



Catalytic activity of neodymium substituted zinc ferrites for oxidative conversion of methane

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ABSTRACT

The catalytic behavior for oxidative conversion of methane in large oxygen excess (methane combustion) and in reducing conditions (oxidative coupling of methane) was comparatively investigated for the first time over pure and neodymium substituted zinc ferrites prepared by combustion method. The catalytic activity proved to be strongly related to the oxide structure, to the specific defects created by substitution as well as to the composition of the reaction mixture. The neodymium substituted ferrites ($\text{ZnFe}_{1.75}\text{Nd}_{0.25}\text{O}_4$, $\text{ZnFe}_{1.5}\text{Nd}_{0.5}\text{O}_4$ and ZnFeNdO_4) exhibited high activity for methane combustion but low activity for coupling reaction. On the other hand, the pure zinc ferrite (ZnFe_2O_4) and ZnNd_2O_4 were active to catalyze methane coupling whereas the activity for methane combustion was low. The catalytic activity of the oxides and the reaction mechanism on simple and mixed oxides is discussed in light of the experimental results.

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1. Introduction

The oxidative coupling of methane (OCM) may prove to be a viable alternative to obtaining higher hydrocarbons starting from methane, which is a relatively cheap and abundant raw material. Due to the great practical impact, the OCM reaction was intensively investigated. The methane catalytic combustion has also a great potential to be applied for gas turbines in order to reduce the NO_x pollution associated to the actually used methane flame burning technology. Thus, the above-mentioned catalytic reactions are related to the superior utilization of natural resources and depollution. The catalytic activity of a broad class of simple and mixed oxides as well as of supported metals has been already investigated. Several reviews have been dedicated to the oxidative conversion of methane over simple and mixed oxides [1,2]. However, in the spite of the intense research there is still enough room for improvements in catalytic performances as well as in stability to obtain ideally tuned materials for a specific practical application.

Neodymium and iron-based oxide materials have been separately studied to some extent. For example, the activity of pure, Zr and Sr doped Nd_2O_3 for OCM reaction was already reported [3,4]. It should be emphasized that the yield to C_2^+ over these materials was relative modest, remaining below 15%. Ferrites have been investigated up now much more for their interesting magnetic

properties. However, the catalytic activity of ZnFe_2O_4 for oxidative dehydrogenation of *n*-butene [5,6]. The photocatalytic behavior of the simple and TiO_2 -added ZnFe_2O_4 was also reported [7,8].

To our knowledge, the catalytic behavior of neodymium substituted zinc ferrites has not been yet investigated. Thus, study of the methane oxidative conversion over simple and Nd substituted zinc ferrite (ZnFe_2O_4) would be a novelty in the catalytic field. The catalytic activity of the ZnNd_2O_4 , having an ordered crystalline structure of K_2NiF_4 type, is also reported here for the first time. As we shall show later, Nd_2ZnO_4 can be a very promising starting material for a novel class of OCM catalysts showing high selectivity to C_2 hydrocarbons as well as high stability in reaction conditions.

The aims of our investigation were (i) to comparatively investigate the catalytic behavior of the pure and neodymium doped zinc ferrites for methane combustion and OCM, (ii) to observe the effect of Fe^{3+} substitution by Nd^{3+} on the catalytic behavior for oxidative conversion of methane in oxygen rich (combustion) and oxygen poor (OCM) atmospheres, and (iii) to get a better understanding on the generation, nature and role of lattice defects on the catalytic reactivity.

2. Experimental

The principle of the preparation procedure consisted in the use of metal coordination compounds as precursors of the final mixed oxides [9,10]. The $\text{ZnFe}_{2-x}\text{Nd}_x\text{O}_4$ ($x=0, 0.25, 0.5, 0.75$ and 1.0) type mixed oxides were prepared starting from the tartarate complexes of the constituent metals. The tartarate precursors were obtained

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by separately dissolving the metal nitrate and tartaric acid in minimum amounts of distilled water followed by the mixing of the resulted solutions. The molar ratio between Me^{n+} and tartaric ion was 1–4. The solutions containing the mixtures of complex metal tartarates were slowly heated and kept at 80 °C for 1 h. After cooling to room temperature, ethanol was added and then the pH was adjusted to 5.5–6 by using a solution of ammonia in ethanol (1:1). The resulted light-yellow precipitate was maintained in liquid phase at 4 °C for 24 h, filtered, washed several times with a mixture of ethanol and water and finally dried on P_4O_{10} . The final step consisted in the air calcination of the precipitates at 800 °C for 1 h.

Activity tests for methane combustion and OCM reactions were performed at atmospheric pressure with 0.1 g of catalyst (0.3–0.8-mm fraction) loaded in a tubular quartz microreactor (i.d. = 8 mm). The blank tests in O_2/CH_4 reactant mixtures with the reactor containing only quartz wool revealed that the homogeneous conversion of CH_4 started from $T > 850$ °C, which was the highest temperature of our study. The catalysts were used as prepared for both, combustion and OCM reactions. The reactor was heated with a furnace connected to a temperature controller (Shimaden, Model SR 25). The reactant gaseous mixtures were prepared using electronic flow controllers (Aalborg). The typical total flow rates of the reaction mixtures were $100\text{ cm}^3\text{ min}^{-1}$ for methane combustion and $24\text{ cm}^3\text{ min}^{-1}$ standard temperature and pressure (STP) for OCM reaction. The corresponding gas hourly space velocity (GHSV) were $60,000\text{ h}^{-1}$ for methane combustion and $14,400\text{ h}^{-1}$ for OCM reaction. The composition of reaction mixtures were 2% CH_4 , 10% O_2 and balance Ar for methane combustion and 41.6% CH_4 , 8.4% O_2 ($CH_4/O_2 = 5/1$) in Ar for OCM reaction. The gaseous mixtures to and from the reactor were analyzed with a Buck Scientific gas chromatograph equipped with TCD detectors. The O_2 , CH_4 were separated and analyzed by using a molecular sieve $13 \times$ column whereas CO_2 , C_2H_6 and C_2H_4 were determined on a Hayasept column.

Temperature programmed reduction (TPR) experiments were carried out in a flow system, with 0.1 g of catalyst, by using a Chembet 3000-Quantachrome Instruments type apparatus equipped with thermal conductivity detectors (TCDs). The gas mixture used in TPR measurements was 3% H_2 in Ar. The typical heating rate was 10 °C min^{-1} and the total flow rate of the oxidizing or reducing gaseous mixtures was 70 ml min^{-1} . A silica gel water trap was interposed between the analyzed sample and the TCD detector in order to ensure a good stability and sensitivity of the detection system.

The crystalline structure of the prepared samples was analyzed with a Rigaku Multiflex diffractometer provided with peak assignment software using $Cu\ K\alpha$ radiation ($\lambda = 1.5405\text{ \AA}$). All the diffraction patterns were recorded in 2θ range of 20–80° by a scanning rate of 2° min^{-1} .

3. Results

At $x=0$, the oxide ($ZnFe_2O_4$) exhibits a cubic structure, which is typical for spinels. The tetrahedral sites of the cubic structure are occupied by zinc ions ($r = 0.6\text{ \AA}$) whereas the octahedral ones by iron ions. As can be seen in Fig. 1, the substitution of Fe^{3+} ($r = 0.87\text{ \AA}$) by Nd^{3+} ($r = 1.16\text{ \AA}$) determines a gradual change in the crystalline structure from cubic to orthorhombic one. Thus, in the Nd substituted ferrites ($ZnFe_{1.75}Nd_{0.25}O_4$, $ZnFe_{1.5}Nd_{0.5}O_4$ and $ZnFeNdO_4$) the initial cubic phase of the pure zinc ferrite coexisted with the newly formed orthorhombic phase of $NdFeO_3$ (see Fig. 1). The formation of the $NdFeO_3$ secondary phase can be explained by the limited solubility of voluminous Nd^{3+} ions in the host spinel lattice. An oxide having a distorted tetragonal K_2NiF_4 structure was obtained for a substitution of $x=2$ ($ZnNd_2O_4$). This structure is formed by $(ZnO_2)^{2-}$ and $(Nd_2O_2)^{2+}$ alternating units in which Nd^{3+} and Zn^{2+}

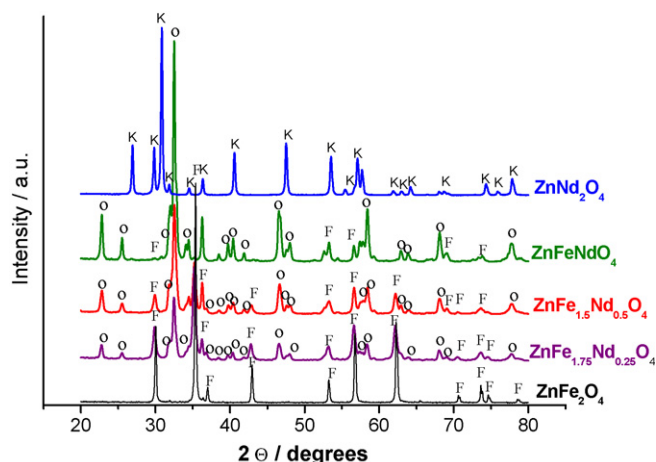


Fig. 1. Comparative XRD spectra of neodymium substituted zinc ferrites. The peak assignments are the following: F, cubic ferrite phase; O, orthorhombic $NdFeO_3$ phase; K, distorted tetragonal K_2NiF_4 -type structure of $ZnNd_2O_4$ phase.

Table 1

The physical surface area (BET) and the specific amount of H_2 consumed in the TPR runs of the investigated oxide catalysts.

Catalyst	S_{BET} ($m^2\text{ g}^{-1}$)	H_2 consumption ($mmol\text{ g}^{-1}_{\text{catalyst}}$)
$ZnFe_2O_4$	6.2	4.79
$ZnFe_{1.75}Nd_{0.25}O_4$	13.5	3.38
$ZnFe_{1.5}Nd_{0.5}O_4$	14.9	2.40
$ZnFeNdO_4$	10.8	0.65
$ZnNd_2O_4$	8.1	0.01

ions are surrounded by 8 and 4 O^{2-} , respectively [11]. It should be emphasized that, the presence of $ZnNd_2O_4$ phase was not observed in the substitutes ferrites.

The physical surface area (BET) of the oxides calcined at 800 °C is relatively small, ranging between 6.2 and $14.9\text{ m}^2\text{ g}^{-1}$ (see Table 1). As expected, the specific hydrogen consumption in TPR runs decreased with the decreasing in the amount of reducible iron in the mixed oxide. The hydrogen consumption in the case of $ZnNd_2O_4$ was negligible as both zinc and neodymium have only one stable oxidation state. Later on we shall discuss in more details the relationship between TPR results, the catalytic activity and reaction mechanism.

From the light-of curbs obtained for methane combustion over simple and Nd^{3+} substituted zinc ferrites presented in Fig. 2 it can be

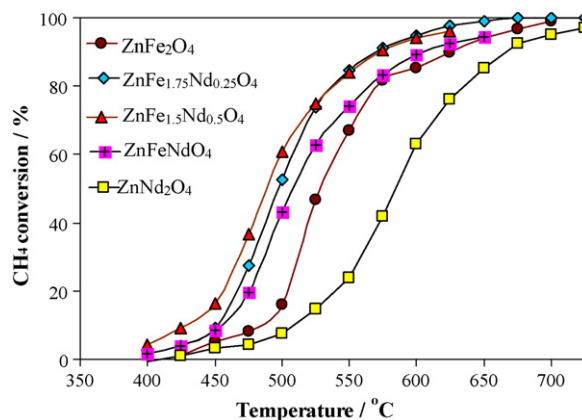


Fig. 2. Conversion of methane in combustion reaction over neodymium substituted zinc ferrites as a function of temperature.

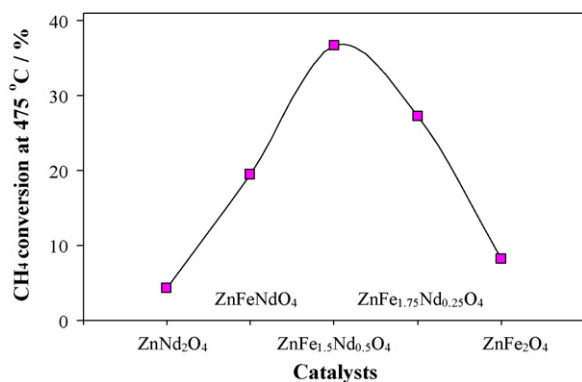


Fig. 3. The effect of Fe³⁺ substitution by Nd³⁺ on the catalytic activity of zinc ferrites (ZnFe₂O₄) for methane combustion.

observed that, the order of the catalytic activity in kinetic domain ($T \leq 500$ °C) was $\text{ZnFe}_{1.5}\text{Nd}_{0.5}\text{O}_4 > \text{ZnFe}_{1.75}\text{Nd}_{0.25}\text{O}_4 > \text{ZnFeNdO}_4 > \text{ZnNd}_2\text{O}_4$. The general remark would be that the catalytic activity for methane combustion is related to the substitution degree of Fe³⁺ with Nd³⁺ in the octahedral positions of the spinel structure. This fact is even better evidenced by Fig. 3 where the catalytic activity in the kinetic domain was plotted as function of Fe³⁺ substitution degree with Nd³⁺. The comparison was made in the kinetic domain (475 °C) in order to evidence the intrinsic catalytic activity of the investigated oxide materials, free from the interference of transport phenomena. It accepted that the lower part of the S-shaped curve of the combustion reactions is within the kinetic regime where the reaction rate increases exponentially with the temperature and does not depend on the flow velocity of the reactant gases. The upper part of the S-shaped curve is within the diffusion regime, where the reaction rate increases only slightly with the temperature and depends markedly on the flow velocity of the gases [12].

The conversion of methane at 475 °C exhibits a maximum of 37% for a degree of iron substitution by neodymium of $x=0.5$. The less active catalysts were the non-substituted materials, ZnFe₂O₄ [X(CH₄ = 8%)] and ZnNd₂O₄ [X(CH₄ = 4%)] having a distorted K₂NiF₄-type structure. It is clear that a certain degree of iron substitution has a positive effect on the catalytic activity for methane conversion in large oxygen excess. The best activity was observed for $x=0.5$ where both perovskite and orthorhombic crystalline structures were present (see Fig. 1). Probably that the highest concentration of the lattice defects working as active sites is reached for $x=0.5$.

The catalytic activity of the simple and of the neodymium substituted ZnFe₂O₄, expressed in term of yield to C₂⁺ (ethane + ethylene), is presented in Fig. 4. Depending on the catalytic material, the temperatures corresponding to the highest yields to C₂⁺ ranged between 775 and 825 °C. One of the reasons of sharp decrease in the yield to C₂⁺ after reaching the maximum activity is the collapse of the crystalline structure in reaction conditions. After reaction, deposits of white ZnO could be observed on the reactor walls as a result of the separation from the ZnFe_{2-x}Nd_xO₄ host lattice followed by sublimation.

The order of the catalytic activities expressed as yields to C₂⁺ were ZnNd₂O₄ > ZnFe₂O₄ > ZnFe_{1.75}Nd_{0.25}O₄ > ZnFeNdO₄ > ZnFe_{1.5}Nd_{0.5}O₄. As can be seen in Fig. 4, the lattice stability in reaction conditions may have influence on the peak catalytic activity. However, the effect on the position of peak activity (see Fig. 4) should be minor as the stability of the investigated oxides reaction resembles. The crystalline structures become unstable in reaction conditions between 775 and 825 °C. Later on we will show that, the stability of the simple and neodymium substituted ferrites (ZnFe_{2-x}Nd_xO₄), with the exception of ZnNd₂O₄, in reducing

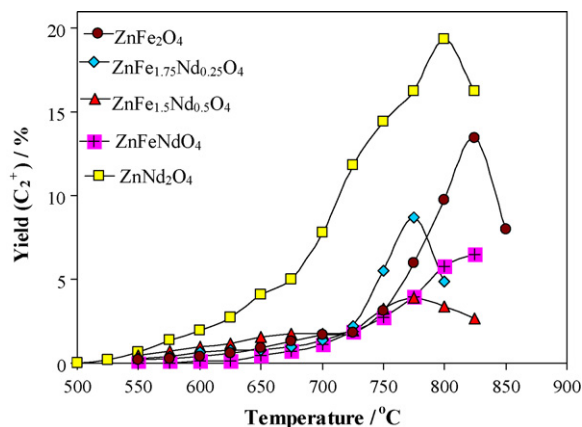


Fig. 4. The catalytic yield to C₂⁺ for OCM reaction of Nd substituted zinc ferrites as a function of reaction temperature.

atmosphere resembles. Similar comment can be made for the contribution of surface area to the overall reactivity of the investigated oxides. The surface areas of the catalytic oxides are relatively small, ranging between 8 and 15 m² g⁻¹ (see Table 1). As in the case of methane combustion, the catalytic activity for OCM reaction shows a significant dependence on the degree of Fe³⁺ substitution with Nd³⁺.

Fig. 5 shows the variation of the catalytic activity and yield to C₂⁺ as a function of Fe³⁺ substitution degree with Nd³⁺. The yield to C₂⁺ and the conversion of methane exhibit the same trend. The yield to C₂⁺ decreased from ~13% for pure ZnFe₂O₄ to ~4% for ZnFe_{1.5}Nd_{0.5}O₄ with the progressive replacement of Fe³⁺ with Nd³⁺. Then, for higher substitution degree of Fe³⁺ with Nd³⁺ the yield to C₂⁺ showed an increasing trend. The highest yield to C₂⁺ of ~19% was observed when Fe³⁺ was completely substituted by Nd³⁺ (ZnNd₂O₄). The comparison between Figs. 3 and 5 reveals a very interesting feature of the investigated materials. The activity for OCM reaction is practically the mirror image of that for methane combustions. The most active catalysts in oxygen excess for methane combustion are the less active and selective for OCM reaction in reducing conditions.

The analysis of the TPR profiles can give useful information regarding the behavior in reducing or oxidizing reaction mixtures. In the case of OCM reaction the optimum reaction temperature is located between 775 and 825 °C. Thus, the oxide catalysts are likely to be in a partial reduced state where the iron is in a mixed

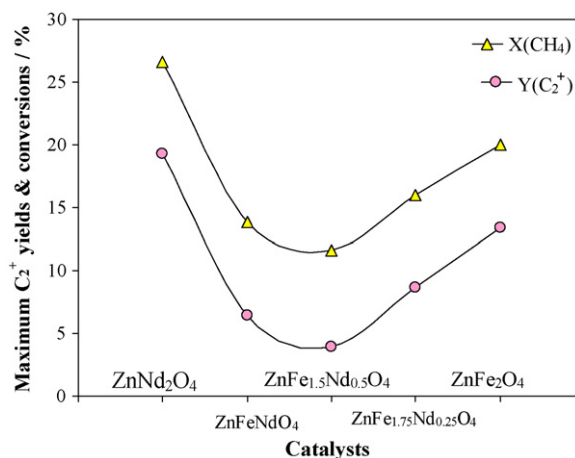


Fig. 5. The effect of Fe³⁺ substitution with Nd³⁺ on the catalytic activity (conversion) and yield of zinc ferrites for OCM reaction.

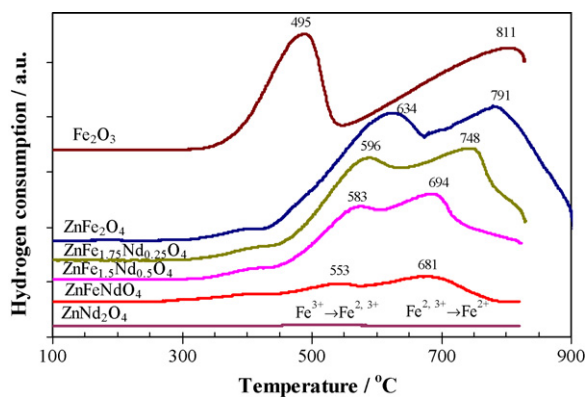


Fig. 6. Temperature programmed reduction of Nd substituted ZnFe_2O_4 .

oxidation state ($\text{Fe}^{2.3+}$). The quantitative analysis of the reduction profiles, based on hydrogen consumption (see Table 1), shows that the reduction of Fe^{3+} to Fe^{2+} takes in two steps, yielding two corresponding TPR peaks. The first reduction step of Fe^{3+} to an intermediate oxidation state ($\text{Fe}^{2.3+}$) is taking place between 553 and 634 °C. The second step consisting in reduction of $\text{Fe}^{2.3+}$ to Fe^{2+} takes place at temperatures between 681 and 791 °C. The temperature of the specific reduction peaks is shifted progressively to lower values as the amount of reducible Fe^{3+} decreases as a result of its substitution with Nd^{3+} . As expected, the hydrogen consumption for ZnNd_2O_4 was negligible, 0.01 mmol g^{-1} (see Table 1). The TPR spectrum of the Fe_2O_3 reference compound presented in Fig. 6 shows also two reduction peaks. The first reduction peak ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2.3+}$) is located at lower temperatures (495 °C) compared to the simple and to the substituted zinc ferrites where $T \geq 553$ °C. The explanation is that the Fe^{3+} located in the lattice of simple and substituted zinc ferrites is more resistant against reduction compared to that of Fe_2O_3 .

4. Discussion

In the case of oxide catalysts it is accepted that the charged surface or bulk oxygen species can activate hydrocarbons. Based on EPR, XPS, IR and Raman evidences, several oxygen species (O^- , O_2^- , O_2^{2-}) have been proposed as active sites for the selective activation of methane in coupling reaction [13]. In contrast, the adsorbed oxygen species having a very short life time on the surface are considered responsible for the total oxidation of methane to CO_2 [14].

In spite of the rich literature concerning the catalytic oxidation of hydrocarbons, the evolution of the structure and of the composition of oxide lattice as a function of reaction conditions is very little analyzed. The simple and neodymium exchanged zinc ferrites showed completely opposite catalytic activity for methane combustion and OCM reactions. Our experimental results suggest that the structure of surface and the bulk is under a permanent change, acting as a mirror of the reaction conditions. This observation is especially evident in the case of the reducible oxides. The activity of the investigated catalysts turned from high to low by changing the ratio between oxidant and reductant. In our view, the discussion about the factors governing the catalytic behavior should focus mainly on the (i) redox behavior of the oxide in reaction mixture and (ii) effect of the doping (in our case the replacement of Fe^{3+} by Nd^{3+}).

The redox behavior in reaction mixture is important because specific lattice defects are created as a result of the removal of lattice oxygen. This process is associated with the reduction of metal cation Fe^{3+} . At high temperatures and in the reducing condition of OCM reaction, oxygen vacancies are likely to be created to compen-

sate the deficit of positive charge resulted by the reduction of Fe^{3+} to Fe^{2+} . On the other hand, when the reaction mixture contains large oxygen excess (methane combustion) the concentration of generated lattice defects should be lower because the gas phase oxygen rapidly replace the lattice or surface consumed oxygen in the catalytic reaction. The general remark is that, the working oxides are in a partially reduced state in the case of OCM reaction whereas in combustion reaction they are in a fully (or close to) oxidation state.

The second factor which should be analyzed more closely is the effect on the catalytic behavior of the substitution of Fe^{3+} by Nd^{3+} in the lattice of ZnFe_2O_4 . An interesting characteristic of the perovskite and spinel type oxides is the possibility of varying the dimension of the unit cell by ion substitution, and thereby the covalency of the B–O bond in ABO_4 structure [2]. Moreover, the partial substitution of B-site may also affect the catalytic activity due to the stabilization of unusual oxidation states and to the simultaneous formation of structural defects. The perovskites with oxygen vacancies and mixed valency (i.e. $\text{Ba}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$) was suggested to contribute largely to the high selectivity to C_2^+ in OCM reaction [15]. Another situation is the introduction of alkali and alkali-earth metals in B sites of LaAlO_3 to form $\text{LaAl}_{1-x}\text{M}_x\text{O}_3$. The substitution of Al^{3+} with Li^+ and Mg^{2+} increased both catalytic activity and selectivity to C_2 hydrocarbons in comparison to the unsubstituted LaAlO_3 perovskites [16].

In our specific case, the substitution of Fe^{3+} with the isoelectronic Nd^{3+} does not create electrically charged lattice defects. But on the other hand, the replacement of small Fe^{3+} (0.78 Å) with the significantly larger Nd^{3+} (1.16 Å) are likely to induce significant lattice strains along with the formation of a new crystalline phase (ZnNdO_3). Previous works observed already that doping B-sites can modify the redox properties as well as the temperatures of the reduction peaks [17,18]. In other words, the oxygen mobility within the crystal lattice may be affected by the substitution at B-site.

In what comes, the effects of the oxides redox behavior in reaction mixture as well as of the doping on the catalytic behavior of simple and substituted zinc ferrites will be discussed in more details.

First we shall analyze the behavior of oxide catalyst in reducing conditions (excess of reductant). Both, heterogeneous and homogeneous steps are considered to be necessary for C_2 formation in OCM reaction. Our observation is that the non-doped catalysts, ZnFe_2O_4 and ZnNd_2O_4 proved to be more active for OCM reaction than the substituted zinc ferrites in B-site ($\text{ZnFe}_{2-x}\text{Nd}_x\text{O}_4$). On the other hand, the pure ferrite (ZnFe_2O_4) was less active than the catalyst having the cations in stable oxidation states (ZnNd_2O_4). It is known that the reducible oxides (i.e. ZnFe_2O_4) exhibit generally lower activity for OCM reaction compared to non-reducible oxides. The specific defects formed by iron substitution with neodymium lead to a severe decrease in catalytic activity and selectivity to C_2^+ (see Fig. 5). In addition to the defects formed by iron substitution with neodymium, other types of defects are generated in reaction conditions (high temperatures and large methane excess) in the lattice of ZnFe_2O_4 and $\text{ZnFe}_{1-x}\text{Nd}_x\text{O}_4$. The formation of these defects was not beneficial for OCM reaction. The synergy between Fe and Nd may have also an important role in determining the catalytic activity and selectivity for OCM reaction.

The explanation for the observed results should take into consideration that the Fe^{3+} in the structure of zinc ferrite is undergoing under reaction conditions to a partial reduction to an intermediate oxidation state $\text{Fe}^{2.3+}$ (Fe_3O_4) generating thus lattice defects. The most likely defects are oxygen vacancies which are formed to compensate the deficit of positive charges resulted by the reduction of Fe^{3+} . The thermodynamic equilibrium $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ is shifted to left hand side in reducing conditions (methane excess) and at high temperatures.

The highest yield to C_2^+ of 19.3% was observed over the nonreducible $ZnNd_2O_4$. This catalyst showed also a stable catalytic activity in time for $T \leq 800^\circ C$. It is likely that the nonreducible $ZnNd_2O_4$, showing little almost no redox properties (see Fig. 6), posses a relevant amount of firmly bound lattice oxygen species which are responsible for the selective activation of methane to $CH_3 \cdot$ [19]. Even in large oxygen excess, the amount of active surface oxygen for methane combustion was low as $ZnNd_2O_4$ showed the lowest activity for methane combustion. An important contribution to the high catalytic activity for OCM reaction should have the synergetic effect between Zn^{2+} and Nd^{2+} ions located in a stable lattice of K_2NiF_4 type. The Zn–Nd couple shows better synergetic effect compared to other investigated systems. For example the highest yield for C_2^+ of Zr doped Nd_2O_3 was only 13%. Probable that the K_2NiF_4 type of lattice structure, assembling the Zn^{2+} and Nd^{3+} ions in an ordered manner, is also beneficial for OCM reaction.

In contrast to OCM reaction, the highest catalytic activity for methane combustion was showed by the neodymium substituted zinc ferrites ($ZnNd_xFe_{1-x}O_4$). It seems that the octahedrally coordinated Nd^{3+} ions have an important contribution to the formation of new types of defects which are beneficial for methane combustion. The introduction of voluminous Nd^{3+} ($r = 1.16 \text{ \AA}$) ions in the place of Fe^{3+} ($r = 0.87 \text{ \AA}$) ions is likely to create mobile and thus active oxygen species for methane combustion. The predominant oxidation state of the iron the lattice should be $3+$ because of the large oxygen excess.

However, if the consecrated Mars van Krevelen redox mechanism is taken under consideration, the local reduction of Fe^{3+} to Fe^{2+} by CH_4 should be the first reaction step. Then the gas phase oxygen should be activated on the resulted active sites by weak adsorption [20]. The large oxygen excess pushes the $Fe^{2+} \rightleftharpoons Fe^{3+}$ equilibrium to right hand side, regenerating the initial oxidized surface. However, electric conductivity measurements are planned to be performed in future to get a better understanding of the interaction between gas phase oxygen and oxide lattice at high temperatures.

5. Conclusions

The catalytic activity of simple and neodymium substituted zinc ferrites was investigated for the first time for methane oxidative conversion. The Nd-substituted ferrites showed the highest catalytic activity for methane combustion whereas the pure ferrite

($ZnFe_2O_4$) and the completely substituted ferrite ($ZnNd_2O_4$) were the most active catalysts for OCM reaction. The redox properties of the simple and substituted ferrites as well as the nature of substitutional element were found to be important parameters in determining the catalytic behavior.

Based on the experimental results, the strategy for future improvement in the catalytic properties of ferrites for methane combustion should take into consideration the finding of suitable substitutional elements for Fe^{3+} . On the other hand, the way to obtain better OCM catalysts consists in the identification of ideal combinations between A and B cations in K_2NiF_4 -type oxides. The theoretically predicted upper bound on OCM yield under conventional packed bed was 28% [21,22]. Hopefully, based on our preliminary results, this upper limit will be reached with the above-mentioned new class of catalytic materials.

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