

Article

# High-Temperature Abatement of N<sub>2</sub>O over FeO<sub>x</sub>/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Catalysts: The Effects of Oxygen Mobility

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**Abstract:** CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> oxides prepared by co-precipitation (Ce+Al) or CeO<sub>x</sub> precipitation onto Al<sub>2</sub>O<sub>3</sub> (Ce/Al) to obtain dispersed CeO<sub>2</sub> and samples with further supported FeO<sub>x</sub> (2.5–9.9 weight% in terms of Fe) were characterized by XRD, XPS, DDPA and Raman. Fe/Ce/Al samples with lower surface concentrations of Fe<sup>3+</sup> were substantially more active in N<sub>2</sub>O decomposition at 700–900 °C. It was related to higher oxygen mobility, as estimated from <sup>16</sup>O/<sup>18</sup>O exchange experiments and provided by preferential exposing of (Fe-)Ce oxides. Stabilization of some Ce as isolated Ce<sup>3+</sup> in Fe-Ce-Al mixed oxides dominating in the bulk and surface layers of Fe/(Ce + Al) samples retards the steps responsible for fast additional oxygen transfer to the sites of O<sub>2</sub> desorption.

**Keywords:** N<sub>2</sub>O decomposition; Fe-Ce-Al mixed oxide; oxygen mobility

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## 1. Introduction

Nitric acid is a key chemical with annual production at above 65 million tons mainly driven by the fertilizer industry. Nitrous oxide (N<sub>2</sub>O) is produced as an unwanted, but inevitable by-product at HNO<sub>3</sub> industrial manufacture by ammonia oxidation. Its emissions by nitric acid plants are growing from 5 to 12 kg N<sub>2</sub>O/ton HNO<sub>3</sub> according to the tendency to high-pressure processes [1]. Meanwhile, nitrous oxide is a potent greenhouse gas characterized by about 300 times the Global Warming Potential of CO<sub>2</sub> and contributes to the greenhouse effect and ozone layer depletion. Therefore, 330–780 thousand tons of N<sub>2</sub>O annually emitted at HNO<sub>3</sub> production are equivalent to 100–240 million tons/y CO<sub>2</sub>e. It can be deleted by placing the catalysts in several points of the ammonia processing flowsheet [2], including that immediately downstream the Pt–Rh gauzes operating at 800–900 °C. A tendency of recent years to increase weight space velocity and reduce the charge of platinum-group metals in the reactor increased the risk of ammonia slipping at gauze ageing or damage. Therefore, efficient conversion of NH<sub>3</sub> to NO + NO<sub>2</sub>, while N<sub>2</sub>O is low is one of the necessary features for N<sub>2</sub>O decomposition catalysts operating in these conditions as well.

Fe-Al-O-based catalytic compositions are efficient both in selective ammonia oxidation to NO and NO<sub>2</sub> [3–5] and in selective N<sub>2</sub>O decomposition under the conditions of the nitric acid plant [4–8] without decrease in NO<sub>x</sub> yield [6,7]. The activity in both reactions was shown to increase by using CeO<sub>2</sub> as the support instead of alumina [4]. It was due to the appearance of the additional pathway of the oxygen supply through oxygen vacancies located in the near subsurface layers of ceria to Fe active sites facilitating the rate-determining step of O<sub>2</sub> desorption. An increase in both ceria and Co(Fe)O<sub>x</sub> dispersion could

additionally promote oxygen diffusion to Fe. In the first case it is because both distributions of oxygen vacancies and oxygen storage and release capability of CeO<sub>2</sub> are related to its particle size [9,10]. The positive effect of the dispersion of Co oxide spinel phase [11,12] or FeOx species over ceria and alumina [4,5,8] onto activity in both reactions was already shown and related to enhanced oxygen diffusion through the active component/support interface periphery [4,11,12]. However, for individual CeO<sub>2</sub> all positive effects resulting from fast oxygen transfer are restricted by its low surface area under the reaction conditions [10]. Several methods to stabilize dispersed CeO<sub>2</sub> particles over Al<sub>2</sub>O<sub>3</sub> after calcination at above 800°C were reported. They include the sol–gel method using aluminum tri-sec-butoxide and Ce(III) nitrates as precursors [13], impregnation of alumina with an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] [14] or stabilization of a complex of the CeO<sub>2</sub> precursor in a homogeneous polymeric matrix (Pechini route) followed by supporting onto alumina [15,16].

In the current study, we used CeO<sub>2</sub> precipitation onto Al<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> coprecipitation methods to increase CeO<sub>2</sub> dispersion in the final supports compared with individual CeO<sub>2</sub>. The reasons for the principally different activity of FeOx/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> samples prepared using these supports have been elucidated.

## 2. Results and Discussion

### 2.1. Phase Composition (XRD)

XRD patterns of Ce/Al and (Ce + Al) samples revealed a mixture of CeO<sub>2</sub>,  $\theta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phases (Figure S1 in Supporting Information). Lattice parameters of CeO<sub>2</sub> in both samples were exactly the same (Table 1) and practically coincided with those for pure CeO<sub>2</sub> calcined at 900 °C ( $a = b = c = 5.412$  Å), while the values of coherent scattering area  $d_{\text{XRD}}$  calculated by the Scherrer equation were lower (40 and 11 nm for Ce/Al and (Ce + Al), respectively, compared with 68 nm for pure CeO<sub>2</sub> [4]). Lattice parameters of  $\gamma$ (+ $\theta$ )-Al<sub>2</sub>O<sub>3</sub> phases cannot be calculated correctly because of low intensity and substantial broadening of corresponding overlapping signals. Therefore, some penetration of Ce ions into their lattices cannot be excluded. At the same time, higher dispersion of alumina species in the (Ce + Al) sample follows from larger widths of the peaks at 45.5° and 67.0° (Figure S1).

**Table 1.** Structural characteristics of Ce/Al and (Ce+Al) based samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Phase Composition (Lattice Parameters)	D <sub>XRD</sub> (nm)
Ce/Al	63	CeO <sub>2</sub> ( $a = b = c = 5.411$ Å) ( $\theta + \gamma$ )-Al <sub>2</sub> O <sub>3</sub>	40 -
3.8 Fe/Ce/Al	50	CeO <sub>2</sub> ( $a = b = c = 5.411$ Å) ( $\theta + \gamma$ )-Al <sub>2</sub> O <sub>3</sub>	41 -
9.9 Fe/Ce/Al	35	CeO <sub>2</sub> ( $a = b = c = 5.411$ Å) ( $\theta + \gamma$ )-Al <sub>2</sub> O <sub>3</sub>	46 -
(Ce + Al)	94	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> ( $a = b = 5.035$ Å, $c = 13.741$ Å) CeO <sub>2</sub> ( $a = b = c = 5.411$ Å) ( $\theta + \gamma$ )-Al <sub>2</sub> O <sub>3</sub>	32 11 tr.
2.5 Fe/(Ce + Al)	70	CeO <sub>2</sub> ( $a = b = c = 5.411$ Å) ( $\theta + \gamma$ )-Al <sub>2</sub> O <sub>3</sub>	12 tr.
6.6 Fe/(Ce + Al)	58	CeO <sub>2</sub> ( $a = b = c = 5.411$ Å) ( $\theta + \gamma$ )-Al <sub>2</sub> O <sub>3</sub> $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> ( $a = b = 5.035$ Å, $c = 13.741$ Å)	14 tr. 39

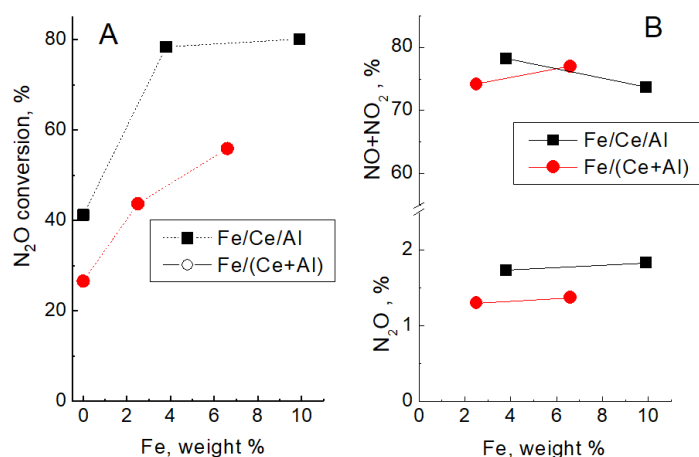
Fe deposition resulted in a decrease in S<sub>BET</sub> value and a consistent increase in D<sub>XRD</sub> of CeO<sub>2</sub> species; the value of effect depended on the quantity of Fe (Table 1). Although CeO<sub>2</sub>

lattice parameters did not change for all Fe content ranges, the formation of Fe-Ce-O solid solution cannot be excluded. Ceria lattice shrinkage was measured in Au/Ce-Fe-O (Ce/Fe = 9) [17], Fe/CeO<sub>2</sub> (Ce/Fe = 4–9) [18] or CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> (Ce/Fe = 2.3) [19] samples prepared by procedures favoring homogeneous distribution of Fe and Ce in the samples before their high temperature treatment. It was due to the replacement of Ce<sup>4+</sup> ions in the typical cubic fluorite lattice (radius 0.097–0.101 nm) by Fe<sup>3+</sup> ions (0.049–0.078 nm, depending on coordination and spin state). However, at smaller Fe content in Fe<sub>x</sub>Ce<sub>1-x</sub>O<sub>2</sub> ( $x \leq 0.05$ , or Ce/Fe  $\geq 20$ ) even a slight increase in lattice parameter compared with pure CeO<sub>2</sub> was observed [18] and related to partial Ce<sup>4+</sup> reduction to the larger (0.123 nm) Ce<sup>3+</sup> ion [20]. Although in our case Ce/Fe ratio varies within 1.1–6.2, these differently directed effects could compensate for each other because Fe was supported onto support already calcined at 900 °C diminishing the efficiency of its incorporation into CeO<sub>2</sub> lattice, while incorporation of some Fe cations into the alumina component is possible as well.

Nevertheless, neither relative intensity and dispersion of  $\gamma$ -, $\theta$ -Al<sub>2</sub>O<sub>3</sub> changed (Figure S1, inserts), nor  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> appeared in both Fe/Ce/Al and Fe/(Ce+Al) samples (Figure S1), unlike Fe/Al<sub>2</sub>O<sub>3</sub> samples with reasonably close S<sub>BET</sub> and Fe content values [4]. Hence, the formation of Fe-Al-O solid solutions in Ce-containing samples is hardly ever possible.

## 2.2. Catalytic Activity in N<sub>2</sub>O Decomposition and NH<sub>3</sub> Oxidation

The activity of Ce/Al and (Ce + Al) based catalysts expressed in terms of N<sub>2</sub>O conversion at 800 °C versus Fe content (Figure 1A) is typical for temperature range 700–900 °C (Figure S2). For every type of support, it increases with Fe content. O<sub>2</sub> and H<sub>2</sub>O expectedly retard the reaction (Figure S3). Conversion values measured for Fe/(Ce + Al) samples are evidently lower than for Fe/Ce/Al. Therefore, better dispersion of CeO<sub>2</sub> species at close Ce content in the sample does not guarantee higher activity even at higher S<sub>BET</sub> values (Table 1).



**Figure 1.** Dependence of N<sub>2</sub>O conversion (A) and (NO + NO<sub>2</sub>) and N<sub>2</sub>O yield at NH<sub>3</sub> oxidation (B) on Fe content at 800 °C for Ce/Al and (Ce + Al) based samples.

For all samples, the conversion of NH<sub>3</sub> and yield of (NO + NO<sub>2</sub>) ( $Y_{\text{NO+NO}_2}$ ) increase, while that of N<sub>2</sub>O ( $Y_{\text{N}_2\text{O}}$ ) decreases with temperature;  $Y_{\text{NO+NO}_2} = 74\text{--}80\%$  and  $Y_{\text{N}_2\text{O}} = 0.5\text{--}1.8\%$  at  $T \geq 800$  °C (Figures S4 A, B, 1B). High stability for 8 h of operation, at least, was shown as well (Figure S4 C). We estimated that at an NH<sub>3</sub> slip of 1% (although such a value is practically impossible) the increment of N<sub>2</sub>O concentration after the Fe-Ce-Al catalyst at 800 °C will be 65–90 ppm. At the average N<sub>2</sub>O concentration downstream of the fresh gauzes of 1500 ppm [2], such an addition will diminish N<sub>2</sub>O conversion only by 4–6%.

### 2.3. Microstructure and Morphology

#### 2.3.1. DDPA

Detailed analysis of dissolution kinetics of Fe, Ce and Al in different samples has been presented in corresponding section of Supporting Information. Herein, we summarized and discussed the main facts that are important for understanding the composition and spatial distribution of different compounds in Fe/(Ce + Al) and Fe/Ce/Al samples.

Mixed oxides of different compositions dissolving consecutively in either HCl or HF (Figure S6) represent most of the 2.5 Fe/(Ce + Al) sample (Table 2). The most abundant compound is Fe-Ce-Al mixed oxide with  $\text{Fe}_{0.03}\text{Ce}_{0.09}\text{Al}$  stoichiometry which (Figure 2A):

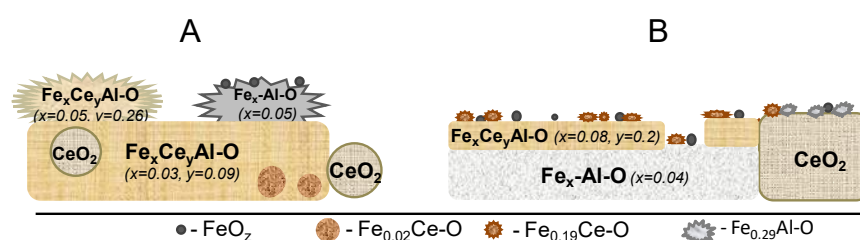
encapsulates the particles of Fe-Ce mixed oxide ( $\text{Fe}_{0.02}\text{Ce}$  stoichiometry);

is partially screened by more disordered Fe-Ce-Al mixed oxide with higher content of Fe and Ce ( $\text{Fe}_{0.05}\text{Ce}_{0.26}\text{Al}$  stoichiometry) and Fe-Al-O compounds dissolving in HCl.

The decreasing Fe/Al ratio in Fe-Al-O compounds points to the formation of mixed oxide with most disordered near-surface layers enriched by  $\text{Fe}^{+}$  (Figure S6 B). At the same time, the protocol of Fe supporting includes using of acidic solutions giving rise to the dissolution of some poorly crystallized alumina detected in the initial support (Figure S5 A, Table 2). In this case, the formation of a  $\gamma\text{-FeAlO}_3$ -like compound with spinel structure is quite possible after following drying and calcination at  $T < 400\text{ }^\circ\text{C}$  [21]. Since the mutual  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  solubility in such structure decreased prominently with calcination temperature rise, its decomposition could happen in our case as well leading to the formation of highly dispersed  $\text{FeO}_x$  species (0.06 mmol/g) on the surface of Fe-Al mixed oxide with  $\text{Fe}_{0.05}\text{Al}$  stoichiometry. Its quantity (1.3 mmole/g) is reasonably close to that of alumina dissolving in HCl in the initial support (1.15 mmole/g) (Table 2). Calculation showed that identified soluble compounds include all Al and Fe in the sample, while about 0.7 mmol/g of Ce, or 25% of its general content in the sample, represent insoluble oxides (Tables S1 in Supplementary Materials, Table 2) which are, more probably, small sized  $\text{CeO}_2$  species with unmodified fluorite lattice (Table 1). Their spatial location in the sample is not clear, but encapsulation by Ce-Al mixed oxide preventing Fe incorporation into the lattice is quite reasonable because the same was detected for the particles of Fe-Ce mixed oxide.

**Table 2.** Stoichiometry/quantity (mmol/g, without account of for O) of compounds dissolved in HCl and HF flows in different samples. Quantities of insoluble Ce compounds were calculated from balance equations.

Sample	Ce + Al	2.5 Fe/(Ce + Al)	3.8 Fe/Ce/Al
HCl	Al/1.15	Fe/0.06	Fe/0.07
		$\text{Fe}_{0.05}\text{Al}/1.30$	$\text{Fe}_{0.29}\text{Al}/0.37$
	$\text{Ce}_{0.05}\text{Al}/0.67$	$\text{Fe}_{0.05}\text{Ce}_{0.26}\text{Al}/0.65$	$\text{Fe}_{0.19}\text{Ce}/0.12$
HF	$\text{Ce}_{0.05}\text{Al}/7.92$	$\text{Fe}_{0.05}\text{Ce}_{0.26}\text{Al}/2.62$	Fe/0.03
	Al/0.45	$\text{Fe}_{0.03}\text{Ce}_{0.09}\text{Al}/8.14$	$\text{Fe}_{0.08}\text{Ce}_{0.2}\text{Al}/2.93$
	Ce/0.069	$\text{Fe}_{0.02}\text{Ce}/0.80$	$\text{Fe}_{0.04}\text{Al}/7.47$
Insoluble Ce	2.4	0.7	2.0

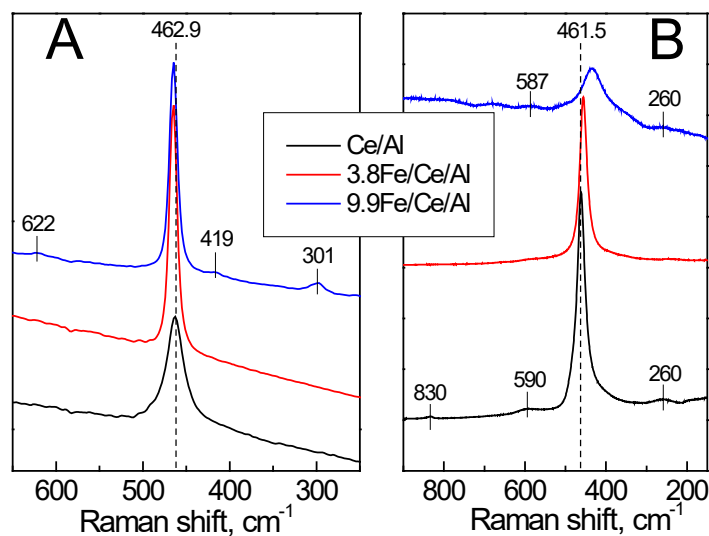


**Figure 2.** Structures formed in 2.5 Fe/(Ce + Al) (A) and 3.8Fe/Ce/Al (B) samples.

The overall quantity of soluble Ce-containing compounds in the 3.8 Fe/Ce/Al sample is substantially lower as compared with the 2.5 Fe/(Ce + Al) sample (Table 2), which can be related to a larger size of CeO<sub>2</sub> particles (Table 1). Most of the dissolved part of the sample is represented by Fe-Al mixed oxide partially screened by Fe-Ce-Al one with Fe<sub>0.04</sub>Al and Fe<sub>0.08</sub>Ce<sub>0.2</sub>Al stoichiometries, correspondingly (Figures S7 C, 2 B, Table 2). Surface layers are composed of more dispersed/disordered binary Fe-Al and Fe-Ce oxides and some FeO<sub>x</sub> dissolved in HCl (Figure S7, Table 2). Completely independent kinetics of their dissolution can be in the case dispersed FeO<sub>x</sub> species are located on the surface of any of binary oxides and even non-dissolved large CeO<sub>2</sub> species with unmodified fluorite lattice including 2.0 mmol/g of Ce, or more than 70% of its content in the sample (Figure 2B, Table 2). A substantially higher quantity of Fe in the surface located Fe-Al-O compounds (Fe<sub>0.29</sub>Al stoichiometry) compared with that in 2.5 Fe/(Ce + Al) could be due to other mechanisms of their formation compared with that in 2.5 Fe/(Ce + Al) sample (see below).

### 2.3.2. Raman

The band at 462.9 cm<sup>-1</sup> in the FT-Raman spectra of Ce/Al sample (Figure 3A) is typical for the F<sub>2g</sub> vibration mode of the fluorite structure of CeO<sub>2</sub> [22,23]. Its width at ~24.5 cm<sup>-1</sup> (Table 3) should correspond to a size of CeO<sub>2</sub> species at about 10 nm [23,24] which is substantially less than the estimated value of D<sub>XRD</sub> at 40 nm (Table 1). At the same time, the particles of 10 nm in a size should be characterized by the Raman band at ~448 cm<sup>-1</sup>, as follows from experimental dependence obtained for CeO<sub>2</sub> and CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composites [15]. Spanier et al. [24] showed that lattice strains in the smaller nanoparticles have the largest contribution to both Raman peak position shift and its broadening compared with other reasons (phonon confinement, particle size distribution, defects, phonon relaxation). Tsunekawa et al. [25] attributed the formation of additional strains to the reduction of Ce<sup>4+</sup> ions to Ce<sup>3+</sup> ions caused by an increasing molar fraction of oxygen vacancies. We supposed that in our case stabilization of additional Ce<sup>3+</sup> within fluorite lattice and appearance of strains can be due to insertion of lower sized Al<sup>3+</sup> cations into the interstitial sites of c-CeO<sub>2</sub> lattice resulting in charge redistribution, such as observed in c-CeO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> composites with close Ce/Al ratio [26]. The intensity of the CeO<sub>2</sub> band in the spectra of Fe/Ce/Al samples does not decrease prominently (Table 3), while its position and especially the width become very close to those in the single crystals [23]. Such changes could be due to better ordering of CeO<sub>2</sub> structure resulting from Al<sup>3+</sup> "extraction" from the lattice after impregnation by acidic Fe-containing solutions that proceed with temperature increase and, to a less extent, some enlargement of crystallized CeO<sub>2</sub> species (Table 1). It is the stabilization of small Fe-Al-O clusters in the points of Al insertion into CeO<sub>2</sub> lattice after their extraction, but not γ-FeAlO<sub>3</sub> phase decomposing at T > 400 °C, that can be responsible for the substantially higher content of Fe in the Fe-Al mixed oxide (Fe<sub>0.29</sub>Al) identified by DDPA compared with that in 2.5Fe/(Ce + Al) sample (Table 2). Bands at 231 (not shown), 301, 419 and 622 cm<sup>-1</sup> in the spectrum of 9.9 Fe/Ce/Al sample are usually related to lattice vibrations in α-Fe<sub>2</sub>O<sub>3</sub> which agrees with XRD data (Table 1).



**Figure 3.** FT-Raman (A) and Raman (B) spectra of Ce/Al-based samples.

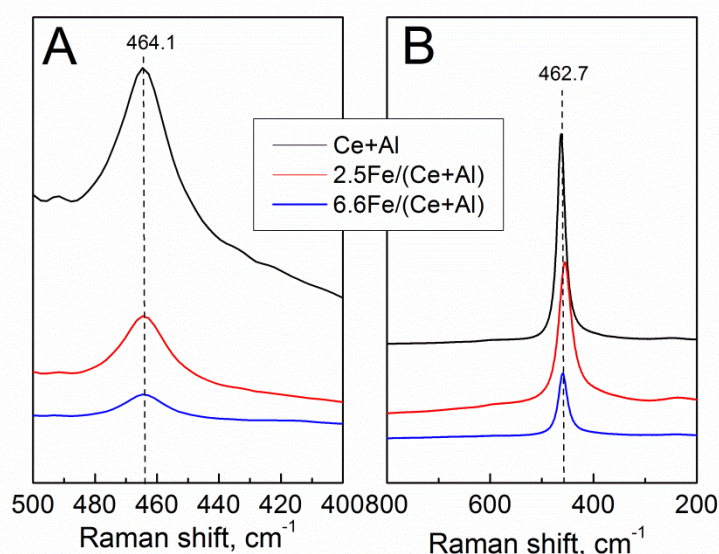
**Table 3.** Position, width (FWHM) and integral intensity of  $F_{2g}$  vibrational mode of  $CeO_2$  in the FT-Raman and Raman spectra.

Sample	Position, $cm^{-1}$		FWHM, $cm^{-1}$		Integral Intensity, Arb.Unit	
	FT-Raman	Raman	FT-Raman	Raman	FT-Raman	Raman
Ce/Al	462.9	461.5	24.5	21.2	0.101	30399
3.8 Fe/Ce/Al	465.1	455.8	10.6	21.8	0.087	27805
9.9 Fe/Ce/Al	464.9	433.0	10.8	66.3	0.079	26155
Ce + Al	464.1	462.7	18.3	17.0	0.219	266717
2.5 Fe/(Ce + Al)	464.0	455.8	17.3	23.4	0.0895	34159
6.6 Fe/(Ce + Al)	464.0	459.6	16.3	20.0	0.0327	19715

The absence of the band at  $\sim 377\text{ cm}^{-1}$  related to  $\alpha\text{-Al}_2\text{O}_3$  phases [27] in the Raman spectra giving information on near subsurface layers of all Ce/Al-based samples (Figure 3B) agrees with XRD and DDPA data.  $F_{2g}$  mode of  $CeO_2$  at  $461.5\text{ cm}^{-1}$  in the spectrum of support is supplemented by the bands at  $\sim 590$ ,  $\sim 260$  and  $\sim 830\text{ cm}^{-1}$  ascribed to the vacancy-interstitial (Frenkel-type) oxygen defects, surface mode, and peroxide ( $O_2^{2-}$ ) stretching vibration at the defective ceria surfaces, respectively [28–30]. These bands disappear in the spectrum of the 3.8Fe/Ce/Al sample because the doping element can annihilate oxygen defects by dopant interstitial compensation mechanism [31]. The low-frequency shift of the  $CeO_2$  band and its broadening (Table 3) typical for smaller particles was detected in the spectra of Fe/Ce/Al samples which contradicts the slight increase in averaged sizes of crystalline  $CeO_2$  particles (Table 1). Therefore, the formation of highly dispersed particles of Fe-Ce mixed oxide in the surface layers of the 3.8Fe/Ce/Al samples was detected by DDPA (Table 2) with inhomogeneous strains due to  $Ce^{3+}$  ions therein [15,28] can be responsible for such changes. Asymmetrical broadening with a low-energy shoulder of  $CeO_2$  band, especially prominent in the 9.9Fe/Ce/Al sample, can result from a higher concentration of such compounds or higher content of  $\alpha\text{-Fe}_2\text{O}_3$  therein. In line with this, bands at  $\sim 260$  and  $\sim 590\text{ cm}^{-1}$  appear again.

The band at  $464\text{ cm}^{-1}$  which is responsible for  $F_{2g}$  mode of fluorite lattice attenuates drastically in Fe/(Ce + Al) samples compared with that in the initial support (Figure 4A, Table 3). It is, more probably, due to the noticeable additional inclusion of Ce into alumina

or Ce-Al mixed oxides with low Ce content where it exists preferentially as isolated  $\text{Ce}^{3+}$  ions in the presence of Fe. Indeed, Ce/Al = 0.05 in Ce-Al mixed oxide detected by DDPA in the (Ce + Al) sample but increased up to 0.09–0.26 after Fe supporting (Table 2). The absolute value of mixed oxides increased as well, while the quantity of insoluble  $\text{CeO}_2$  decreased from 2.4 mmol/g to 0.7 mmol/g (Table 2). At the same time, the position of  $\text{CeO}_2$   $F_{2g}$  mode in Fe/(Ce + Al) samples changed non-substantially pointing to the absence or low degree of ceria lattice modification by foreign atoms compared with the support. In this case, a slightly higher FWHM compared with that in Fe/Ce/Al samples is due to the particle size effect, which is true for crystallized particles, at least (Table 1) [15].



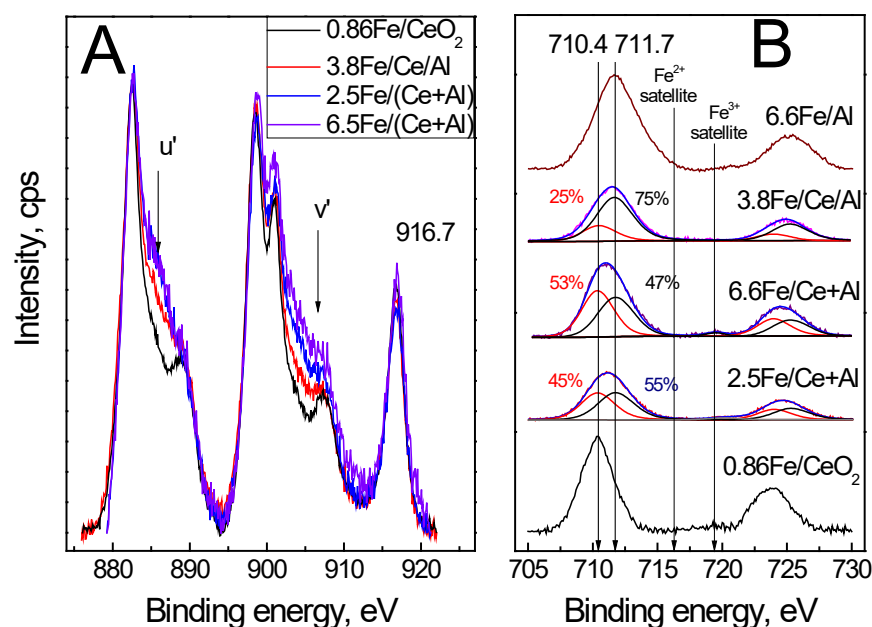
**Figure 4.** FT-Raman (A) and Raman (B) spectra of (Ce + Al) based samples.

The band at  $\sim 377\text{ cm}^{-1}$  related to  $\alpha\text{-Al}_2\text{O}_3$  phases [27] was absent in the Raman spectra of near subsurface layers of (Ce + Al) based samples as well which agrees with XRD data (Figure S1, Table 1). After iron supporting, they undergo changes that are very similar to those in the bulk of the sample (Figure 4B, Table 3). An even more prominent drop in the intensity of the Ce band compared with that for the bulk can be related to the additional formation of Fe-Ce-Al mixed oxide with high Ce content ( $\text{Fe}_{0.05}\text{Ce}_{0.26}\text{Al}$  stoichiometry) (Table 2). Nevertheless, the close  $\text{CeO}_2$  band position and FWHM values in FT-Raman and Raman spectra point to a more uniform distribution of elements in the bulk and surface layers of these samples as compared to those in Ce/Al-based samples. This agrees with DDPA data on the preferential formation of Fe-Ce-Al-O mixed oxides in the 2.5 Fe/(Ce + Al) sample, while obviously spatially divided Fe-Al-O, Fe-Ce-O and more  $\text{CeO}_2$  were found in the 3.8 Fe/Ce/Al sample.

#### 2.4. Surface Composition (XPS)

The normal complex formed due to shake-down satellites from an O1s to Ce 4f electron transfer in the Ce 3d spectra of all  $\text{CeO}_2$  containing samples (Figure 5A) was supplemented by the features marked as  $v'$  and  $u'$  due to the presence of  $\text{Ce}^{3+}$  [10]. An increase in  $\text{Ce}^{3+}$  fraction from 8% of total surface Ce concentration in  $\text{CeO}_2$  (spectrum not shown for shortness) up to 20% in 0.86 Fe/ $\text{CeO}_2$  sample was related to the formation of Fe-Ce-O solid solution or Fe-Ce mixed oxide [4,32]. Similar compounds of  $\text{Fe}_{0.19}\text{Ce}$  stoichiometry have been detected in the 3.8Fe/Ce/Al sample (Table 2, Figure 2). Therefore, there are two reasons that explain the further increase in  $\text{Ce}^{3+}$  fraction in 3.8Fe/Ce/Al (25%) and especially Fe/(Ce + Al) (31–33%) samples (Table 4): stabilization of both isolated Ce cations in

alumina-based structure of Fe-Ce-Al mixed oxides (Table 2) and Ce located on CeO<sub>x</sub>-AlO<sub>x</sub> boundary in the same oxides as Ce<sup>3+</sup>; lower CeO<sub>2</sub> particle sizes (12 nm (2.5 Fe/(Ce + Al)) and 41 nm (3.8 Fe/Ce/Al), Table 1) compared with that in Fe/CeO<sub>2</sub> (55 nm [4]) favoring reduction in Ce<sup>4+</sup> [25].



**Figure 5.** Ce 3d (A) Fe 2p (B) spectra of Fe-Ce-Al-O samples including contributions of Fe<sub>2</sub>O<sub>3</sub> (710.4 eV) and FeOOH (711.7 eV)-like structures to overall Fe2p spectrum. 6.6 Fe/Al<sub>2</sub>O<sub>3</sub> and 0.86 Fe/CeO<sub>2</sub> samples were studied by Pinaeva et al. [4].

**Table 4.** Surface (XPS) composition of different Fe-Ce-Al-O samples.

Sample	Ce <sup>3+</sup> , % of Total	Ce <sub>s</sub> , <sup>a</sup> at. %	Ce <sub>exp</sub> , rel.units <sup>b</sup>	Ce/Al	Fe <sub>s</sub> <sup>a</sup> at. % <sup>a</sup>	Fe <sub>exp</sub> , rel.units <sup>b</sup>
3.8 Fe/Ce/Al	25	3.7	184	0.12	1.6	80
2.5 Fe/(Ce + Al)	31	2.4	171	0.075	1.7	117
6.6 Fe/(Ce + Al)	33	2.7	159	0.096	2.7	166

a: calculated supposing C-containing compounds are absent under reaction conditions; accounting of C does not change the order of values. b: calculated as  $\text{Fe}(\text{Ce})_{\text{exp}} = \text{Fe}(\text{Ce})_{\text{s}} \cdot \text{SSA}$ .

Surface Ce concentration (Ces) and Ce/Al ratios in all samples (Table 4) are substantially lower than should follow from its integral composition ( $\text{Ce}/\text{Al} \approx 0.3$ , Table S1), which agrees in general with higher dispersion of Al-containing compounds. The highest Ces and Ce/Al values were measured in the 3.8 Fe/Ce/Al sample (Table 2). However, the concentration of exposed Ce (Cexp) in the Fe/Ce/Al and Fe/(Ce + Al) samples differ not so prominently because of higher S<sub>BET</sub> values in the last (Table 1). It is problematic to estimate Ces in the Fe-Ce-Al-O compounds of the samples. This value should be slightly higher in 2.5Fe/(Ce + Al) sample ( $\text{Ce}/\text{Al} = 0.26$  instead of  $\text{Ce}/\text{Al} = 0.2$  for 3.8Fe/Ce/Al sample, Table 2). Surface areas of crystallized CeO<sub>2</sub> particles in Fe/(Ce + Al) and Fe/Ce/Al samples as formally estimated from their absolute content (Table S1) and sizes (Table 1) are quite close. However, encapsulation of about 29% of Ce composing Fe-Ce-O mixed oxides ( $\text{Fe}/\text{Ce} = 0.02$ , 0.8 mmol/g, Table 2) by Fe-Ce-Al mixed oxide was found for 2.5 Fe/(Ce + Al) sample (Figure 2A). This allows supposing bulk location of some CeO<sub>2</sub> species as well thus decreasing Ces value therein. In addition, preferential exposing of highly dispersed



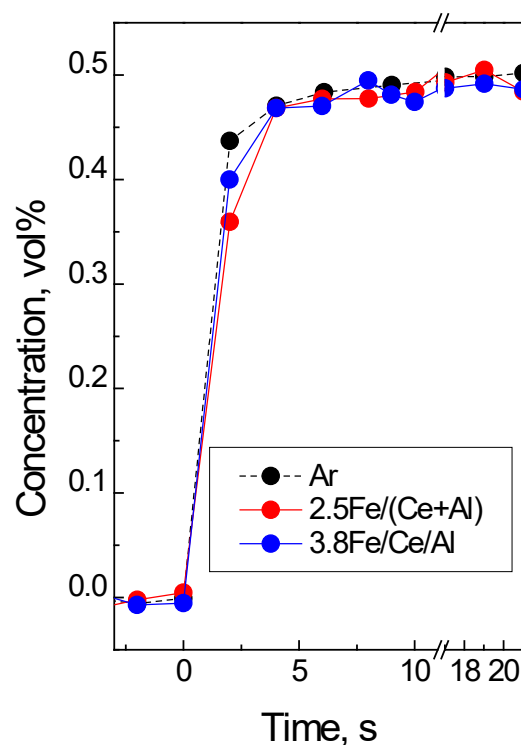
Fe-Ce-O compound with  $\text{Fe}_{0.19}\text{Ce}$  stoichiometry can additionally contribute to higher  $\text{Ce}_s$  value in the 3.8 Fe/Ce/Al sample. Hence, a substantial part of  $\text{Ce}_s$  in the Fe/(Ce + Al) samples composes Fe-Ce-Al mixed oxides with a high concentration of  $\text{Ce}^+$ , while the fraction of  $\text{CeO}_2$ -like structures is higher and seems to be responsible for greater  $\text{Ce}_s$  value in Fe/Ce/Al samples.

The 3.8 Fe/Ce/Al sample is characterized by the lowest Fe surface concentration ( $\text{Fe}_s$ ) and the quantity of exposed Fe as related to a weight unit ( $\text{Fe}_{\text{exp}}$ ) (Table 4). BE values of the  $\text{Fe}2p_{3/2}$  spectra ranging from 710.9 eV to 711.7 eV (Figure 5B) evidence presence of  $\text{Fe}^{3+}$  in oxyhydroxide environment (like in  $\alpha$ - or  $\gamma$ - $\text{FeOOH}$ ), and in the oxide (like  $\text{Fe}_2\text{O}_3$ ) structures [33–35], correspondingly dominating in 6.6 Fe/ $\text{Al}_2\text{O}_3$  and 0.86 Fe/ $\text{CeO}_2$  samples [4]. Although the positions of the Fe  $2p_{3/2}$  peak for  $\text{Fe}^{2+}$  in  $\text{Fe}_{0.94}\text{O}$ ,  $2\text{FeO}\cdot\text{SiO}_2$  or  $\text{Fe}_{0.01}\text{Mg}_{0.99}\text{O}(100)$  single crystal were characterized by the values between 709.0 and 710.4 eV, its absence or low content in our samples follows from the absence of distinct satellite at 714.6–716 eV [36,37].  $\text{FeOOH}$  usually undergoes a dehydroxylation reaction at 250–300 °C resulting in  $\text{Fe}_2\text{O}_3$  [38]. At the same time, tetrahedral  $\text{Fe}^{3+}$  cations coordinating both terminal and bridging OH groups were found on the surface of both Fe-Al-O solid solution and highly dispersed  $\text{FeO}_x$  species resulting from the decomposition of  $\gamma$ - $\text{FeAlO}_3$ -like structures [21]. In accordance with this, the  $\text{Fe}2p_{3/2}$  band at 711.7 eV (dominates in 3.8Fe/Ce/Al sample) can be subscribed to:  $\text{Fe}^{3+}$  ions in Fe-Al mixed oxides, including those with  $\text{Fe}_{0.29}\text{Al}$  stoichiometry (Table 2) formed by “extraction” of Al from  $\text{CeO}_2$  lattice after Fe supporting; highly dispersed  $\text{FeO}_x$  species resulted from the decomposition of Fe-Al-O.

The band at 710.4 eV can characterize  $\text{FeO}_x$  species on the surface of  $\text{CeO}_2$  or  $\text{Fe}^{3+}$  ions in the Fe-Ce-O compounds (Table 2, Figure 2). Its high abundance in Fe/(Ce + Al) samples (45–53% of total  $\text{Fe}_s$ ) contradicts lower  $\text{Ce}_s$  values compared with that in 3.8 Fe/Ce/Al sample. However, the substantial part of the surface Fe in Fe/(Ce + Al) samples composes Fe-Ce-Al mixed oxides with reasonably high Ce content ( $\text{Ce}/\text{Al} = 0.26$ , Table 2). It resulted from the inclusion of additional Ce from  $\text{CeO}_2$  into the surface layers of alumina or Ce-Al mixed oxide of the initial support with Fe participation. Therefore, preferential formation of Fe-Ce-O oxide-like compounds is quite possible in Fe-Ce-Al mixed oxides. The contribution of Fe-Ce-Al mixed oxides into the surface composition in the 3.8 Fe/Ce/Al sample is not high which follows from the preferential dissolution of  $\text{FeO}_x$ , binary Fe-Al-O and Fe-Ce-O compounds in HCl (Table 2) and substantially less prominent decrease in integral intensity of  $\text{F}_{2g}$  vibrational mode of  $\text{CeO}_2$  in the near-surface layers of Fe/Ce/Al samples compared with corresponding support (Table 3).

### 2.5. $\text{O}_2$ Adsorption/Desorption

$\text{O}_2$  transients recorded during the He/0.5vol.% $\text{O}_2$  switch following 60 s stay in He flow revealed the delay of  $\text{O}_2$  response compared with Ar (Figure 6) corresponding to adsorption of reasonably close quantities of oxygen ( $3 \times 10^{19}$ – $5 \times 10^{19}$  oxygen atom/g) by reduced sites in the 2.5 Fe/(Ce + Al) and 3.8 Fe/Ce/Al samples.



**Figure 6.** Responses of O<sub>2</sub> and inert label (Ar) during the switch from He to He + 0.5vol.% O<sub>2</sub> flow over different samples. T = 800 °C.

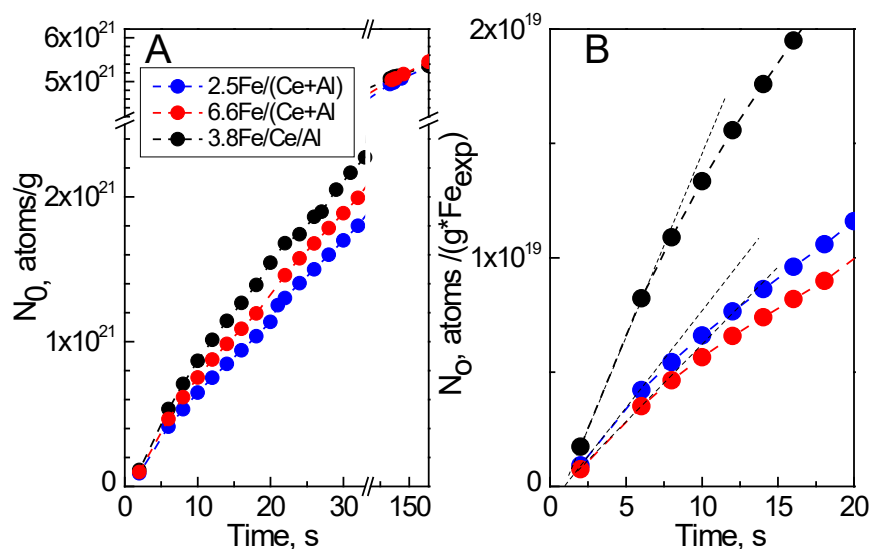
Differently paired Fe<sup>2+</sup> and Ce<sup>3+</sup> ions resulting from the reduction in the oxygen absence are the most evident sites for O<sub>2</sub> dissociative adsorption as coordinatively unsaturated surface metal cations. They can form in the surface layers of FeO<sub>x</sub> clusters, including those resulted from the decomposition of  $\alpha$ -FeAlO<sub>3</sub>; Fe-Al-O mixed oxide of Fe<sub>0.29</sub>Al stoichiometry formed in 3.8Fe/Ce/Al sample by Al “extraction” from CeO<sub>2</sub> lattice during calcination; highly dispersed Fe-Ce mixed oxides (Fe<sub>0.19</sub>Ce stoichiometry (Table 2); Fe-Al-Ce-O mixed oxides with high Ce content (Fe<sub>0.05</sub>Ce<sub>0.26</sub>Al or Fe<sub>0.08</sub>Ce<sub>0.2</sub>Al stoichiometry).

Reduction of isolated Fe<sup>3+</sup> in the Fe-Al-(Ce)-O mixed oxides with of Fe<sub>0.03</sub>Ce<sub>0.09</sub>Al stoichiometry (most of Ce stabilized as Ce<sup>3+</sup> and unlikely can participate in any redox processes) requires transport of second oxygen atom through the occasional vacancies on the surface or in the bulk of alumina and thus be slow.

## 2.6. Oxygen Mobility (<sup>18</sup>O SSITKA)

The rates of oxygen exchange in Fe/Ce-Al-O samples in the period of 0–60 s after the <sup>16</sup>O/<sup>18</sup>O switch can be ordered as 3.8 Fe/Ce/Al > 6.6 Fe/(Ce + Al) > 2.5 Fe/(Ce + Al), as follows from the slope of N<sub>O</sub>(t)/g dependencies (Figure 7A). It does not correlate with S<sub>BET</sub> values of the samples (Table 1) and Fe<sub>s</sub> or Fe<sub>exp</sub> values (Table 4). Moreover, the difference between 3.8 Fe/Ce/Al and Fe/(Ce + Al) samples becomes even more prominent when related to one surface Fe site (Figure 7B). Fast exchange proceeding with reasonably close to initial rate value in these samples during about 20–25 s includes a higher quantity of oxygen atoms (N<sub>O</sub> = 1 × 10<sup>21</sup>–2 × 10<sup>21</sup> O atoms/g) than can be related to Fe, even with an account of that located in the bulk (~1.0 × 10<sup>21</sup> O atoms/g in the 6.6 Fe/(Ce + Al) sample with the highest Fe content). Therefore, efficient exchange in the near-surface layers of Ce-containing compounds contributes to N<sub>O</sub> as well. Indeed, substantially more profound and faster oxygen exchange took place in Fe/CeO<sub>2</sub> samples compared with Fe/Al<sub>2</sub>O<sub>3</sub> [4]. However, both Ce

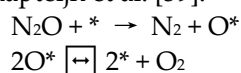
content and  $C_{exp}$  values are reasonably close in all samples (Table 4). We consider that the higher rate of exchange in the 3.8 Fe/Ce/Al sample can be due to preferential exposure of Fe-Ce mixed oxide or crystallized  $CeO_2$ , including that bonded with clusters of  $FeOx$  or Fe-Al mixed oxides, while in 2.5 Fe/(Ce + Al) sample substantial part of Fe and Ce are included as preferentially isolated ions into Fe-Ce-Al mixed oxides that still retain alumina-like structure. Although Fe-Ce mixed oxide was detected in the 2.5 Fe/(Ce + Al) sample (Table 2, Figure S6), it obviously locates in bulk (Figure 2), like part of  $CeO_2$ , and thus does not contribute to the fast oxygen exchange.



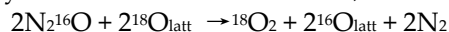
**Figure 7.** Time dependencies of the quantity of exchanged oxygen ( $N_o$ ) as related to weight unit (A) or one surface Fe site (B) in  $^{18}O$  SSITKA experiments for different samples.  $T = 800$  °C.

## 2.7. Discussion

In accordance with the simplified redox scheme of  $N_2O$  decomposition proposed by Kapteijn et al. [39]:

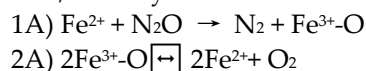


one active (reduced) site is sufficient for  $N_2$  to evolve, but two neighboring  $O^*$  are necessary for the desorption of  $O_2$ . Factually, two neighboring active sites for  $N_2O$  adsorption are desired for efficient reaction running, especially provided oxygen desorption from the surface is the rate-controlling step of this reaction [39]. Potential quantities of such reduced sites under reaction conditions in 2.5 Fe/(Ce + Al) and 3.8 Fe/Ce/Al samples are quite close (Figure 6). At the same time, the isotopic transient experiment  $^{18}O_2/N_2^{16}O$  performed on  $LaMnO_3$  at 900 °C revealed that there is direct oxygen transfer to the catalysts' bulk from  $N_2O$  molecule, and  $O_2$  formed involves lattice oxygen [40]:

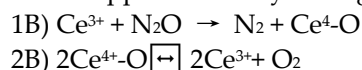


This means that catalytic activity should depend on oxygen exchange properties.

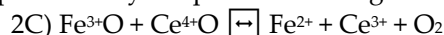
In  $CeO_2$ -containing compounds a simplified redox scheme realized in Fe oxides or  $FeOx/Al_2O_3$  systems:



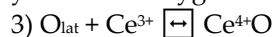
is supplemented by analogous steps for  $Ce^{3+}/Ce^{4+}$  redox pair:



And step corresponding to the additional pathway of oxygen species recombination provided by the presence of neighboring  $\text{Fe}^{3+}$  and  $\text{Ce}^{4+}$ :



In addition, reoxidation of  $\text{Ce}^{3+}$  due to fast oxygen diffusion from  $\text{CeO}_2$  lattice ( $\text{O}_{\text{lat}}$ ) by extended oxygen vacancies arising after insertion of  $\text{Fe}^{3+}$  ions into the fluorite lattice:



Can become an alternative pathway for the supply of the second oxygen atom which is necessary for  $\text{O}_2$  desorption and enhancing recombination of oxygen adspecies by steps 2B and 2C without adsorption of the second  $\text{N}_2\text{O}$  molecule. Pure  $\text{CeO}_2$  revealed insubstantial activity as related per surface area unit compared with  $\text{FeO}_x/\text{CeO}_2$  and even  $\text{Fe}/\text{Al}_2\text{O}_3$  samples [4]. Therefore, the contribution of this pathway is high in  $\text{Fe}/\text{Ce}/\text{Al}$  samples containing substantial quantities of both  $\text{Fe}-\text{Ce}-\text{O}$  mixed oxide and bulky  $\text{CeO}_2$  bonded with  $\text{FeO}_x$  or  $\text{Fe}-\text{Al}-\text{O}$  clusters. Stabilization of a substantial fraction of  $\text{Ce}$  as isolated  $\text{Ce}^{3+}$  cations composing mixed  $\text{Fe}-\text{Ce}-\text{Al}$  oxides in the  $\text{Fe}/(\text{Ce} + \text{Al})$  samples diminishes substantially the efficiency of oxygen transfer to  $\text{Fe}^{3+}-\text{O}$  sites.

### 3. Materials and Methods

#### 3.1. Catalysts Preparation

Two procedures were used to prepare the supports with a  $\text{CeO}_2 : \text{Al}_2\text{O}_3$  weight ratio of 1 : 1. In the first of them, the precursor of  $\text{CeO}_2$  was deposited from 0.75 M  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.0%, Vekton, Saint-Petersburg, Russia) water solution using 1 M  $(\text{NH}_4)_2\text{CO}_3$  (99.3 %, Vekton, Saint-Petersburg, Russia) as a precipitation agent onto  $\text{Al}_2\text{O}_3$  (the product of thermochemical activation of hydrargillite calcined at 500 °C) characterized by BET surface area at 210  $\text{m}^2\text{g}^{-1}$ ). After washing by  $\text{H}_2\text{O}$  unless the pH of the filtrate was 7 and drying at 60 °C overnight, the sample was calcined at 900 °C for 5 h and denoted below as  $\text{Ce}/\text{Al}$ . In the second procedure, the water solution of  $(\text{NH}_4)_2\text{CO}_3$  was added dropwise to a water solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98.5%, Ecos, Saint-Petersburg, Russia) and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  mixed in the necessary proportion unless  $(\text{Ce} + \text{Al})/\text{CO}_3$  (mole) = 2.5 value was reached. Thus, the obtained gel was dried at 60 °C for 22 h followed by calcination at 500 °C for 2h and at 900 °C for 5h resulting in a sample denoted below as  $(\text{Ce} + \text{Al})$ .

$\text{FeO}_x$  was supported by incipient wetness impregnation of  $\text{Ce}/\text{Al}$  and  $(\text{Ce} + \text{Al})$  by water solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98.5 %, Vekton, Saint-Petersburg, Russia) with necessary concentration with added citric acid (99.8 %, Vekton, Saint-Petersburg, Russia) in 10 wt.% excess to the stoichiometric amount and ethyleneglycole (99.0 %, Ecos, Saint-Petersburg, Russia), dried in air at 150 °C for 3 h and then calcined at 900 °C for 4 h. In the commonly used abbreviation  $n \text{ Fe}/\text{support}$ , “n” corresponded to  $\text{Fe}$  weight % concentration in the sample.

#### 3.2. Characterization

XRD patterns were recorded using D8 diffractometer (Bruker, Germany) with  $\text{CuK}\alpha$  monochromatic radiation. Each sample was scanned in the range of  $2\theta$  from 10° to 70° with a step 0.05°. The surface composition of the samples was investigated by X-ray photoelectron spectroscopy (XPS) using spectrometer SPECS (SPECS, Germany) with  $\text{Al K}\alpha$  irradiation ( $h\nu = 1486.6 \text{ eV}$ ). The positions of the peaks of  $\text{Au } 4f_{7/2}$  (84.0 eV) and  $\text{Cu } 2p_{3/2}$  (932.67 eV) core levels were used for calibration of the binding energy (BE) scale. In Raman spectroscopy depth of light penetration depends on the wavelength of monochromatic radiation provided by different sources. We believe that green light (514.5 nm line of an  $\text{Ar}^+$  laser with 2 mW power reaching the sample) provides information about the structure of preferentially near-surface layers of the samples, while data on the bulk composition are obtained with near-infrared (NIR) radiation at 1064 nm line (provided by an Nd-YAG laser with 100 mW power output) (Bruker Optik GmbH, Ettlingen, Germany). FT-Raman spectra (3700–100  $\text{cm}^{-1}$ , 300 scans, resolution 4  $\text{cm}^{-1}$ , 180° geometry) were collected using an RFS 100/S spectrometer (Bruker Optik GmbH, Ettlingen, Germany). Horiba Jobin Yvon

T64000 spectrometer (HORIBA Scientific, Palaiseau, France) with micro-Raman setup and backscattering geometry for experimental spectra collection was used to measure the Raman spectra. The spectral resolution was not worse than  $1.5 \text{ cm}^{-1}$ . The detector was a silicon-based CCD matrix, cooled with liquid nitrogen. The band at  $520.5 \text{ cm}^{-1}$  of Si single crystal was used to calibrate the spectrometer.

The method of differential dissolution phase analysis (DDPA) [41] was used to reveal the composition and, in some cases, morphology and particle depth distribution of the compounds and phases (including X-Ray amorphous ones) formed in the samples. For this about 10 mg of the sample loaded in a quartz microreactor was dissolved in the flow (3.6 mL/min) of water-based solution with the composition changing from HCl (pH = 2) to 3M HCl (with continuous temperature increase from  $20 \text{ }^\circ\text{C}$  to  $90 \text{ }^\circ\text{C}$ ), and finally to 3.6 M HF. Compounds dissolving in milder conditions (HCl (pH = 2) and 1–3M HCl) were reasonably supposed to form in the surface layers of the samples. Better crystallized structures, as a rule, dissolve in HF or even remain insoluble. Change of the outlet mixture composition in time was analyzed by ICP AES 262477-364A spectrometer (BAIRD, Zoeterwoude, The Netherlands) using the spectral lines at 238.2, 308.2, and 413.8 nm which are characteristic for Fe, Al and Ce, respectively.

### 3.3. Kinetic Measurements and Catalytic Tests

For  $^{16}\text{O}/^{18}\text{O}$  exchange experiments, the sample was first heated to  $800 \text{ }^\circ\text{C}$  in 0.58 vol %  $^{16}\text{O}_2 + \text{He}$  flow and kept at this temperature for 30 min. After, this gas mixture was replaced stepwise by the same one containing  $^{18}\text{O}_2$  and Ar (1 vol.%) as an inert tracer. All responses were analyzed using QMS 200 gas analyzer (Stanford Research Systems, Sunnyvale, USA) as time variation of the  $^{18}\text{O}$  atomic fraction in the gas phase  $\alpha_g(t) = \frac{(^{16}\text{O}^{18}\text{O} + 2 \cdot ^{18}\text{O}^{18}\text{O})}{2 \cdot (^{16}\text{O}^{18}\text{O} + ^{18}\text{O}^{18}\text{O} + ^{16}\text{O}^{16}\text{O})}$ . Time dependencies of exchanged oxygen for different samples as related to the mass unit ( $N_o$ ) were calculated using the formulae  $N_o(t) = N_A \cdot \frac{2 \cdot C_{\text{O}_2} \cdot U}{g} \cdot \int_0^t (\alpha_g^{\text{input}} - \alpha_g) dt$ , where  $\alpha_g^{\text{input}}$ : isotope fraction in the inlet mixture (0.95),  $C_{\text{O}_2}$ : inlet  $\text{O}_2$  concentration (mol/mol),  $U$ : flow rate of the reaction mixture (mole/s),  $N_A$ : Avogadro number. Dynamics of oxygen adsorption/desorption at  $800 \text{ }^\circ\text{C}$  was elucidated from the experiments on the stepwise replacement of He by 0.5 vol. %  $\text{O}_2 + 1 \text{ vol. } \% \text{Ar} + \text{He}$  mixture and vice versa flowing the reactor. ( $\text{O}_2 + \text{He}$ )/He switch was performed after at least 30 min sample stay in  $\text{O}_2$  containing flow, while He/( $\text{O}_2 + \text{He}$ ) one followed in about 60 s. All kinetic measurements were performed with the sample ( $g = 0.025 \text{ g}$ , particles of 250–500  $\mu\text{m}$  in a size) loaded into a reactor (quartz tube, i.d. = 3 mm). The gas flow rates of all mixtures amounted to  $16.7 \text{ cm}^3/\text{s}$ .

The catalytic activity for samples with particles of 250–500  $\mu\text{m}$  in a size was measured in a fixed-bed U-shaped reactor (3 mm i.d. quartz tube) at ambient pressure in the temperature range  $700\text{--}900 \text{ }^\circ\text{C}$ . For  $\text{NH}_3$  oxidation, mixture 1%  $\text{NH}_3 + 20\% \text{ O}_2$  in  $\text{N}_2$  was fed to the reactor charged by 0.015 g of the sample with a flow rate of  $6.9 \text{ cm}^3/\text{s}$ . Concentrations of  $\text{NH}_3$  and  $\text{NO}_x$  ( $x = 0.5\text{--}2$ ) in the outlet mixture were measured by infrared spectroscopy. For  $\text{N}_2\text{O}$  decomposition, a gas mixture of 0.15 vol%  $\text{N}_2\text{O}$  in He flowed the reactor charged with 0.038 g of the sample with a flow rate of  $16.7 \text{ cm}^3/\text{s}$ . In some experiments about 3 vol. %  $\text{O}_2$  (+3 vol. %  $\text{H}_2\text{O}$ ) were added to the inlet mixture. Outlet mixture composition was analyzed by gas chromatograph equipped with Porapack T (i.d. = 3mm,  $l = 3 \text{ m}$ , for  $\text{N}_2\text{O}$  analysis) and NaX (i.d. = 3mm,  $l = 2 \text{ m}$ , for  $\text{N}_2$  analysis) columns.  $\text{N}_2\text{O}$  or  $\text{NH}_3$  conversion ( $X_{\text{N}_2\text{O}(\text{NH}_3)}$ ) and yield ( $Y_i$ ) values calculated as  $X_{\text{N}_2\text{O}} = \frac{(C_{\text{N}_2\text{O}}^0 - C_{\text{N}_2\text{O}})}{C_{\text{N}_2\text{O}}^0} \cdot 100\%$ ,  $X_{\text{NH}_3} = \frac{(C_{\text{NH}_3}^0 - C_{\text{NH}_3})}{C_{\text{NH}_3}^0} \cdot 100\%$ , and  $Y_i = \frac{n \cdot C_i}{C_{\text{NH}_3}^0} \cdot 100\%$ , ( $C_i$  and  $C_i^0$ : outlet and inlet concentrations of  $i$ th compound,  $n$ : number of N atoms in the  $i$ th molecule) were considered as a measure of samples activity.

#### 4. Conclusions

FeO<sub>x</sub> (2.5–9.9 weight.% in terms of Fe) was supported by impregnation of mixed CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support prepared either by co-precipitation (Ce + Al) or CeO<sub>2</sub> precipitation onto Al<sub>2</sub>O<sub>3</sub> (Ce/Al). Preferentially Fe-Ce-Al mixed oxides both in the surface layers and in the bulk were formed in Fe/(Ce + Al) samples, while the substantial spatial division of ceria and alumina-based compounds remains intact in Fe/Ce/Al samples. The stabilization of Ce<sup>3+</sup> in Fe-Ce-Al mixed oxides was shown to inhibit oxygen mobility in the near-surface layers of Fe/(Ce + Al) samples. It results in retardation of the additional pathway of oxygen supply to the sites responsible for O<sub>2</sub> desorption and explains the lower activity of Fe/(Ce + Al) samples in N<sub>2</sub>O decomposition.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12090938/s1>, Figure S1: XRD patterns of Ce/Al (A) and (Ce + Al) (B) based samples with different content of Fe, Figure S2: Dependence of N<sub>2</sub>O conversion on the temperature for Ce/Al (A) and (Ce + Al) (B) based samples, Figure S3: Effect of O<sub>2</sub> and H<sub>2</sub>O presence in the inlet flow on N<sub>2</sub>O conversion over 3.8 Fe/Ce/Al and 2.5 Fe/(Ce + Al) samples. T = 800 °C, Figure S4: Temperature dependence of the conversion (A) yield of (NO + NO<sub>2</sub>) and N<sub>2</sub>O (B) at NH<sub>3</sub> oxidation over different Fe/Ce-Al-O based samples. Stability tests for 9.9 Fe/Ce/Al sample (C) at 800 °C, Figure S5: Differential dissolution curves of Ce and Al (A) and identified compounds (B) at stepwise consecutive change of flow composition from HCl (pH = 2) to 1-3M HCl (1) and then to 3.6 M HF (2) over (Ce + Al) sample, Figure S6: Differential dissolution curves of Fe, Ce and Al (A) and identified compounds (B) at stepwise consecutive change of flow composition from HCl (pH = 2) to 1-3M HCl (1) and then to 3.6 M HF (2) over 2.5 Fe/(Ce + Al) sample, Figure S7: Differential dissolution curves of Fe, Ce and Al (A) and initially (B) and finally (C) identified Fe-Ce-Al compounds at stepwise consecutive change of flow composition from HCl (pH = 2) to 1–3M HCl (1) and then to 3.6 M HF (2) over 3.8Fe/Ce/Al sample; Table S1: Quantity of Fe, Ce, Al (as prepared, dissolved and insoluble) in different samples (mmol/g). Quantities of insoluble compounds were calculated from balance equations.

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