modes of the NO_3^- ions which bear significant resemblance to the reference Ba-nitrate and Fenitrate spectra given in the insets of Figures 15 and 17. Furthermore, all of these dried samples present the lattice phonon band at 143 cm⁻¹ which clearly indicates the presence of crystalline Ba(NO₃)₂. In addition, a low frequency band at 520 and a weak shoulder at ~ 433 cm⁻¹ corresponding the symmetric A_{1g} (Fe-OH)₂ stretching mode of Fe(H₂O)₆³⁺ ion can also be observed [127]. These observations point to the fact that Fe(NO₃)₃ and Ba(NO₃)₂ domains co-exist on the dried samples which yield similar nitrate-related overlapping bands in the Raman spectra. It is also seen that the most prominent bands (the insets of Figures 20 and 21) of the dried samples are blue shifted to higher wavenumbers in comparison with those of the reference Ba(NO₃)₂ spectrum. These shifts can be attributed to the presence of surface or amorphous NO₃⁻ species on the support surface with lower degree of crystallinity.

Annealing of Fe/Ba/Al storage materials at 423 K preserves the iron and barium nitrates on the surface (Figures 20 and 21). A very weak band at 300 cm⁻¹ that is indicative of the presence of α - Fe₂O₃ structure is also visible for the 10Fe/8Ba/Al sample annealed at 423 K. As the annealing temperature increases, insets of Figures 20 and 21 reveal that the symmetric stretching, bending and phonon lattice bands shift to lower wavenumbers than that of the dried Fe/Ba/Al samples. This temperature dependent behavior resembles the similar trend observed for the Fe-free NO_x -storage materials and can be attributed to the decomposition of the surface NO₃⁻ species during annealing. Thus nitrate-related Raman bands observed at T > 423 K can be assigned to the presence of thermally stable bulk-like nitrates remaining on the surface of the Fe/Ba/Al storage materials.

Samples analyzed after annealing at 623 K in Figures 20 and 21 are still dominated by the strong nitrate features, however they also unveil an important aspect, the hematite formation. Hematite formation at 623 K is evident in the 5Fe/8Ba/Al and 5Fe/20Ba/Al samples (Figures 20a and 20b) as weak shoulders at about 300 and 1320 cm⁻¹. They are more clearly discernable in the samples with higher Fe content such as 10Fe/8Ba/Al and 10Fe/20Ba/Al samples (Figures 23a and 24b) as a result of the stronger bands at ~225, 295, 411, 618, and 1328 cm⁻¹. As expected, these changes can be readily attributed to the decomposition of the deposited ferric nitrate on the surface and the formation of α - Fe₂O₃. Comparing the relative stabilities of nitrate species on the Ba/Al and the Fe/Al systems (Figures 15 and 17), it can be argued that Ba-nitrates are significantly more stable than Fe nitrates at 623 K. Thus these results imply that the Fe-nitrate decomposition is probably completed to a great extent in the studied Fe/Ba/Al systems at 623 K. Therefore, the Raman spectra of the Fe/Ba/Al samples at 623 K contain Raman bands mostly due to of the presence of thermally stable bulk-like Ba-nitrates and α - Fe_2O_3 , respectively.

Thermal behavior and the structural changes in the Fe/Ba/Al system at 873 K show interesting variations depending on the relative composition of the Fe/Ba/Al storage-material. According to Figures 20a and 20b, Fe/Ba/Al systems with a lower Fe content of 5 wt. % still contain highly stable nitrates which are still present at 873 K. This is in contrast with the iron-free 8Ba/Al system (Figure 15a) having an identical Ba/Al weight ratio where all of the nitrates decompose below 873 K, i.e. at a significantly lower temperature than that of the 5Fe/(8 or 20Ba)/Al systems. It is also evident from Figures 20a and 20b that the 5Fe/(8 or 20 Ba)/Al systems at 873 K also contain hematite and magnetite domains. Therefore, these observations suggest that addition of 5 wt. % Fe to the 8Ba/Al system leads to a thermal stabilization of the formed nitrates and prevents their complete decomposition at 873 K. One possible explanation for this behavior is that at lower Fe loadings such as 5 wt. %, Fe domains may prefer to spread in a more uniform fashion on the alumina support material by forming small Fe₂O₃ and Fe₃O₄ crystallites, providing an extensively broad and an active interface for the $Ba(NO_3)_2$ interaction and stabilization. Thus, under these conditions, interaction of Ba(NO₃)₂ domains with the alumina support material is profoundly altered. This argument is also consistent with the observation that no significant amount of Fe_2O_3 or Fe_3O_4 signals were detected in the XRD experiments given in Figures 18a and 18b, supporting the lack of large Fe_2O_3 or Fe_3O_4 crystallites on the surface under the conditions described above.

In contrast to the 5Fe/(8 or 20Ba)/Al systems, thermal behavior of the NO_x - storage materials with a higher Fe loading of 10 wt. % displays dissimilar structural properties at 873 K. At 873 K, 10Fe/(8 or 20Ba)/Al systems almost completely lack any nitrate bands in their Raman spectra (Figures 21a and 21b). In these relatively iron-rich samples, only Fe₂O₃ and Fe₃O₄ related Raman bands exist at 873 K, suggesting the complete decomposition of Fe and Ba nitrates on the surface. These experimental findings can also be explained by using an argument in accordance with the ones discussed earlier. Therefore, it can be suggested that higher loadings of Fe in the Fe/Ba/Al system results in the formation of larger Fe₂O₃ and Fe₃O₄ crystallites leading to a phase segregation between the Fe and Ba domains. The weakening in the interaction between the Fe and Ba domains leads to a structural configuration where the interaction of the Ba domains with the alumina support starts to approach towards the Ba/Al system in which in the absence of Fe domains, Ba domains directly interact with the alumina support.

Raman spectra of the Fe/Ba/Al systems annealed at $T \ge 1073$ K are almost exclusively dominated by the Fe₂O₃ and Fe₃O₄ features regardless of the relative composition of the Fe/Ba/Al structure. Intensities of the hematite and magnetite Raman signals also increase with increasing annealing temperature to 1273 K, suggesting ordering of the crystal structure as well an increase in the particle size.

Besides, standard molar enthalpy (heat) of formation at 298.15 K ($\Delta_f H^\circ$) for some of Ba- and Fe- related species that were observed in XRD and Raman data can be noted as: $\Delta_f H^\circ_{(\text{barium nitrate})} = -988.0 \text{ kJ/mol}; \Delta_f H^\circ_{(\text{barium oxide})} = -548.0 \text{ kJ/mol}; \Delta_f H^\circ_{(\text{iron (III) oxide})} = -824.2 \text{ kJ/mol and } \Delta_f H^\circ_{(\text{iron (II, III) oxide})} = -1118.4 \text{ kJ/mol [136]}.$

Assignment of Raman bands for the spectra of 8(20)Ba/Al and 5(10)Fe/Al and 5(10)Fe/8(20)Ba/Al systems are summarized in Table 3.

Table 3. Raman bands assigned for Ba- and Fe- related nitrate and oxide features[50, 51, 119, 122-133].

Ba(NO ₃) ₂	Defect-rich BaO	Fe(NO ₃) ₃ .9H ₂ 0	α-Fe ₂ O ₃
lattice phonon band: 134 cm^{-1}	lattice mode: 350-500 cm ⁻¹	lattice mode: 259 and 277 cm ⁻¹	lattice modes: 820, 952, 1060 and 1111 cm ⁻¹
v_{sym} 1045 cm $v_{bending}$: 730 cm ⁻¹ $v_{antisym}$ of LO: 1634 cm ⁻¹		V _{sym} (nitrate): 1054 Cm ⁻¹ V _{bending} (nitrate): 720 cm ⁻¹ V _{antisym} (nitrate) of LO: 1634 cm ⁻¹	A _{1g} : 232 and 506 cm ⁻¹
$v_{antisym}$ of TO: 1357 and 1406 cm ⁻¹		$v_{antisym (nitrate)}$ of TO: 1250-1700 cm ⁻¹	E _g : 252, 293, 299, 417 and 618 cm ⁻¹
		$v_{sym A_{1g}}$ (Fe-OH ₂): 433 and 520 cm ⁻¹	magnon scattering mode: 1323 and 1332 cm ⁻¹

3.1.2 BET Results

BET surface areas of the NO_x free samples were also analyzed. Results are given in Table 4.

Table 4. BET surface area results for the samples Al, 8(20)Ba/Al, 5(10)Fe/Al, and 5(10)Fe/8(20)Ba/Al samples annealed at 873 K.

	Al	8Ba/Al	20	Ba/Al	5Fe/Al		10Fe/Al
BET (m^2/g)	223	185	12	6	199		175
error (± m ² /g)	0.2	0.2	0.1		0.5		0.2
	5Fe/8Ba/Al	10Fe/8Ba	/Al	5Fe/20Ba/Al		10Fe/20Ba/Al	
BET (m ² /g)	146	160		145		115	
error $(\pm m^2/g)$	0.2	0.2		0.1		0.2	

BET measurements indicated that impregnation of Ba- and Fe- species to the γ -Al₂O₃ both resulted in a decrease in the surface areas. It can be also seen that as the loadings of the Ba and Fe increase, the surface areas are further reduced.



Figure 22. (a) Ba $3d_{5/2}$ region of the XPS spectra corresponding to 10Fe/20Ba/A1 samples after annealing at 1073 K and 623 K. (b) Fe 2p region of the XPS spectra corresponding to 5Fe/8Ba/A1 after annealing at 1073 K and 623 K.

Figures 22a shows Ba $3d_{5/2}$ core level shifts of 10Fe/20Ba/Al samples annealed to 623 and 1073 K, respectively. The Ba $3d_{5/2}$ binding energy at 779.4 eV (Figure 22a) denotes the BaO feature present in the sample after the decomposition of Ba(NO₃)₂ [137]. The binding energy shift to 779.9 eV (Figure 22a) is in close agreement to the corresponding value for a pure BaAl₂O₄ (779.7 eV) crystal phase [138]. It should be noted that the photoelectron spectra is surface sensitive, probing the top-most 50-100 A. Thus photoelectron studies are also consistent with the
current Raman and XRD data indicating the transformation of BaO species into BaAl₂O₄ domains on the surface of the 10Fe/20Ba/Al samples.

The relatively wide range of XPS binding energies reported in the literature for Fe₂O₃ [139] and Fe₃O₄ [140] makes it difficult to definitively validate the formation of Fe₂O₃ that the Raman data and XRD patterns indicate. The direction of the Fe 2p core level shifts with increasing annealing temperature, however, suggests the formation of Fe₂O₃. Figure 22b shows the Fe 2p orbitals of the 5Fe/8Ba/Al sample after annealing to 623 K (709.1 eV) and 1073 K (709.9 eV), respectively (with Fe 2p_{3/2} binding energy positions in parentheses). An accompanying +0.8 eV binding energy shift in the Fe 2p orbitals indicate greater electron density deficiency, consistent with a Fe(^{+2/+3}) transformation into a fully Fe(⁺³)-bearing mineral oxide (e.g., Fe₂O₃). In comparing the core level shifts of samples with higher Fe loadings, 10Fe/20Ba/Al, an identical trend for the Fe 2p_{3/2} binding energy shift was observed between the 623 and 1073 K annealing temperatures.

3.1.4 TEM and EELS analysis

3.1.4.1 Al and 20Ba/Al



Figure 23. TEM micrographs were given for Al and Ba/Al samples. (a) Al, (b) 20Ba/Al. 20Ba/Al sample was initially thermally treated at 873 K.

Representative TEM micrograph of Al reveals that γ -Al₂O₃ have rod like porous grains with small particle sizes. This is in agreement with the XRD data (shown in Fig 16a, first spectrum at the bottom) that shows broad features indicating small particles of alumina.

When Ba-species are impregnated onto the support, surface morphology of the 20Ba/Al sample looks similar to that of Al (Fig 25b). This suggests a relatively good dispersion of Ba-species that is difficult to differentiate from the underlying γ -Al₂O₃ morphology.

3.1.4.2 10Fe/20Ba/Al



Figure 24. TEM micrograph and EELS spectra for 10Fe/20Ba/Al sample. The sample was initially thermally treated at 873 K. EELS spectra were acquired for four randomly chosen areas on the micrograph.

Representative TEM image for the 10Fe/20Ba/Al sample annealed at 873 K is shown in Figure 24. Comparison of the surface morphology of the Fe/Ba/Al samples resemble to that of γ -Al₂O₃ and BaO/ γ -Al₂O₃ samples (data shown in Fig 25) and display a complex surface structure with grains. Further spatially-resolved elemental information can be attained via electron energy loss spectroscopy (EELS). Figure 24 presents EELS data collected from various independent zones of the same sample in an attempt to obtain some statistical knowledge associated with the relative amounts of Fe and Ba and the relative dispersion of these species on the catalyst surface. EELS measurements obtained from four different regions on the

catalyst surface indicate Ba distribution seems to be relatively more uniform compared with the Fe distribution. This is particularly evident as Fe signal completely vanishes at certain locations on the surface while Ba signal is always detectable in all of the analyzed cases. It should be noted that our detailed TEM studies on γ -Al₂O₃, BaO/ γ -Al₂O₃ and Fe/Ba/ γ -Al₂O₃ indicated that contrast differences in the obtained TEM images cannot be correlated with the presence of a specific phase. In other words, the contrast difference is likely arising from the sample thickness effects.

3.2 NO_x storage behaviors of the synthesized materials from gas phase

This chapter focuses on NO_x uptake of synthesized materials from gas phase followed by FTIR and TPD which allow monitoring of changes in the surface properties of storage sites using NO_2 (g) as a probe molecule.

In order to understand the complex NO_x adsorption features of a very intricate ternary oxide system (Fe/Ba/Al), the simpler structural subunits, Al, Ba/Al and Fe/Al, were analyzed in a separate fashion. Moreover, NO_x storage behavior of BaAl₂O₄ sample was also examined. After having understood the NO_x interactions of these simpler subunits separately, combinations of these simpler units having more complex structures were analyzed. Finally the NO_x uptake and storage of the complex Fe/Ba/Al system was examined in the light of the complimentary data that belongs to simpler structural subunits. This analysis approach was given by Scheme 2. <u>Analysis of samples: from simple to complex structures</u>
i) Al
ii) 8(20)Ba/Al and BaAl₂O₄
iii) 5(10)Fe/Al
iv) Target system: 5(10)Fe/8(20)Ba/Al

Scheme 2. The list of the samples with varying structural complexities analyzed via FTIR spectroscopy.

3.2.1 FTIR Results

3.2.1.1 Al

 NO_x adsorption on various oxide systems have been thoroughly studied in the literature [140-153]. A summary of the commonly observed surface NO_x species are given in Table 5. Current FTIR results can be analyzed in the light of the information given in Table 5 as well as other relevant reports [140-153].

Figure 25 shows the IR results of the adsorption experiments on the γ -Al₂O₃ sample. The spectral window within 1000-2500 cm⁻¹ yields a large number of overlapping IR features. This series of IR spectra is very similar to those previously reported ones [13, 48, 66, 141, 142]. Based on the results of previous reports, the resulting IR bands can be assigned to a nitro compound, different types of nitrites and nitrates on γ -Al₂O₃: bridging nitrite (v₃; 1230-1205 cm⁻¹), monodentate nitrite (v₃; 1470-1450 cm⁻¹ and v₁; 1065-1050 cm⁻¹), bridging nitrate (v₃; 1650-1600 cm⁻¹ and 1225-1170 cm⁻¹ and v₁; 1030-1000 cm⁻¹), bidentate nitrate (v₃; 1565-1500 cm⁻¹ and 1300-1260 cm⁻¹ and v₁; 1040-1010 cm⁻¹), monodentate nitrate (v₃; 1530-1480 cm⁻¹ and 1290-1250 cm⁻¹ and v₁; 1035-970 cm⁻¹) [12, 15, 143]. Intensities of the nitrite features (monodentate and bridging) reach a maximum and then disappear where the nitrate related bands continue to grow with increasing doses of NO₂. IR spectra given in Fig 27a suggests that the nitrate formation on alumina at 323 K goes through a nitrite precursor [12]. This behavior is explained by disproportionation reaction of the NO₂ given below [66].

Species	Frequencies	Adsorbate	Adsorbent
(ads)	(cm ⁻¹)		
N ₂	2260-2180	N ₂	Metals
N ₂ O	2305-2220, 1339-1195	N ₂ O, NO	Oxides
N ₂ O ₂ ²⁻	1384, 1190, 1150, 830	NO	MgO
trans- N ₂ O ₂	1750-1730	NO	Y-Zeolites
cis- N ₂ O ₂	1902-1840, 1795-1735	NO	Oxides
NO	1820-1103	NO	Oxides
NO	1980-1720	NO	Oxides
NO ⁺	2260-1830	NO, NO ₂	Oxides
NO ₂ -	1330-1208, 1230-1180, 900-850	NO	Oxides
ONO-	1470-1400, 1185-1120	NO	Oxides
N ₂ O ₃	1920, 1555, 1305	NO	Y-Zeolites
NO ₂	1632, (1320)	$NO + O_2$	V_2O_5/Al_2O_3
N ₂ O ₄	1740, (1380)	NO ₂	CuO
NO ₂ ⁺	2200-1980	NO, NO ₂	Oxides
NO ₃ -	monodentate: 1570-1458, 1331-1250, 1035-970	NO, NO ₂	Oxides
	bidentate: 1600-1500, 1310-1225, 1040-1003	NO, NO ₂	Oxides
	bridging: 1660-1590, 1260-1225, 1030-1000	NO ₂	Oxides

Table 5: Infrared Bands Assigned to N_xO_y Adsorbed Species [152].

$$2NO_2 \leftrightarrow NO^+NO_3^- \tag{8.1}$$

$$Al^{3+-}O_2^{-} + NO^+NO_3^{-} \leftrightarrow NO_3^{-}...Al^{3+}O^{2-}...NO^+$$

$$(8.2)$$

$$NO_2^- + NO_2 \leftrightarrow \dots NO_3^- + NO$$
 (8.3)



Figure 25. FTIR spectra for NO₂ (g) adsorption on Al. (a) FTIR spectra of stepwise NO₂ adsorption on the Al sample at 323 K. Inset shows 1400-1100 cm⁻¹ region for 323 K adsorption experiment. (b) Temperature-dependent (323 - 923 K) FTIR spectra for NO₂ (g) adsorbed Al sample.

The IR spectra recorded during all the NO₂ adsorption experiments display a development of a broad feature in the 1920-1980 cm⁻¹ frequency range which can be attributed to the alumina-bound N₂O₃ (formed by the reaction of NO₂ and NO) [144] and/or NO⁺ adsorbed on alumina [66, 145]. Formation of the N₂O₃ species was suggested to occur via the following reaction: [66]

$$NO_2 + NO \rightarrow N_2O_3$$
 (8.4)

A couple of very weak bands are also observed near 2250 cm⁻¹ that can be assigned to the adsorbed N₂O. This feature disappears after outgassing at increasing temperatures [146].

Figure 25a shows that as the nitrate coverage increases, IR bands shift to the higher wavenumbers [13]. This behavior is reversible. As can be seen in Figure 25b, with increasing temperatures, IR bands shift to the lower wavenumbers due to

decreasing surface coverage and desorption of nitrates from the alumina surface. The relative stabilities of different types of nitrates during temperature treatment cannot be differentiated due to the overlapping features of the nitrate bands. It is readily seen in Fig. 27b that all of the detected nitrate bands disappear above 773 K.

3.2.1.2 8(20)Ba/Al

The IR features observed for $8wt\%BaO/\gamma-Al_2O_3$ and $20wt\%BaO/\gamma-Al_2O_3$ (see Fig 28 and 29) are in accord with those previously reported for $BaO/\gamma-Al_2O_3$ [48, 50, 54, 147]. FTIR spectra of stepwise NO₂ adsorption on both 8wt%BaO and $20wt\%BaO/\gamma-Al_2O_3$ at 323 K (Fig 28a and 29a) indicate that during the initial phase of the NO₂ adsorption, as can be seen from the main component of the broad band at ~1226 cm⁻¹, bridging nitrites are dominant, whereas with further NO₂ exposure, nitrates become the prevailing species formed on the surface of Al₂O₃ and BaO components.



Figure 26. FTIR spectra for NO₂ (g) adsorption on 8Ba/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 8Ba/Al sample at 323 K. Inset shows 1400-1100 cm⁻¹ region for 323 K adsorption experiment. (b) Temperature-dependent (323 - 923 K) FTIR spectra for NO₂ (g) adsorbed 8Ba/Al sample.



Figure 27. FTIR spectra for NO₂(g) adsorption on the 20Ba/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 2Ba/Al sample at 323 K. Inset shows 1400-1100 cm⁻¹ region for 323 K adsorption experiment. (b) Temperature-dependent (323 - 923 K) FTIR spectra for NO₂(g) adsorbed 20Ba/Al sample.

Such a transformation between two different NO_x species on the surface is also consistent with the observation of a isosbestic point at ~1222 cm⁻¹. Various types of nitrates can be identified in Figures 26a and 27a based on the previous reports in the literature [13, 48, 66, 141, 142] which reveal that surface/bidentate (1300-1310 and 1585-1600 cm⁻¹) and bulk/ionic (1305-1325 and 1434-1472 cm⁻¹) nitrates are present on the baria sites. In addition, the small feature centered around 1745-1770 cm⁻¹ can be attributed to the $v_1 + v_4$ combination band for bulk Ba(NO₃)₂. The formation and transformation mechanisms of NO_x species observed upon NO₂ adsorption on BaO/ γ -Al₂O₃ was proposed to be as follows by Szanyi et al. [144]:

$$BaO + 2NO_2 \rightarrow NO_3^{-}...Ba...NO_2^{-}$$
(9.1)

$$NO_3^-...Ba...NO_2^- + NO_2 \rightarrow NO_3^-...Ba...NO_3^- + NO$$
 (9.2)

As expected, bulk-like/ionic nitrate features are more pronounced in the spectra corresponding to the higher Ba loading (i.e. 20wt%BaO/ γ -Al₂O₃ with respect to that of 8wt%BaO/ γ -Al₂O₃ case. On the other hand, nitrates on alumina sites (~ 1610 and 1265 cm⁻¹) are less visible in the 20 wt%BaO case (Figures 26a and 27a). This can be associated to the covering of the alumina sites by the BaO phase with increasing loading [144].

Comparison of Figure 25 with Figures 26 and 27 reveals that the broad band at ~1920-1980 cm⁻¹ which is clearly visible in the case of γ -Al₂O₃ (Figure 25) is barely visible for the BaO/ γ -Al₂O₃ system (Figures 26 and 27). This is consistent with the fact that BaO domains with a very high affinity towards NO_x species, cover a large fraction of the support (γ -Al₂O₃) surface leaving a very limited amount of exposed bare γ -Al₂O₃ sites for the formation of the weakly-bound molecular N₂O₃ species whose formation mechanism was described in detail above [148]. Observation of the larger N₂O₃ band for the 8Ba/Al system (Figure 26) having a larger fraction of exposed alumina support sites with respect to that of the 20Ba/Al system (Figure 27) also support this argument. Thus rather than the weakly-bound molecular N₂O₃ species, in the presence of BaO, NO₂ adsorption leads to the formation of strongly bound nitrite and nitrate species on BaO/ γ -Al₂O₃.

Thermal stabilities of the NO₂ saturated BaO/ γ -Al₂O₃ surfaces with different BaO loadings are given in Figures 26b and 27b. It is apparent that ionic nitrate features are more evident than the bidentate nitrates at elevated temperatures. This result shows that the ionic nitrates are thermally more stable than the bidentate ones. Alumina related nitrates have the lowest thermal stability. Hence, it can be concluded that the presence of BaO increases the thermal stability of nitrates. As will be discussed below, the presence of BaAl₂O₄ sites on the BaO/ γ -Al₂O₃ surface also needs to be taken into account. On the other hand, solely based on Figures 26b and 27b, the thermal stability of the barium aluminate related nitrates could not be distinguishably identified from the temperature dependent IR spectra for the Ba/Al samples due to the overlapping features of the bulk (ionic) nitrates and the nitrates on the barium aluminate sites. Although the nitrate species formed on pure (bulk) BaAl₂O₄ material are stable up to 723 K (see below), nitrate thermal stability could be different on pure $BaAl_2O_4$ and the $BaAl_2O_4$ nano-domains on the BaO/γ - Al_2O_3 surface. It is visible in Figures 26b and 27b that almost all of the surface NO_x species desorb at a temperature below 873 K.



Figure 28. FTIR spectra for NO₂ (g) adsorption on pure BaAl₂O₄. (a) FTIR spectra of stepwise NO₂ adsorption on the BaAl₂O₄ sample at 323 K. Uppermost spectra were taken after saturating the surface with 8 Torrs of NO₂ (g). Inset of the figure shows 1400-1100 cm⁻¹ region for the stepwise spectra during the initial uptake. (b) Temperature-dependent (323 – 923 K) FTIR spectra for NO₂ (g) adsorbed BaAl₂O₄ sample.

As mentioned above, it is important to consider the possible existence of $BaAl_2O_4$ (barium aluminate) sites on the BaO/γ - Al_2O_3 surface due to the high temperature (1023 K) pretreatment of the surface before the FTIR experiments which may lead to solid state reactions resulting in the formation of $BaAl_2O_4$ spinel. Hodjati et al studied NO_x adsorption on bulk BaO and barium aluminate surfaces where overlapping IR features were found in the spectral window within 1800-1200 cm⁻¹ [101]. NO_x adsorbed on barium aluminate (BaAl_2O_4) revealed couple of bands at

1360-1430 cm⁻¹ assigned as N-bound nitrates and a broad band at 1605-1630 cm⁻¹ which was attributed to the bridged nitrates [101]. To the best of our knowledge, this report was the only present work in the literature regarding the FTIR analysis of surface NO_x species on $BaAl_2O_4$. Therefore, we have also performed NO_2 adsorption experiments on a BaAl₂O₄ sample (Figure 28). It should be noted that due to the relatively low inherent surface area of the BaAl₂O₄ material, overall FTIR signal intensities (Figure 28) upon NO2 adsorption are more than an order of magnitude lower than that of the γ -Al₂O₃ and BaO/Al₂O₃ samples (Figures 25-27) which have significantly higher specific surface areas. Parallel to the findings of Hodjati et al. [101], overlapped nitrate bands at 1360-1430 cm⁻¹ and 1605-1630 cm⁻¹ were observed in Figure 28. It can be easily seen from Figure 28a that at lower coverages a band centered at around 1207 cm⁻¹ was observed. This feature disappeared at subsequently higher doses. This feature can be assigned to a nitrite feature suggesting that the formation of nitrates on BaAl₂O₄ surface also follows a nitrite route similar to γ -Al₂O₃ and BaO/Al₂O₃. Hence, it is visible that the vibrational frequencies of the nitrates formed on the barium aluminate surface (1434-1472 cm⁻¹) coincide with that of the bulk nitrates found on the BaO/Al₂O₃ surface. Therefore, the presence of BaAl₂O₄- related nitrate species overlapping with the bulk nitrates should not be excluded in the BaO/Al₂O₃ case (Figures 26-27). Our XRD results (Figure 14) reveal that barium aluminate formation was found to be more pronounced for 20Ba/Al than the 8Ba/Al case. This observation is also in agreement with the findings of Szailer et al where the transformation of BaAl₂O₄ formation was suggested to be at the expense of the bulk BaO phase [96].

3.2.1.3 5(10)Fe/Al

FTIR spectra showing NO₂ adsorption on 5(10)Fe/Al significantly resemble the IR features for NO₂ adsorbed on the γ -Al₂O₃ surface (Figures 27, 31 and 32). This similarity was also observed by Goodman et al. who studied HNO₃ adsorption on γ -Fe₂O₃ and α -Al₂O₃ where the assigned nitrate stretching bands had very close frequencies [150].



Figure 29. FTIR spectra for NO₂ (g) adsorption on the 5Fe/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 5Fe/Al sample at 323 K. Inset of the figure showed 1400-1100 cm⁻¹ region. (b) Temperature-dependent (323 - 923 K) FTIR spectra for NO₂ (g) adsorbed 5Fe/Al sample.



Figure 30. FTIR spectra for NO₂ (g) adsorption on the 10Fe/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 10Fe/Al sample at 323 K. Inset of the figure showed 1400-1100 cm⁻¹ region. (b) Temperature-dependent (323 - 923 K) FTIR spectra for NO₂ (g) adsorbed 10Fe/Al sample.

Fig 31a and 32a show that bridging nitrite related bands (v_3 ; 1230-1205 cm⁻¹ $v_a(NO_2)$ and 1320-1330 cm⁻¹ $v_s(NO_2)$) and monodentate nitrite (v_3 ;1470-1450 and v_1 ;1065-1050 cm⁻¹) are formed very quickly prior to the nitrate species upon exposure to NO₂, suggesting that NO₂ adsorption on the Fe/Al sample also follows a nitrite route as well. Different than γ -Al₂O₃ case, at the initial NO₂ doses, just nitrite formation was observed in 5(10)Fe-Al and isosbestic point for the conversion is not as obvious as in the spectra for γ -Al₂O₃. Furthermore, an additional band at 1180-1195 cm⁻¹ with concomitant band 1250-1350 cm⁻¹, which can be assigned to a nitrite species, is also detected at the initial NO₂ doses and becomes less visible at higher coverages (Figures 29a and 30a). In a former FTIR work, Guglielminotti and Boccuzzi studied NO+H₂ coadsorption on the Fe/ZrO₂ surface and assigned such a band at 1190 cm⁻¹ to a (chelating nitrito type) nitrite species [151].

Additionally, during the initial doses of NO₂, formation of nitrosyl features coordinated to the Fe²⁺ and/or Fe³⁺ sites are also visible via the vibrational features located at 1805-1835 cm⁻¹ [143]. After subsequently higher NO₂ doses, these nitrosyl features on the surface start to form dinitrosyls with the participation of Fe²⁺ ions (Fe²⁺(NO)₂) which is evident due to the observation of features at 1830 cm⁻¹ and 1735 cm⁻¹ [143]. At even higher coverages, these dinitrosyls species are transformed into nitro species which is evident by the presence of the band at 1650-1375 cm⁻¹ and 1350-1250 cm⁻¹. It is apparent that the accommodation of nitrosyls favorably on the Fe-sites allows an alternative and an easy transformation route for the formation of nitro in the Fe/Al system. Such an interpretation is also consistent with the presence of the nitro band in the Fe/Al system (Figures 29 and 30). Formation mechanism of the nitro species via the nitrosyls precursor on the Fe/Al surfaces can be summarized as follows:



It should be noted that unlike γ -Al₂O₃, transformation of nitrites into nitrate species requires a larger NO₂ exposure on the Fe/ γ -Al₂O₃ surface. This is consistent with the stabilizing effect of Fe sites on the weakly-bound molecular species such as (di)nitrosyls and N₂O₃.

Besides this, the bands related to bridging nitrate (v_3 ; 1650-1600 cm⁻¹ and 1225-1170 cm⁻¹, v_1 ;1030-1000 cm⁻¹), bidentate nitrate (v_3 ;1565-1500 cm⁻¹ and 1300-

1260 cm⁻¹ and v₁;1040-1010 cm⁻¹), and monodentate nitrate (v₃;1530-1480 and 1290-1250 cm⁻¹ and v₁;1035-970 cm⁻¹) also become visible at higher doses in Figures 29 and 30. Despite the similarity of the nitrate bands for both Al and Fe/Al surfaces, the presence of Fe in Al sample causes visible changes in the relative intensities of the nitrate signals. Fe leads to increase in the relative intensity of bidentate nitrates with respect to others. This interpretation is consistent with the former work of Busca and Lorenzelli who showed that the adsorption of NO₂, NO and N₂O on α -Fe₂O₃ (hematite) leads to bidentate nitrates (v₃; 1540 and 1200 cm⁻¹; where the nitrate vibrational modes were characterized by a frequency separation of $\Delta v \sim 340$ cm⁻¹ [152]. Therefore, it can be suggested that in the Fe/Al system iron forms mostly bidentate nitrates upon higher NO₂ exposures and the alumina related monodentate nitrates are hindered indicating that alumina sites are partially covered by Fecontaining domains.

When thermal stability of the nitrates on Al and Fe/Al are compared, it can be seen in Figures 29b and 30b that nitrate bands formed on Fe/Al sample decompose and desorb from the surface at 723 K. This result suggests that the presence of iron sites on the alumina leads to a slight decrease in the thermal stability of nitrates.

Both stepwise NO_x saturation and temperature dependent FTIR experiments result in similar characteristics in terms of both relative IR intensities and thermal behaviors of the adsorbed species in the 5Fe/Al and 10Fe/Al systems. This indicates that the increasing the Fe loading from 5 wt % to 10 wt % does not have a very significant influence on neither the relative intensities nor the line-shapes of the IR spectra. However, it can still be stated that the monodentate nitrates associated to the alumina sites are relatively more attenuated in the 10Fe/Al case (Figures 29 and 30) which may indicate a more extensive blocking of the alumina support sites by Fecontaining domains.

3.2.1.4 5(10)Fe/8(20)Ba/Al

Figure 31-34 show the FTIR spectra for the 5(10)Fe/8(20)Ba/Al mixed oxide samples. Similar to the findings for Fe/Al samples, just nitrite related bands are observed at the initial doses of NO₂ for all of the mixed 5(10)Fe/8(20)Ba/Al samples whereas the nitrite and nitrate features simultaneously formed in 8(20)Ba/Al case. As in the case of Fe/Al samples (Figures 29a and 30a), at least two different types of nitrites exist during the initial stages of uptakes which are evident by the presence of two different vibrational bands at 1230-1205 cm⁻¹ and at 1180-1195 cm⁻¹ (Figures 31a-34a) where this second type of nitrites are not visible in the case of Fe-free Ba/Al samples. Upon further NO₂ exposure, all of the nitrite related bands disappear and instead, nitrate bands (v₃; 1600-1200 cm⁻¹ and v₁; 1040-1000 cm⁻¹) attributed to alumina, baria and iron sites appear dominantly in Figure 31a-34a. This indicates that formation of nitrites precede the nitrate formation on the Fe-Ba/Al system.

Similar to the Fe/Al system, nitrosyls are also formed on Fe/Ba/Al surface (1805-1835 cm⁻¹) during the initial introduction of NO₂, which later transformed into adsorbed nitro species (1650-1375 cm⁻¹ and 1350-1250 cm⁻¹.) with increasing the number doses of NO₂ for all of the spectra for the Fe/Ba/Al mixed oxide systems (see Figures 31a-34a).

In Figures 31-34, peaks located at 1300-1310 and 1585-1600 cm⁻¹ are most likely due to v_3 modes of bidentate surface nitrates bound to BaO sites whose vibrational frequencies are slightly different than the ionic/bulk nitrates (1305-1325 cm⁻¹ and 1434-1472 cm⁻¹). The small signal at 1745-1770 cm⁻¹ can be attributed to the combination band for bulk-like nitrate as discussed earlier (Figures 30-33) [144]. It should be remembered that BaAl₂O₄ sites can also have a contribution to the 1360-1430 cm⁻¹ band that overlaps with bulk-like nitrates. Luo et al. also claimed that the bulk BaAl₂O₄ serve as additional storage phase in the Fe-Ba/Al system [110]. Moreover, shoulders at 1250-1260 and 1610-1620 cm⁻¹ reveal that the nitrates adsorbed on the iron sites and exposed alumina surface are also apparent in the figures through 31 to 34. After discussing these overall band assignments of the adsorbed species on the Fe-Ba/Al system, the effect of the varying loadings of Fe on Ba/Al the system is elucidated in detail below. FTIR results due to the NO₂ adsorption on 5Fe-8Ba/Al sample (see Figure 33) reveal that while nitrate bands adsorbed on BaAl₂O₄ and BaO (ionic nitrates) diminish, bidentate nitrates become more evident with respect to that of the 8Ba/Al spectra (see Figure 26).This trend is also valid when the results of 5Fe-20Ba/Al and 20Ba/Al are compared. Similarly, Luo et al. reported that NO_x is mainly stored as bidentate type nitrates when NO/air is adsorbed to Fe-Ba/Al₂O₃ sample [110]. It might be suggested that the introduction of 5 wt% Fe into the 8(20)Ba/Al system leads to decrease in the formation of bulk BaO which in turn, can hinder the formation of BaAl₂O₄ sites. Therefore, one of the major differences in the IR spectra for the Fe containing and the Fe-free systems could be the relative differences in the BaAl₂O₄ sites in those two different cases. Therefore, it can be concluded that the presence of 5 wt% Fe loading enhances the bidentate nitrates by lowering the formation of BaAl₂O₄ phase in 5Fe-8(20)Ba/Al structure.



Figure 31. FTIR spectra for NO₂ (g) adsorption on the 5Fe/8Ba/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 5Fe/8Ba/Al sample at 323 K. Last red color spectrum was taken after saturating the surface with 8 Torr of NO₂ (g). Inset of the figure showed 1400-1100 cm⁻¹ region for the stepwise spectra upto 25 doses. (b) Temperature-dependent (323 – 923 K) FTIR spectra for NO₂ (g) adsorbed 5Fe/8Ba/Al sample.



Figure 32. FTIR spectra for NO₂ (g) adsorption on the 10Fe/8Ba/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 10Fe/8Ba/Al sample at 323 K. Last red color spectrum was taken after saturating the surface with 8 Torr of NO₂ (g). Inset of the figure showed 1400-1100 cm⁻¹ region for the stepwise spectra up to 25 doses. (b) Temperature-dependent (323 – 923 K) FTIR spectra for NO₂ (g) adsorbed 10Fe/8Ba/Al sample.



Figure 33. FTIR spectra for NO₂ (g) adsorption on the 5Fe/20Ba/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 5Fe/20Ba/Al sample at 323 K. Last red color spectrum was taken after saturating the surface with 8 Torr of NO₂ (g). Inset of the figure showed 1400-1100 cm⁻¹ region for the stepwise spectra up to 25 doses. (b) Temperature-dependent (323 – 923 K) FTIR spectra for NO₂ (g) adsorbed 5Fe/20Ba/Al sample.



Figure 34. FTIR spectra for NO₂ (g) adsorption on the 10Fe/20Ba/Al. (a) FTIR spectra of stepwise NO₂ adsorption on the 10Fe/20Ba/Al sample at 323 K. Last red color spectrum was taken after saturating the surface with 8 Torr of NO₂ (g). Inset of the figure showed 1400-1100 cm⁻¹ region for the stepwise spectra up to 25 doses. (b) Temperature-dependent (323 – 923 K) FTIR spectra for NO₂ (g) adsorbed 10Fe/20Ba/Al sample.

In order to see the effect of the different loadings of Fe in Ba/Al system, NO₂ adsorption results for 5Fe-8(20)Ba/Al are compared with that of the 10Fe-8(20)Ba/Al results. Interestingly, increasing the Fe loading to 10 wt% leads to a different behavior where 10Fe-8Ba/Al and 10Fe-20Ba/Al surfaces reveal smaller bidentate nitrate signals and more pronounced nitrate signals associated with bulk BaO sites and BaAl₂O₄ sites. This could be due to the sintering of the Fe sites at higher Fe loadings as well as a change in the interaction between the Ba sites and the underlying alumina surface leading to an altered (more bulk-like) BaO morphology and increased BaAl₂O₄ formation. In comparison with the 5Fe-8Ba/Al and 5Fe-20Ba/Al, formation of nitrosyls on the iron sites is less visible on the 10Fe-8Ba/Al

and 10Fe-20Ba/Al cases which are also in agreement with the fact that NO_x storage capacity decreases at higher iron loadings.

Besides this, thermal stability of the nitrates in Ba-Fe/Al system seems to be slightly lower than that of the Ba/Al system (Figure 26b, 27b and 31b-34b). Most of the adsorbed species desorb below 723 K in the Fe-Ba/Al system. This indicates that the interaction of the adsorbed NO_x with the Ba sites is weakened in the presence of iron so that desorption take place at relatively lower temperatures. Further TEM and TPD experiments are underway to account for the fundamental reasons that could be associated with these observations.

3.2.2 TPD



Figure 35. TPD profiles for 30, 32 and 46 amu signals corresponding to 8 Torr NO_2 adsorption on 8Ba/Al (see 2.3.2. for the detailed experimental protocol).

Figure 35 presents TPD profiles of NO₂ adsorption on 8 wt%BaO/ γ -Al₂O₃ at 323 K.

TPD profiles reveal that NO_x desorption takes place in two temperature regimes similar to those previously reported ones [48, 96]. Based on the combined FTIR and TPD results, the desorption feature at ~ 400 K is associated with nitrite desorption and decomposition on the alumina and baria sites and nitrate desorption from the support, whereas the broad and complex desorption envelope at T > 650 K is due to the desorption and decomposition of strongly bound nitrates on the baria sites [96]. NO₂ related signal (46 amu) centered at ~700 K is attributed to the decomposition of bidentate nitrates whereas NO (30 amu) and O₂ (32 amu) signals at ~745 K are due to the decomposition of ionic Ba nitrate. NO_x desorption is also accompanied by N₂O desorption and H₂O desorption (not shown in the Figure) as a result of desorption from the walls of the chamber [96].

4 CONCLUSIONS

4.1 Conclusions: Part I

In the current study, we present detailed spectroscopic (Raman, XPS), and diffraction (XRD) results, in an attempt to bring a better fundamental understanding to the thermal structural and morphological changes in the mixed-oxide (Fe/Ba/Al₂O₃) NO_x-storage systems within 300-1273 K. The results demonstrated that the crystallinity and the structure of the Ba-nitrates on the support surface strongly depend on their interaction with the γ -alumina support material and the presence of Fe species as an additive into the Ba/Al system. Some of the main conclusions of the current work can be summarized as follows:

(a) The deposited Ba(NO₃)₂ via solution precursors on the γ -Al₂O₃ surface by incipient wetness impregnation method exhibits distinctively different thermal stabilities depending on the Fe loading in the Fe/Ba/Al samples. Introduction of 5 wt. % Fe mainly in the form of α - Fe₂O₃ (hematite) into the 8(20)Ba/Al samples resulted in the formation of relatively thermally stable bulk nitrate species on the surface. A further increase in the Fe content to 10 wt. % leads to formation of bulk nitrate species however with a considerably lower thermal stability, which is close to that of the 8(20)Ba/Al system.

(b) The chemical compositions of the studied NO_x-storage materials have also a substantial effect on the temperatures at which BaAl₂O₄ formation and the γ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃ phase transformation start to be observed. The increased Ba content in the storage materials tends to favor BaAl₂O₄ at T \geq 873 K. However, BaAl₂O₄ formation is hindered in the presence of hematite (α -Fe₂O₃) where the suppression of the BaAl₂O₄ formation is more pronounced in the case of Fe-rich samples.

(c) The presence of different Fe loadings, mainly in the form of α - Fe₂O₃ in the Fe/Al and Ba-Fe/Al systems leads to a depression of the γ -Al₂O₃ $\rightarrow \alpha$ -Al₂O₃

phase transformation temperature and favors the corundum formation above 1073 K. This effect can be suppressed to a certain extent in the presence of the Ba component, particularly when the BaO content is increased to 20 wt. %.

(d) TEM data showed small rod-like grains for both Al and 20Ba/Al samples. Besides, TEM and EELS data showed that relative dispersion of Ba species are higher than the dispersion of Fe domains on the 10Fe/20Ba/Al sample.

4.2 Conclusions: Part II

 NO_2 (g) adsorption experiments were performed on Ba/ γ -Al₂O₃ and Fe-Ba/ γ -Al₂O₃ surfaces and the NO_x storage behavior of these systems were followed by FTIR spectroscopy in a comparative manner. Thermal stability of the adsorbed species due to NO₂ (g) adsorption were also discussed by acquiring temperature-dependent FTIR spectra. Besides, a representative TPD profile showing desorbed species from NO_x saturated surface was also given for 8Ba/Al sample. Some of the main conclusions of the current work can be summarized as follows:

(a) Upon initial exposures of NO₂ at 323 K, nitrites and nitrates are formed on the alumina support. In addition to nitrites and bidentate nitrates, nitrosyl features are also present in 5(10)Fe/Al and 5(10)Fe/8(20)Ba/Al system at the lower doses of NO₂.

(b) Unlike the 8(20)Ba/Al system, ionic nitrates are not detected on the 5(10)Fe/Al and 5(10)Fe/8(20)Ba/Al samples during the initial doses of NO₂.

(c) The surface nitrates are found to have bidentate while bulk-like ones have ionic type configuration on BaO species. It was suggested that the vibrational bands which were attributed to the bulk-like nitrates could also have some contribution from nitrates associated with the $BaAl_2O_4$ sites.

(d) In contrast to the 5Fe-8(20)BaO systems, bidentate nitrates become less visible for 10Fe-8(20)BaO samples.

(e) Temperature dependent IR spectra reveal that thermal stability of the nitrates is slightly lowered by the addition of iron to Ba/Al samples.

(f) TPD profile is found to be in agreement with FTIR data that decomposition of NO_x takes place at lower temperature from the support compared to that of storage sites in 8Ba/Al system. Moreover, bulk (ionic) nitrates are thermally more stable than the surface (bidentate) ones.

5 REFERENCES

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