DIRECT DECOMPOSITION OF NITRIC OXIDE ON PEROVSKITE TYPE CATALYSTS

Daniela D. Stoyanova\textsuperscript{1}, Srdjan P. Petrovic\textsuperscript{2}, Petya Z. Georgieva\textsuperscript{1}, Ana Terlecki-Baricevic\textsuperscript{2}, Dimitar R. Mehandjiev\textsuperscript{1}

\textsuperscript{1}Institute of General and Inorganic Chemistry
Bulgarian Academy of Sciences
“Acad. G. Bonchev” str., block 11
1113 Sofia, Bulgaria
E-mail: dsto@svr.igic.bas.bg
\textsuperscript{2}Department of Catalysis and Chemical Engineering
Institute of Chemistry, Technology and Metallurgy
11000 Belgrade, Serbia

ABSTRACT

The purpose of this work is to study the activity of perovskite type LaTi\textsubscript{x}Mg\textsubscript{y}Fe\textsubscript{z}O\textsubscript{3} catalysts in NO decomposition in a neutral medium in absence of a reducing agent. The catalysts are characterized by XPS analyses and their specific surface area determination. It is found that direct nitric oxide decomposition proceeds manifesting the catalyst samples high efficiency. It takes place above a certain temperature in oxidizing agents’ absence. A process is elaborated the basis of this effect aiming to form catalytically active complexes on the surface of the catalyst samples.

Keywords: direct decomposition of NO, perovskites, XPS, specific surface area.

INTRODUCTION

The catalytic reduction of NO by CO (or by using some other reducing agents) is used as a method of neutralization of this harmful gas present in industrial waste gases and exhaust gases from internal combustion engines. It has been investigated on a large number of catalyst compositions of various chemical natures [1 - 10]. The direct decomposition of NO as a result of a catalytic process, however, is an important and difficult task still not solved. Some investigations report that NO catalytic reduction by CO proceeds in parallel with its decomposition. It can be assumed that the decomposition of NO (described with the equation above) taking place on this particular type of catalysts (the perovskite type catalyst in this case) can also occur in a neutral medium in absence of a reducing agent. In view of this consideration we formulate the objectives of the present work as studying the decomposition reaction of NO in a neutral medium using this specific type of catalysts in absence of reducing and oxidizing agents and verifying our previous observation.

EXPERIMENTAL

Preparation and characterization. The catalyst samples were synthesized by mixing the oxides La\textsubscript{2}O\textsubscript{3} (99.99 \%), MgO (96.0 \%), TiO\textsubscript{2} (99.0 \%) and Fe\textsubscript{2}O\textsubscript{3} (99.5 \%) in various ratios, grinding for 1 hour in a planetary ball mill model Fritsch Pulverisette 5 and calcinating at a temperature of 1000°C in the course of 10 hours. All initial chemical reagents used in this study were delivered by Johnson Matthey GmbH Alfa Aesar. The procedure described provided to synthesize the following...
catalyst samples: LaTi\(_{0.4}\)Mg\(_{0.1}\)Fe\(_{0.4}\)O\(_{3}\); LaTi\(_{0.4}\)Mg\(_{0.4}\)Fe\(_{0.2}\)O\(_{3}\); and LaTi\(_{0.1}\)Mg\(_{0.5}\)Fe\(_{0.5}\)O\(_{3}\). They were denoted as MF (10:40); MF (40:20); TF (40:13); and TF (10:53), correspondingly.

The express BET method, based on low-temperature adsorption of nitrogen, i.e. at the boiling temperature of liquid nitrogen equal to 77K, was applied to measure the specific surface area of the catalyst samples. The relative error of the method was ca 8 %.

XPS spectra were recorded on VG Escalab II spectrophotometer. The surface concentration of the ions was calculated on the basis of the spectra obtained using the respective photoelectron peak areas of each element.

**Catalytic activity test.** The catalytic activity test was carried out in a continuous flow reactor [13]. A sample of the tested catalyst (from a sieve fraction ranging from 0.3 mm to 0.6 mm) of a volume of 0.8 cm\(^3\) was charged as a fixed bed in a quartz reactor of an internal diameter of 8 mm. Argon of 99.999 vol % purity was used as a carrier gas. The feed concentration of NO was 1200 ppm, the rest being argon. The hourly space velocity, \(W\), was equal to 26 000 h\(^{-1}\). The inlet concentration of NO was continuously controlled by NDIR gas-analyzer Infralyt 2106. The outlet NO concentration was monitored by UNOR 5 (Maihak) gas analyzer.

**RESULTS AND DISCUSSION**

Table 1 lists the experimental data referring to the chemical composition (at %) and the specific surface area of the catalyst samples. The lanthanum content in all catalyst samples was 20 at %, while that of oxygen was 60 at %.

Table 1 shows that the catalyst samples differ in the contents of the three basic components – Ti, Mg and Fe, which is in correspondence with the ratios pre-set during the mixing the ball mill charge. The catalyst sample TF (10:53) has the highest Fe content, while TF (40:13) has the lowest one. The specific surface areas of the catalyst samples are also different, although not varying considerably. MF (40:20) has the greatest surface area.

The X-ray diffraction analysis shows results coinciding with those reported in ref. [14]. It evidences that, regardless of the varying compositions, the main crystallized phase is perovskite of an orthorhombic structure. Furthermore, La\(_2\)O\(_3\) phase is found in all samples studied. It is most strongly manifested in case of TF (10:53) sample. Fig. 1 illustrates the results referring to the catalytic activities of the samples. It shows the grams of NO decomposed over 1 g of a catalyst sample per one hour (Ig) at a given temperature.

The data presented confirm the conclusions made in our previous work [12] that the decomposition of NO is initiated on the catalyst sample at temperatures higher than 250°C in accordance with the stoichiometric Eq. (2). One has the impression that the temperature increase brings about activity decrease in case of MF (40:20) sample but activity increase in the presence of MF (10:40), TF (40:13) and TF (10:53). It is obvious that different kinds of catalytically active complexes (CAC) of various compositions and structures [15] are formed depending on the ratio between the two basic

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ti</th>
<th>Mg</th>
<th>Fe</th>
<th>(S_o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF (10:40)</td>
<td>8.0</td>
<td>2.0</td>
<td>8.0</td>
<td>2.4</td>
</tr>
<tr>
<td>MF (40:20)</td>
<td>8.0</td>
<td>8.0</td>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>TF (40:13)</td>
<td>8.0</td>
<td>10.0</td>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>TF (10:53)</td>
<td>2.0</td>
<td>10.0</td>
<td>10.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition in at %, and specific surface area \(m^2\) g\(^{-1}\) of the synthesized samples.
Daniela D. Stoyanova, Srdjan P. Petrovic, Petya Z. Georgieva, Ana Terlecki-Baricevic, Dimitar R. Mehandjiev

catalytically active components (iron and titanium on the surface of the catalysts). It is quite possible that magnesium and lanthanum ions could also be involved in these CACs influencing the catalytic activity too. If we take into account the values of the specific surface areas determined, the amount of decomposed NO per 1m² surface area of a given catalyst sample for one hour at the given temperature (the data are not presented) will follow an analogous pattern. MF (10:40) and the TF (10:53) samples are the most active catalyst samples at temperatures higher than 400°C. The activity of MF (10:40) is the only one that decreases. This indicates that the magnitude of the specific surface area affects the catalyst activity evaluated on the basis of Ig, although the differences between the samples in regard to this parameter are not great. In fact the activity of MF (10:40) is higher in view of this factor (see Fig. 1).

Fig. 2 shows the degree of purification, η %, in presence of the three most active catalyst samples aiming to illustrate the efficiency in NO removal in the course of a model mixture purification under the conditions described.

It is seen that the catalysts have high purification efficiency, reaching a conversion degree of up to 90 %. The juxtaposition of the data on the chemical composition (Table 1) to the results referring to the catalytic activity (Fig. 2) shows that the catalysts richer in iron are more active. Yet the data in Table 1 correspond to the total content of iron in the samples, but the catalytic activity, as it is known, is basically determined by the chemical composition, the concentration and the oxidation state of the ions on the surface. The XPS analysis carried out shows that lanthanum is present as La³⁺, iron - as Fe²⁺ and Fe³⁺, while titanium - as Ti⁴⁺. This evaluation is made on the basis of the data on the binding energies of La3d₅/₂, Fe2p and Ti2p₃/₂ respectively (Fig. 3a,b,c).

These investigations provide the estimation of the surface concentration of the basic ions on the surface of the catalyst samples studied. The results are listed in Table 2.

Figs. 4 and 5 represent the values of Ig and Is, respectively, versus iron ions surface concentration determined by XPS analysis. This is done to check the effect of the surface and bulk concentration of iron. It becomes quite clear that the activity dependences on iron bulk and surface content are analogous, i.e. the cata-

Table 2. Chemical composition of the surface layer of the studied catalyst samples in at % derived from XPS-analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>La</th>
<th>Ti</th>
<th>Mg</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF (10:40)</td>
<td>11.7</td>
<td>6.8</td>
<td>3.0</td>
<td>2.8</td>
<td>75.6</td>
</tr>
<tr>
<td>MF (40:20)</td>
<td>9.2</td>
<td>5.5</td>
<td>12.6</td>
<td>1.4</td>
<td>71.2</td>
</tr>
<tr>
<td>TF (40:13)</td>
<td>8.0</td>
<td>4.2</td>
<td>18.3</td>
<td>0.7</td>
<td>68.7</td>
</tr>
<tr>
<td>TF (10:53)</td>
<td>8.4</td>
<td>1.4</td>
<td>18.2</td>
<td>2.9</td>
<td>69.1</td>
</tr>
</tbody>
</table>
lytic activity in respect to the direct NO decomposition increases with increase of the surface concentration of iron ions. One has the impression that small changes in the concentration are leading to considerable increase of the catalyst samples efficiency. These results show that the catalytically active complexes (CAC) are mainly formed with the participation of iron ions.

On the other hand, an interesting effect is observed with respect to the dependence of the catalytic activity on the catalyst bed temperature increase. The catalytic activity starts to decrease from a certain temperature onwards. This leads to the assumption that another type of interaction between the ions involved in the CAC structure appears in the course of temperature increase. This second type of interaction affects the catalytic activity to a certain extent.

Two types of Moessbauer spectra are observed in studying the same samples [14]. The spectrum of MF (10:40), MF (40:20) and TF (40:13) is a quadrupole doublet due to Fe\(^{3+}\) ions present in a high-spin state and octahedral coordination. Another tendency is also observed: a weakening of this signal with iron content increase in the catalyst samples. In case of TF (10:53) sample a sextet is also registered in addition to the

Fig. 4. Amount (mg) of decomposed NO per 1 g of catalyst per 1 hour (Ig) at catalyst bed temperature $T = 400^\circ$C, depending on the Fe content (at %), determined by chemical analysis (curve 1) and superficial concentration of Fe ions, determined by XPS analysis (curve 2).

Fig. 5. Amount (mg) of decomposed NO per 1 m² of the specific surface area (Is) of a given catalyst sample per 1 hour at $T = 400^\circ$C, depending on the Fe content (at %), determined by chemical analysis (curve 1) and superficial concentration of Fe ions, determined by XPS analysis (curve 2).
doublet. The appearance of this sextet is due to Fe\(^{3+}\) located closely to one another, which provides an exchange interaction between them. The decrease of iron ions content results in a decrease of the strength of this exchange interaction, which in turn leaves the doublet only as in case of the other samples. It can be assumed that more than one iron ion is participating in the CAC formation. The presence of exchange interaction between these ions promotes the catalytic action efficiency. That is the reason that TF (10:53) is the most active catalyst sample. Such an interaction probably exists in the other catalyst samples as well, but it is rather weak and therefore it cannot be registered. The increase of the catalytic process temperature leads to disruption of this exchange interaction and this determines the catalytic activity decrease. This explains also the decrease of the activity of TF (10:53) and MF (40:20) (see Figs. 1 and 2). Such an effect, called „magneto-catalytic effect“ [16, 17] is observed at the temperature of Neel in case of anti-ferromagnetic oxide catalysis of the oxidation of CO or organic compounds [18]. At this specific temperature the exchange interaction between the ions in the structure of the catalyst is disrupted and the kinetic parameters of the reactions, the activation energy and the pre-exponential factor, change. This is manifested by the catalytic activity change [16].

CONCLUSIONS

Direct decomposition of nitric oxide proceeds on catalysts of the perovskite type of the general formula LaTi\(_x\)Mg\(_{2-x}\)Fe\(_2\)O\(_4\) above a certain temperature in the absence of oxidizers. The catalysts manifest high efficiency providing a conversion degree of 80 % in nitric oxide removal from gaseous mixtures. This action is determined by the formation of catalytically active complexes (CAC) on the surface of the catalyst samples involving Fe\(^{3+}\)-ions. The latter play the main role in the mechanism of the reaction. The crystalline structure of the catalysts enables the realization of exchange interaction between the Fe\(^{3+}\)-ions, which results in a higher efficiency of the CAC.

REFERENCES