
Ceramics in Environmental Applications

CHARACTERIZATION OF MnO-DOPED LANTHANUM HEXALUMINATE ($\text{LaMnAl}_{11}\text{O}_{19}$) IN TERMS OF SELECTIVE CATALYTIC REDUCTION OF NO_x BY ADDITION OF HYDROCARBON REDUCTANT (HC-SCR)

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ABSTRACT

Environmental pollution by vehicles, turbines and aircrafts has enormously increased in the last decade. New generation lean-burn combustion engines which are more effective and require less fuel consumption will raise the emission of nitrogen oxides (NO_x) even more. Thus, especially in urban areas, more stringent environmental regulations are to be released which can only be met by development of new catalytic materials and concepts.

Rare earth oxide catalysts are reported to offer highly effective conversion of NO_x by methane (CH_4) in the terms of selective catalytic reduction (HC-SCR). Especially La_2O_3 is reported to have a high NO reduction by CH_4 to N_2 , although its technical realization as catalyst material has not yet been reported and can be challenging due to the hygroscopic property of La_2O_3 .

Complex oxide compounds containing La_2O_3 however can be suitable alternatives and promising candidates for technical application as catalysts. In this study, $\text{LaMnAl}_{11}\text{O}_{19}$ is characterized in terms of HC-SCR with methane. Phase and morphological characterization of the powder synthesized by sol-gel route and coatings by electron-beam physical vapor deposition (EB-PVD) deposition was presented. $\text{LaMnAl}_{11}\text{O}_{19}$ crystallizes to the magnetoplumbite phase at about 1000°C and is then thermally stable up to 1400°C .

FTIR spectra of pressed sol-gel powder showed that NO is adsorbed superficially and oxidized by the surface. The addition of oxygen led to changes of the spectrum in the nitrite-nitrate region and the formation of NO^+ and N_2O_4 species. The EB-PVD coated $\text{LaMnAl}_{11}\text{O}_{19}$ layer was catalytically characterized at 200° , 400° and 600°C and showed catalytic activity towards NO depending on temperature.

INTRODUCTION

In the last decade, the need for low fuel consumption and high efficiency turbines and motors has promoted the use of lean-burn techniques leading to an increase in the combustion temperature. The consequent increase of cyclic process parameters raises the emission of NO_x and leads to formation of oxygen rich exhaust gases. On the other hand, more stringent regulations have been released by legislators such as CEAP, LAER or EURO regarding emissions. As an intermediate precaution, NO_x and hydrocarbon (HC) emissions are reduced to 0.3 g/km for diesel engines and almost to zero for petrol engines with the EURO4 regulation which is to apply from 2005. Further adjustment of the diesel and petrol engine regulations has been discussed for the future regulations¹. From 2008, with the new CEAP6 regulation for aircraft turbines, NO_x emissions are to be reduced to a level far below the former CEAP2 regulation². It is to be expected that total emission further increases with the increase of the worldwide air traffic. European commission aims to achieve efficient and environment-friendly energy generation by targeting low to zero emission in power plant technologies and aircraft traffic.

Referring to these considerations more stringent regulations are anticipated in the future, particularly, for turbine engines operated in urban areas, emphasizing the necessity for

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employment of catalysts ³. These catalysts must be able to reduce NO_x in net oxidizing conditions. Today's technologies allow various numbers of possibilities for NO_x reduction. In general, those can be divided into two main categories; primary and secondary catalytic systems. Primary system is mostly based on catalytic combustion, implying that a part of the air/fuel mixture is reacted heterogeneously over a catalyst before the actual combustion occurs ^{4,5}. For these types of catalysts, it is necessary to use premixed combustion which may bring enormous problems regarding liquid fuels, especially for aircraft turbines.

Secondary systems in turn achieve the reduction of NO_x in the exhaust gas. There are two promising secondary systems for the reduction of NO_x-emission under lean-burn conditions. One of those is the storage-reduction technology (NO_x-SR). This technology allows the storage of NO_x by adsorption on the surface of the catalyst during the lean-burn phase and subsequently, desorption and reduction of the absorbed NO_x during the following fat-burn phase. Because the second phase is much faster than the storage phase, a significant NO_x reduction can be achieved in total ⁶.

The second promising candidate technology is the selective catalytic reduction of NO_x (SCR) with addition of ammonia or hydrocarbons as reductant ⁷. For stationary systems ammonia is widely used, although for mobile systems hydrocarbons are preferred. As the reductant and NO_x react over the catalyst, NO_x is converted to N₂ and O₂ and thus, reduced. The problem regarding the systems working with ammonia addition is the production of non-reacted NH₃ which inflows the environment and/or forms corrosive products. In turn, the hydrocarbons (fuel, kerosene) are more easily applicable on mobile systems.

MnO-doped La-hexaluminate has been suggested as a promising material for the above mentioned catalytic systems. Earlier studies on rare earth lanthanide oxides report high catalytic activity as SCR-catalyst material. With La₂O₃ and Sr/La₂O₃, a high conversion of NO_x with methane is shown with or without oxygen ^{8,9}. Due to highly hydroscopic property of La₂O₃, its technical realization as catalyst material is difficult, making it necessary to direct the investigations towards finding out more stable chemical compounds of La-oxides for this application.

MATERIALS AND METHODS

Manganese (II) oxide doped lanthanum hexaluminate (LaMnAl₁₁O₁₉) has been produced by means of two processing routes. Figure 1 shows the procedure for sol-gel synthesis of lanthanum manganese hexaluminate powder. After drying at 200°C, the powder was calcined for 1 hour at various temperatures from 600°C to 1400°C. The detailed synthesis procedure is described elsewhere¹⁰.

XRD-measurements of the calcined powder were performed with a step size of 0,020° at 2θ angles from 10° to 80° on a Siemens D5000 diffractometer using nickel-filtered CuKα radiation. The samples were characterized microstructurally and compositionally by Energy Dispersive X-ray spectroscopy (EDX) supported Scanning Electron Microscope (SEM Leitz LEO 982). X-ray diffractograms of the used LaMnAl₁₁O₁₉ powder showed that the crystallization to magnetoplumbite phase occurs above 1100°C. Therefore, the powder was pre-calcined for 1 h at 1000°C in order to carry out the FTIR measurements.

The FTIR spectra were recorded on a Bomem MB 102 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4cm⁻¹. The detailed setup is described elsewhere¹¹.

Beside the sol-gel synthesized powder, EB-PVD (Electron-Beam Physical Vapor Deposition) manufactured $\text{LaMnAl}_{11}\text{O}_{19}$ coatings were analyzed. For deposition of coatings, a two-source 150 kW electronic beam coater was used consisting of separated chambers for loading, preheating, and deposition. Ingots which meet the special requirements of the EB-PVD deposition were bottom fed in the crucibles during evaporation to ensure continuous and constant deposition conditions. The substrates were rotated during the vacuum evaporation. SEM, EDX, and XRD-analysis of the EB-PVD coating layers were carried out as described above.

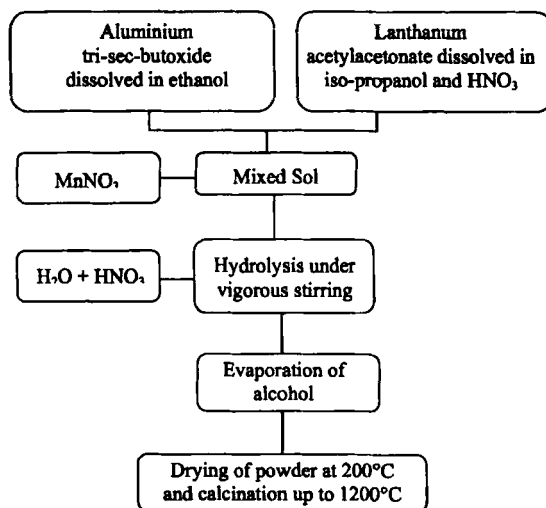


Figure 1: Sol-gel route synthesis of $\text{LaMnAl}_{11}\text{O}_{19}$

For the catalytic characterization of the hexaluminate coatings, a user-specific and computer controlled experimental setup consisting of a gas-mixer, a tube-furnace, a gas-tight, ceramic specimen holder, and two electrochemical gas sensors from Sensoric GmbH was employed. As carrier gas synthetic air and as test gas nitrogen monoxide (NO) were used. In order to achieve a maximum surface area, a small honeycomb structured component was built by bonding pieces of the layers together. The size of this component was similar to that of the cross sectional area of the specimen holder being about 10 mm long.

RESULTS AND DISCUSSION

Production and Characterization of Materials

XRD-analysis of the sol-gel synthesized MnO-doped La-hexaluminate powder after calcining for one hour at various temperatures up to 1200°C showed that the powder was amorphous up to 900°C and crystallized to the magnetoplumbite phase at about 1000°C. Since the crystallization occurred without the formation of other phase(s) which is mostly encountered in the case of undoped La-hexaluminate, it can be attributed that the formation of the

magnetoplumbite phase at MnO-doped La-hexaluminate is due to a crystallisation process and not due to a reaction between LaAlO_3 and Al_2O_3 .

Scanning electron microscopy (SEM) investigation of the sol-gel-synthesized and 1200°C calcined powder shows the formation of hexagonal, plate-like grains with random crystal growth, leading to an interlocking and high surface morphology (Fig.2). The high surface area of the morphology supports the catalytic effect of the material.

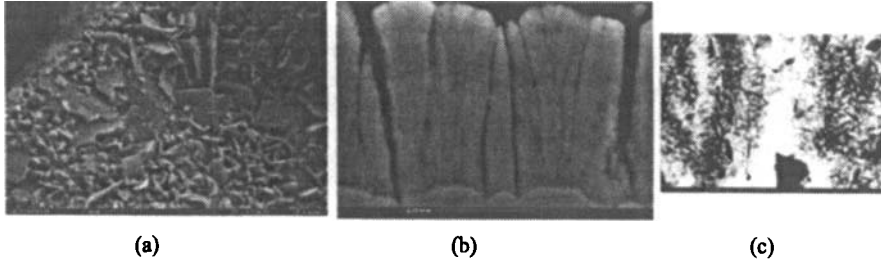


Figure 2: SEM micrographs of sol-gel synthesized and calcined $\text{LaMnAl}_{11}\text{O}_{19}$ powder morphology on the surface of a particle (a). SEM micrographs of 1100°C heat-treated EB-PVD manufactured MnO-doped La-hexaluminate coating showing the columnar morphology (b); Back scatter image detail of the interlocking microstructure after heat-treatment (small picture at c).

EB-PVD processing of $\text{LaMnAl}_{11}\text{O}_{19}$ with multiple beam patterns delivered a stoichiometric layer. Since the vapor pressures of individual oxides within $\text{LaMnAl}_{11}\text{O}_{19}$ composition, i.e. MnO , La_2O_3 and Al_2O_3 exhibit strong differences, EB-PVD- manufacturing of this composition requires less power than that of PYSZ evaporation and subsequently leads to lower substrate temperature. Therefore, the as-received EB-PVD coatings were amorphous and a heat-treatment process was needed for its crystallization. SEM micrographs shown in Figure 3 display the columnar EB-PVD-coating (Fig. 2b) and the formation of interlocking plate-like morphology of magnetoplumbite phase after heat-treatment as detected in back-scatter SEM-modus (Fig. 2c).

Magnetoplumbite phase of La-hexaluminate has a highly defective crystal structure, consisting of $[\text{AlO}_6]^{+}$ spinel blocks, intercalated by mirror planes of composition $[\text{LaAlO}_3]^0$. The introduction of Mn(II) , a divalent ion, in the spinel block forms an electrically neutral structure. This promotes the formation of magnetoplumbite phase, with an interlocking needle-like morphology. Once formed, the phase is stable up to 1400°C .

FTIR-Measurements

The specimen for the FTIR measurements was prepared as described above and activated by heating for 1 h in vacuum, followed by 100 Torr oxygen for 1h and again vacuum for 1 h. All steps were performed at 500°C .

The FTIR spectrum of the activated sample was recorded at ambient temperatures and taken as a background reference. Each shown spectrum is subtracted by this background reference. On the surface of the activated samples only absorptions in the hydroxyl-stretching-region and the surface-carbonate-region were observed. The weak bands at 3862 cm^{-1} and 3675 cm^{-1} are attributed to $\text{Al}^{3+}\text{-OH}^{12}$ and $\text{La}^{3+}\text{-OH}^{13}$.

NO was added to the activated catalyst at room temperature for 20 minutes. The addition of NO resulted in an adsorption of NO on the surface which was disproportionate with time. Bands were observed at 1610 cm^{-1} , corresponds to the banding mode of adsorbed water, at 1398 cm^{-1} , identified as NO_2^- species, at 1208 cm^{-1} , characteristic for hyponitrite ($\text{N}_2\text{O}_2^{2-}$) and a defused adsorption at 1512 cm^{-1} , which is typical for surface nitrates.

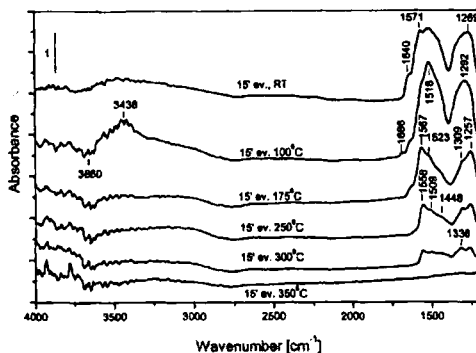


Figure 3: Temperature controlled vacuum diffraction of adsorbed surface species under NO/O_2

The addition of 60 Torr of oxygen into the reactor (containing 30 Torr of NO) led to great changes in the spectrum. The nitrosyl bands disappeared and the nitrite-nitrate region changed drastically. New bands at 2229 cm^{-1} and 1752 cm^{-1} belonging to NO^+ species and adsorbed N_2O_4 appeared indicating that oxidation of NO took place. The adsorption of NO_2 can occur by disproportionation under the participation of Lewis acid-base pairs and/ or surface hydroxyls ¹⁴.

Evacuation of the reactor for 15 min at ambient temperatures resulted only in a few changes in the spectrum, associated to the disappearance of NO^+ and N_2O_4 bands (Fig. 3). After evacuation temperature controlled diffraction was done. At $100\text{ }^\circ\text{C}$ only changes in the shapes and intensities were observed, indicating that a rearrangement of the NO_3^- -species occurs. Remarkable decomposition of the surface NO_x species begins at $175\text{ }^\circ\text{C}$ (Fig. 3). From the thermal stability and the magnitude of the ν_3 spectral splitting the nitrates bands, it was assigned that mono-, bi- and bridged species form (Fig. 3). The high temperature stable species can be identified as NO^{2-} species ¹³. Detailed analyses of the desorption process of the surface nitro-nitrate structures are underway, in order to investigate the decomposition to NO and/or NO_2 , or to N_2 and O_2 .

Adsorption of NO/O_2 for 30 min was repeated and then evacuated for 10 min at room temperature. Then methane (CH_4) was added to the FTIR cell and heated for 15 min at various temperatures (Fig. 5). The heating to $250\text{ }^\circ\text{C}$ led to a loss of the adsorbed nitrate species. The subtraction spectrum in Fig. 6B shows a parallel re-adsorption of the adsorbed H_2O (bands 3875 cm^{-1} and 3675 cm^{-1}). Heating to $350\text{ }^\circ\text{C}$ for 20 min showed a strong decrease in the nitrite-nitrates bands, accompanied by the adsorption of H_2O (band 1610 cm^{-1}). This indicates that the oxidation of CH_4 took place leading to the formation of adsorbed water. Further increase of temperature up to $450\text{ }^\circ\text{C}$ for 20 min raised the adsorption of water instead of decreasing. The subtraction spectra showed the formation of a new band at 1372 cm^{-1} corresponding to bidentate carbonates and negative bands due to the nitrite-nitrate species consumption (Fig. 5B). The changes of the

spectra in the Lanthanum-NO species region could not be observed, due to the spectral bandwidth of the employed FTIR.

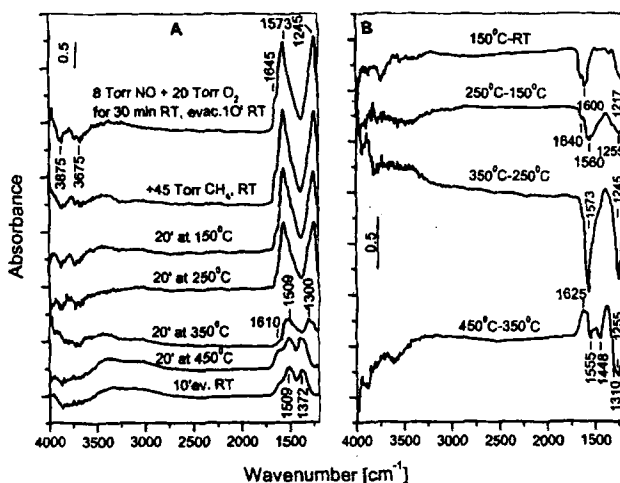


Figure 4: Spectra (left) and subtraction spectra (right) of an adsorbed NO/O₂ catalyst surface under CH₄ atmosphere (0,06 bar) at various temperatures

Catalytic Characterization

With the as-received EB-PVD MnO-doped La-hexaluminat layers catalytic experiments were performed. Before performing the catalytic experiments, a dry run with no specimen was carried out in order to examine the operation of the experimental setup. A "background" graph was recorded at several temperatures up to 900°C and with NO concentrations of 25 and 50 ppm at a total flow rate of 400 ml/min. Synthetic air was used as carrier gas, thus there was an oxygen rich atmosphere of about 20% of excess oxygen and a humidity of 50 %. The results were reproducible. During background tests, no formation of nitrogen dioxide (NO₂) was detected at any temperature and with all NO concentrations. In turn, it was detected that the measured NO concentration decreases with increasing temperature, assuming that this decrease is either due to adsorption effects at walls of the ceramic holder or decomposition of NO to N₂ and O₂. Relying on these assumptions, all the measured results shown here were corrected by the pre-measured background values.

The experiments were carried out with as-received i.e. amorphous/crystalline layers of EB-PVD manufactured MnO-doped La-hexaluminat. NO reduction and conversion was observed at temperatures 200, 400 and 600 °C. Simultaneously an increase in NO₂-concentration has been detected which was almost compatible to the concentration reduction of NO at the corresponding temperature (Fig. 5). Percentage ratio of NO reduction to the theoretical expected NO concentration seems to depend on the NO concentration and on temperature. The temperature dependence is likely due to the catalytic activity temperature of LaMnAl₁₁O₁₉, whereas the concentration dependence is probably to the present surface area of the honeycomb structure. Comparison of the measured concentrations of NO and NO₂ with the theoretically expected

concentrations indicates some negligible deficit which is presumably due to the conversion of the gas to another species, which can not be detected with the present setup.

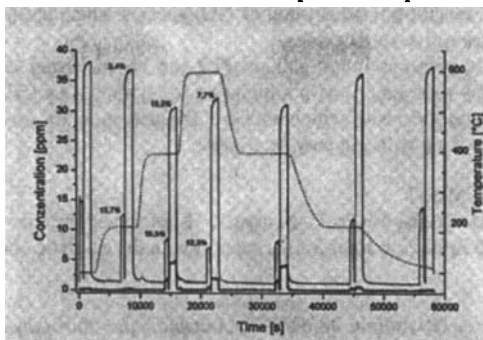


Figure 5: Catalytic activity of LaMnAl₁₁O₁₉ EB-PVD layer under NO+synthetic air atmosphere at different temperatures (NO: dotted; NO₂: continuous; temperature: dashed). The numbers show the NO reduction in percentage to the theoretical expected concentration

Considering these results and observed FTIR-spectra, it can be presumed that chemisorption of O₂ occurs on oxygen defect sites, leading to the formation of charged oxygen species which might promote the formation of NO₂ and the adsorption of NO_x species on surface sites of LaMnAl₁₁O₁₉. Moreover, it must be noted that the FTIR measurements are carried out under low pressure atmospheres, whilst the catalytic measurements at atmospheric pressure. It is known that thermal stability of the adsorbed surface nitrates increases with pressure which may explain the observed discrepancy between two different experiments. The decomposition of the adsorbed (surface) nitrates to O₂ and N₂ upon increase of the temperature is not unlikely, although it can not be definitely disclosed. New measurements with a better equipped experimental setup are underway.

CONCLUSION

FTIR spectra show adsorption of NO under oxygen and oxygen free atmospheres. On adsorption of NO at room temperature, surface-nitrates form, most likely as anionic nitrosyl and nitro-species. The adsorbed NO undergoes disproportionation with time involving surface OH groups. Oxygen addition changes the spectrum, mainly due to the oxidation of NO, NO⁺ and N₂O₄ surface species. The evacuation leads to the disappearance of NO⁺ and N₂O₄ and results in slight changes in the nitrate region of the spectrum. Under vacuum nitrates are stable up to 300°C.

Catalytic characterization of EB-PVD layer of LaMnAl₁₁O₁₉ confirms the promotion of NO-oxidation. The FTIR measurements were carried out under vacuum, It is likely that the decomposition and desorption temperatures under atmosphere pressure differ and are higher from those. Activity temperatures around 700°C under combustion conditions therefore seem to be feasible.

Due to the limitations in bandwidth of the employed FTIR equipment, the behavior of NO species at La-surface sites could not be characterized in order to determine HC-SCR mechanism. Regarding the methane at FTIR spectra in Fig. 5, it can be assumed that the Mn-surface sites

were blocked by adsorbed NO-species which are likely non-reactive towards CH₄. Doping LaMnAl₁₁O₁₉ with single-oxidation-state ions, like Mg, it may force that the Mn-ion remains in 2⁺-oxidation state resulting in adsorption of NO_x-species which are more reactive with methane or formation of free active surface-sites.

According to previous investigations, NO can be converted over rare earth metal oxide catalysts, especially over La₂O₃, with a high rate to N₂ and O₂ by CH₄ in the present of oxygen. Therefore further experiments which involve the detection of La-sites and modification of LaMnAl₁₁O₁₉ by doping with Mg may be eligible.

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