CATALYTIC BEHAVIOUR OF NEODYMIUM SUBSTITUTED ZINC FERRITES IN OXIDATIVE COUPLING OF METHANE

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The catalytic behavior for oxidative conversion of methane, oxidative coupling of methane was 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 as well as to the specific defects created by substitution. The pure zinc ferrite (ZnFe$_2$O$_4$) and ZnNd$_2$O$_4$ exhibited high activity for coupling reaction whereas the neodymium substituted ferrites (ZnFe$_{1.75}$Nd$_{0.25}$O$_4$, ZnFe$_{1.5}$Nd$_{0.5}$O$_4$ and ZnFeNdO$_4$) was low active in this reaction. The catalytic activity of the oxides and the reaction mechanism on simple and mixed oxides is discussed in light of the experimental results.

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 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.\cite{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.

The catalytic activity of pure, Zr and Sr doped Nd$_2$O$_3$ for OCM reaction was already reported.\cite{3, 4} 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$_2$O$_4$ for oxidative dehydrogenation of n-butene.\cite{5, 6} Thus, study of the methane oxidative conversion over simple and Nd substituted zinc ferrite (ZnFe$_2$O$_4$) would be a novelty in the catalytic field. The catalytic activity of the ZnNd$_2$O$_4$, having an ordered crystalline structure of K$_2$NiF$_4$ type, is also reported here for the first time. As we shall show later, Nd$_2$ZnO$_4$ 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 investigate the catalytic behavior of the pure and neodymium doped zinc ferrites for oxidative coupling of methane, (ii) to observe the effect of Fe$^{3+}$ substitution by Nd$^{3+}$ on the catalytic behavior for oxidative conversion of methane in oxygen poor (OCM) atmospheres, (iii) to get a better understanding on the generation, nature and role of lattice defects on the catalytic reactivity.

EXPERIMENTAL

The principle of the preparation procedure consisted in the use of metal coordination compounds as precursors of the final mixed oxides.\cite{7, 8} The ZnFe$_{2-x}$Nd$_x$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 solutions containing the mixtures of complex metal tartarates were slowly heated and kept at 80 °C for 1h. 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$_2$O$_5$. The final step consisted in the air calcination of the precipitates at 800 °C for 1 h.

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Activity tests for 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 O2/CH4 reactant mixtures with the reactor containing only quartz wool revealed that the homogeneous conversion of CH4 started from T > 850°C, which was the highest temperature of our study. The reactor was heated with a furnace connected to a temperature controller (Shimden, Model SR 25). The reactant gaseous mixtures were prepared using electronic flow controllers (Aalborg). The typical total flow rates of the reaction mixtures for OCM reaction were 24 cm³/min STP (standard temperature and pressure). The corresponding GHSV (gas hourly space velocity) were 14400 h⁻¹. The composition of reaction mixtures for OCM reaction were 41.6% CH4, 8.4% O2 (CH4/O2 = 5/1) in Ar. The gaseous mixtures (O2, CH4, CO2, C2H6 and C2H4) to and from the reactor were analyzed with a Buck Scientific gas chromatograph equipped with TCD detectors.

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 (TCD). The gas mixture used in TPR measurements was 3% H2 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 silicagel 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.

RESULTS

At x = 0, the oxide (ZnFe₂O₄) exhibits a cubic structure, which is typical for spinels (see Fig. 1a). The tetrahedral sites of the cubic structure are occupied by zinc ions (r = 0.6 Å) whereas the octahedral ones by iron ions. As can be seen from X-ray diffraction (Fig. 2), the substitution of Fe³⁺ (r = 0.87 Å) by Nd³⁺ (r = 1.16 Å) determines a gradual change in the crystalline structure from cubic to orthorhombic one.

Thus, in the Nd substituted ferrites (ZnFe₁₋ₓNdₓO₄, ZnFe₁₋ₓNdₓO₄ and ZnFeNdO₄) the initial cubic phase of the pure zinc ferrite coexisted with the newly formed orthorhombic phase of NdFeO₃ (see Fig. 1 b). The formation of the NdFeO₃ secondary phase can be explained by the limited solubility of voluminous Nd³⁺ ions in the host spinel lattice. An oxide having a distorted tetragonal K₂NiF₄ structure (Fig. 1 c) was obtained for a substitution of x=2 (ZnNd₂O₄). This structure is formed by (ZnO₂)⁴⁻ and (Nd₂O₂)⁴⁺ alternating units in which Nd³⁺ and Zn²⁺ ions are surrounded by 8 and 4 O²⁻, respectively. It should be emphasized that, the presence of ZnNd₂O₄ 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 m² 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.
Fig. 2 – Comparative XRD spectra of neodymium substituted zinc ferrites. The peak assignments are the following: F– cubic ferrite phase; o–orthorhombic NdFeO₃ phase, K–distorted tetragonal K₂NiF₄ type structure of ZnNd₂O₄ phase.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET} / m² g⁻¹</th>
<th>H₂ consumption / mmol g⁻¹ catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFe₂O₄</td>
<td>6.2</td>
<td>4.79</td>
</tr>
<tr>
<td>ZnFe₁.75Nd₀.25O₄</td>
<td>13.5</td>
<td>3.38</td>
</tr>
<tr>
<td>ZnFe₁.5Nd₀.5O₄</td>
<td>14.9</td>
<td>2.40</td>
</tr>
<tr>
<td>ZnFeNdO₄</td>
<td>10.8</td>
<td>0.65</td>
</tr>
<tr>
<td>ZnNd₂O₄</td>
<td>8.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Fig. 3 – The catalytic yield to C₂⁺ for OCM reaction of Nd substituted zinc ferrites as a function of reaction temperature.

Fig. 4 – The effect of Fe³⁺ substitution with Nd³⁺ on the catalytic activity (conversion) and yield of zinc ferrites for OCM reaction.

The order of the catalytic activities expressed as yields to C₂⁺ were ZnNd₂O₄ > ZnFe₂O₄ > ZnFe₁.75Nd₀.25O₄ > ZnFeNdO₄ > ZnFe₁.5Nd₀.5O₄. As can be seen in Fig. 3, 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. 3) should be minor as the stability of the investigated oxides 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, with the exception of ZnNd2O4, in reducing 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). The catalytic activity for OCM reaction shows a significant dependence on the degree of Fe³⁺ substitution with Nd³⁺.

Fig. 4 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 ZnFe₁.₅Nd₀.₅O₄ 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 analysis of the TPR profiles (see Fig. 5) can give useful information regarding the behavior in reducing reaction mixtures. In the 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 oxidation state (Fe²⁺, Fe³⁺). The quantitative analysis of the reduction profiles, based on hydrogen consumption (see Table 1), shows that the reduction of Fe³⁺ to Fe²⁺ takes in two steps, yielding two corresponding TPR peaks. The first reduction step of Fe³⁺ to an intermediate oxidation state (Fe²⁺, Fe³⁺) is taking place between 553 and 634 °C. The second step consisting in reduction of Fe²⁺, Fe³⁺ to Fe²⁺ 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 Fe³⁺ decreases as a result of its substitution with Nd³⁺. As expected, the hydrogen consumption for ZnNd₂O₄ was negligible, 0.01 mmol g⁻¹ (see Table 1). The TPR spectrum of the Fe₂O₃ reference compound presented in Fig. 5 shows also two reduction peaks. The first reduction peak (Fe³⁺ → Fe²⁺, Fe³⁺) is located at lower temperatures (495 °C) compared to the simple and to the substituted zinc ferrites where T ≥ 553 °C. The explanation is that the Fe³⁺ located in the lattice of simple and substituted zinc ferrites is more resistant against reduction compared to that of Fe₂O₃.

**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⁻, O₂⁻, O₂²⁻) have been proposed as active sites for the selective activation of methane in coupling
reaction.10 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 CO2.11

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. 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. 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 Fe3+ by Nd3+).

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 Fe3+. At high temperatures and in the reducing condition of OCM reaction, oxygen vacancies are likely to be created to compensate the deficit of positive charge resulted by the reduction of Fe3+ to Fe2+. The general remark is that, the working oxides are in a partially reduced state in the case of OCM reaction.

The second factor which should be analyzed more closely is the effect on the catalytic behavior of the substitution of Fe3+ by Nd3+ in the lattice of ZnFe2O4. 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 AB2O4 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. Ba1-xCa7FeO3-δ) was suggested to contribute largely to the high selectivity to C2+ in OCM reaction.12 Another situation is the introduction of alkali and alkaline-earth metals in B sites of LaAlO3 to form LaAl1-xMxO3. The substitution of Al3+ with Li+ and Mg2+ increased both catalytic activity and selectivity to C2 hydrocarbons in comparison to the unsubstituted LaAlO3 perovskites.13

In our specific case, the substitution of Fe3+ with the isoelectric Nd3+ does not create electrically charged lattice defects. But on the other hand, the replacement of small Fe3+ (0.78 Å) with the significantly larger Nd3+ (1.16 Å) are likely to induce significant lattice strains along with the formation of a new crystalline phase (ZnNdO3).

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 C2 formation in OCM reaction. Our observation is that the non-doped catalysts, ZnFe2O4 and ZnNd2O4 proved to be more active for OCM reaction than the substituted zinc ferrites in B-site (ZnFe2-xNd1-xO4). On the other hand, the pure ferrite (ZnFe2O4) was less active than the catalyst having the cations in stable oxidation states (ZnNd2O4). It is known that the reducible oxides (i.e. ZnFe2O4) 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 C2+ (see Fig. 4). 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 ZnFe2O4 and ZnFe1-xNd1-xO4. 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 Fe3+ in the structure of zinc ferrite is undergoing under reaction conditions to a partial reduction to an intermediate oxidation state Fe2+, Fe3+ (Fe2O4) 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 Fe3+. The thermodynamic equilibrium Fe2+ ⇌ Fe3+ is shifted to left hand side in reducing conditions at high temperatures. In addition to the defects formed by iron substitution with neodymium, other types of defects are generated in reaction conditions in the lattice of ZnFe2O4 and ZnFe1-xNd1-xO4. 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 highest yield to C2+ of 19.3% was observed over the nonreducible ZnNd2O4. This catalyst showed also a stable catalytic activity in time for T ≤ 800 °C (see Fig. 5. It is likely that the
nonreducible ZnNd₂O₄, showing little almost no redox properties, posses a relevant amount of firmly bound lattice oxygen species which are responsible for the selective activation of methane to CH₃. The highest yield for C₂⁺ of Zr doped Nd₂O₃ was only 13%. Probable that the K₂NiF₄ type of lattice structure, assembling the Zn²⁺ and Nd³⁺ ions in an ordered manner, is also beneficial for OCM reaction.

CONCLUSIONS

The catalytic activity of simple and neodymium substituted zinc ferrites was investigated for the first time for coupling oxidative of methane (OCM) reaction. The pure ferrite (ZnFe₂O₄) and the completely substituted ferrite (ZnNd₂O₄) 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.

REFERENCES