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The influence of O_2 on oxidative coupling of methane over oxide catalysts using N_2O as oxidant

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Abstract

The study of the influence of molecular oxygen on N_2O decomposition under conditions of oxidative coupling of methane (OCM) and on the simple reaction of N_2O decomposition (without methane) was carried out over SrO and Li/Bi_2O_3 . It was found that molecular oxygen caused the decrease in the rate of N_2O decomposition over all the catalysts studied under conditions of OCM. However, the overall catalytic activity over Bi-containing catalysts are significantly lower than that for SrO. Poisoning by molecular oxygen was established over Li/Bi_2O_3 for N_2O decomposition without methane. Over SrO molecular oxygen was not shown to inhibit the decomposition of nitrous oxide in the absence of methane. It was established that the defect structure of SrO was changed under catalytic conditions. The participation of structural defects for N_2O decomposition and CO_2 formation was proposed.

Keywords: O_2; Oxidative coupling; Methane; Oxide catalysts; N_2O

1. Introduction

Since 1980, the catalytic direct methane conversion has received renewed attention due to the development of some active and selective catalysts [1–3]. Among the most intensively studied and effective catalysts used for this reaction are the alkaline earth and rare earth oxides. Most studies were carried out using oxygen as an oxidant. Some works have been done on Sm_2O_3 and Li/MgO with a high content of alkali promoter (5 wt.%) using nitrous oxide as oxidant [4–6]. The conversion of CH_4 was an order of magnitude greater with O_2 than with N_2O over all the studied catalysts, but C_2-selectivity was greater with N_2O. In recent years we found that M/CaO (M=Li or Na) with a low amount of alkali promoter (<2 at.%) and SrO were very active catalysts for N_2O decomposition and methane conversion [7,8]. This may be due to the various activation ways for N_2O and the formation of different oxygen species over different catalysts.

The study of the reaction of N_2O decomposition under the reaction conditions is a useful test for the nature of defects [9,10]. Previously, it has been shown [11,12] that the rate of N_2O decomposition under reaction conditions of oxidative coupling of methane (OCM) did not depend on O_2 partial pressure over one group of catalysts, such as Li/CaO, Na/CaO and Bi_2O_3. Therefore, competition was not observed for the activation centres between two kinds of oxidant (N_2O and O_2). In contrast, for the other catalyst group (SrO, Li/Bi_2O_3 and Er/Bi_2O_3) the reaction of N_2O

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decomposition was inhibited by molecular oxygen under OCM conditions, that is, activation of both oxidants carried out on the same centres over the second group of catalysts. Two mechanisms for N_2O decomposition have been suggested: (1) over active sites including metal ions with the multivalent state [13] (such as impure transition metal ions Fe^{3+} for CaO doped by Li/Na or host ions of Bi^{3+} for Bi_2O_3), (2) over oxygen vacancies [9]. For the first group of catalysts N_2O decomposition proceeds according to the first mechanism; a second mechanism over oxygen vacancies is supposed for the second group of catalysts.

This communication presents the results on N_2O decomposition under conditions of OCM and without methane over SrO and Li/Bi_2O_3 catalysts together with an IR spectroscopy study aimed to elucidate the nature of activation centres for oxidants (O_2 and N_2O). A particular interest was the structure of the catalysts after the treatment by reaction mixtures.

2. Experimental

Catalysts were prepared from high purity grade materials: $SrCO_3$ (Fe<0.001, Mn<0.0005), Bi_2O_3 (Fe<0.003, Mn<0.001), LiOH (impurity content: 0.0001–0.001 at.%). Li/Bi_2O_3 was prepared by impregnating the original oxide with lithium hydroxide followed by drying and calcination in air for 3 h at 1023 K. After calcination the actual alkali concentration was determined by atomic adsorption analysis on an AAS-1 apparatus. We used Li/Bi_2O_3 catalysts with a low amount of alkali promoter (0.2 at.%) within the range of solid solution formation. The SrO catalyst was prepared by calcination of high purity $SrCO_3$ in oxygen for 2 h at 1523 K to remove the carbonates.

Catalytic activity was examined at 1023–1053 K in a microcatalytic quartz fixed bed reactor. 30–40 mg of catalysts with a mesh size of 0.125–0.5 mm were used with a total gas flow of 40–60 ml min^{-1} at 1 atm. A 'Biochrom-1' gas chromatograph was used to analyse the product stream. Separation of the various components was achieved using NaX zeolite and Porapak Q columns.

The BET method was applied to determine the surface areas of the catalysts (SrO: 0.2 $m^2\ g^{-1}$; Li/Bi_2O_3: 0.1 $m^2\ g^{-1}$).

The N_2O decomposition was studied under the following conditions:

- ■ $CH_4:N_2O:O_2:He=30:10:X: (60-X)$, where $X=0$–15 vol.%
- ■ $N_2O:O_2:He=10:X: (90-X)$, where $X=0$–15 vol.%

All catalytic experiments presented here were performed under conditions where contribution from non-catalytic reactions was less than 10% of catalytic reactions.

IR spectra were recorded with 'Specord 75' spectrometer. Prior to IR study the catalysts were treated under reaction conditions at 1023 K. Then the gas flow was switched to helium and heating was stopped. The sample was cooled to room temperature in the He flow. Then the sample was pressed in the KBr matrix and the IR spectrum was recorded. The mass of sample used for the IR study was strictly 5 mg in order to estimate the concentration of defects. The calculation of the defect concentration was based on area under the absorption curve in the IR spectra.

3. Results and discussion

The rates of formation of OCM products and N_2O decomposition as a function of the partial pressure of O_2 in CH_4–N_2O–O_2, N_2O–O_2 reaction mixtures for two catalysts of Li/Bi_2O_3 and SrO are shown in Figs. 1 and 2. One can see that the addition of molecular oxygen in the CH_4–N_2O reaction mixture has a similar

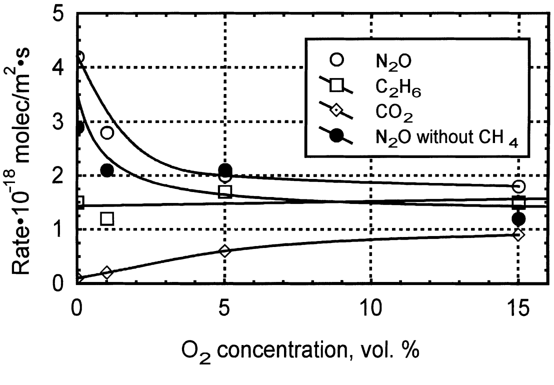

Fig. 1. The rates of N_2O decomposition, C_2H_6 and CO_2 formation for reaction mixture $CH_4:N_2O:O_2=30:10:X$ (where $X=0$–15) vol.% and N_2O decomposition for reaction mixture $N_2O:O_2=10:X$ (where $X=0$–15) vol.% versus oxygen concentration over Li/Bi_2O_3 catalyst ($T=1053$ K).

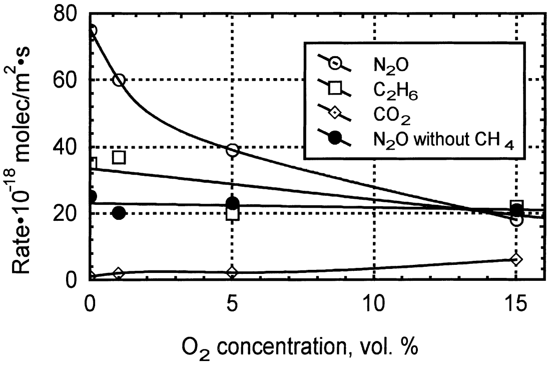

Fig. 2. The rates of N_2O decomposition, C_2H_6 and CO_2 formation for reaction mixture CH_4:N_2O:O_2=30:10:X (where X=0–15) vol.% and N_2O decomposition for reaction mixture N_2O:O_2=10:X (where X=0–15) vol.% versus oxygen concentration over SrO catalyst (T=1023 K).

influence on the catalytic behaviour of both catalysts (SrO and Li/Bi_2O_3). Firstly, the rate of N_2O decomposition decreases when the concentration of O_2 increases. Secondly, the rate of CO_2 formation increases up to one order of magnitude when concentration of O_2 in CH_4–N_2O–O_2 is changed from 0 to 15 vol.%. However, the overall catalytic activities of SrO and Li/Bi_2O_3 are different. The rates of N_2O decomposition, C_2H_6 and CO_2 formations over Li/Bi_2O_3 are more than one order of magnitude lower than that for SrO. The studying of the simple reaction of N_2O decomposition (without methane) showed that the molecular oxygen inhibits N_2O decomposition over Li/Bi_2O_3, while over SrO such effect is not established. This means that over SrO the different sites are responsible for the activation of O_2 and N_2O without methane (reaction mixture N_2O–O_2) and the same centres are likely to be responsible for oxidant activation in reaction mixture with methane (CH_4–N_2O–O_2).

The hyperbolical character of the fall of the rates of N_2O decomposition over all catalysts studied may testify to the presence of two types of active catalysts sites. The sum fraction of active centres is inhibited by oxygen at low partial pressures of O_2 (<5 vol.%). The other fraction is not inhibited by O_2 and is responsible for N_2O activation with formation of C_2H_6.

As it was mentioned above [12], doping Bi_2O_3 by Li or Er results in the change of mechanisms of N_2O decomposition in the presence of methane as well as without methane. It is well known [14] that 20 at.% Er/Bi_2O_3 is an oxygen ion conductor with a high concentration of oxygen vacancies, which may serve as sites for N_2O decomposition. The similar behaviour of Li/Bi_2O_3 and Er/Bi_2O_3 in reactions studied is assumed to indicate the same mechanisms for N_2O decomposition with and without methane over these catalysts. As far as SrO is concerned it has been shown by Tre'yakov [15] that intrinsic defects in the SrO lattice are Frenkel defects (oxygen vacancies and interstitial oxygens). So, taking into consideration the type of the intrinsic defects in the catalysts studied and following Winter [9] we suggest that the activation of both oxidants may occur over oxygen vacancies. According to Winter anion pair vacancies are responsible for activation of O_2 but single anion vacancies are responsible for activation of N_2O, as may be illustrated by the following scheme:

$$(e) + (e) \Leftrightarrow (e)(e) \qquad (1)$$

$$N_2O + (e) \Rightarrow N_2 + O^- \qquad (2)$$

$$O^- + O^- \Leftrightarrow O_2^{2-} \qquad (3)$$

$$O_2^{2-} \Leftrightarrow O_2 + (e)(e) \qquad (4)$$

where (e) is the single anion vacancy with one electron and (e)(e), the anion pair vacancy with two electrons.

To explain the differences in the catalytic behaviour of SrO and Bi-containing systems without methane we have analysed the scheme of N_2O decomposition. The overall rate of N_2O decomposition depends on the number of reaction sites available for N_2O decomposition, while this number is determined by competition between two reactions (Eqs. (2) and (4)). It is well known that SrO forms stable strontium peroxide in OCM conditions. This means that the steady concentration of single anion vacancies is very low under a flow of N_2O–O_2 reaction mixture. According to equilibrium 1, the concentration of anion pair vacancies is even lower. In this case the poisoning effect of O_2 on N_2O decomposition does not occur (Fig. 2). Due to the low concentration of both pair and single vacancies the rates of N_2O decomposition without methane are considerably lower than that with methane (under OCM conditions). The addition of methane to N_2O–O_2 reaction mixture results in interaction of methane with O^- or O_2^{2-} and, therefore, the steady concentration of both single and pair anion vacancies increases.

The rate of N_2O decomposition in the presence of methane rose approximately four times in comparison with the rate of N_2O decomposition without methane. In this case O_2 and N_2O begin to compete for active catalysts sites. Concerning Bi-containing catalysts the peroxide of bismuth is not stable under OCM conditions, therefore, the steady concentration of active catalyst sites is similar for both reaction mixtures (CH_4–N_2–O_2 and N_2O–O_2). In accordance of that the rates of N_2O decomposition in both cases (with and without methane) display similar values. Therefore, the poisoning effect of O_2 on N_2O decomposition does not depend on the presence of methane in the reaction mixture (Fig. 1).

Thus, the stabilisation of active oxygen species on the catalyst surface may influence the peculiarities of the oxidant activation.

It should be noted that for the reaction mixture CH_4–N_2O (without oxygen) the rate of N_2O decomposition (W_{N_2O}) is approximately twice as much as the rate of C_2H_6 formation ($W_{C_2H_6}$) over SrO (Fig. 2). With increasing O_2 concentration in the reaction mixture the rate of N_2O decomposition drops and at O_2 concentration >5 vol.% W_{N_2O} became close to $W_{C_2H_6}$. This means that the selectivity of 100% on ethane formation was observed using N_2O as oxidant. This effect was also established for Li/Bi_2O_3 (Fig. 1). This fact may be an evidence for similar mechanisms of C_2H_6 formation from oxygen species created by N_2O decomposition over the SrO and Li/Bi_2O_3 catalysts studied.

Previously Anshits et al. [11] reported that two temperature ranges were found for OCM reaction using N_2O as an oxidant over SrO. In the temperature range 923–1023 K the rate of N_2O decomposition considerably exceeds the rate of C_2H_6 formation, while in the range 1023–1123 K the rates of N_2O decomposition and C_2H_6 formation gradually become close. At T=1023 K $W_{N_2O} = W_{O_2} + W_{C_2H_6}$ and $W_{C_2H_6} = W_{O_2}$, where W_{O_2} is the rate of formation of molecular oxygen from N_2O decomposition. This means that the reaction of N_2O decomposition proceeds by two parallel routes with formation of molecular oxygen and the formation of oxygen species which are responsible for C_2H_6 formation. Taking into consideration the scheme of N_2O decomposition mentioned above we may suppose that N_2O decomposition may proceed over both types of active centres: pair and single vacancies in the reaction mixture CH_4–N_2O (without oxygen). When N_2O decomposition occurs over pair vacancies, the molecular oxygen is formed. When N_2O decomposes over single vacancies, the atomic uncharged oxygen or/and O^- is assumed to be formed. These oxygen species may activate methane with the formation of CH_3 radicals and ethane as coupling product.

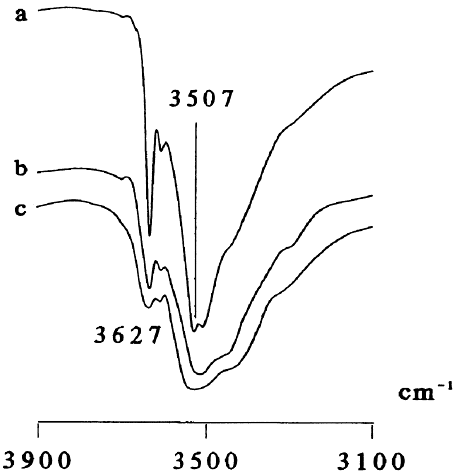

Fig. 3. IR absorption spectra of steady state SrO (1023 K) in the OH band region after treatment in the reaction mixture: (a) CH_4:N_2O=30:10; (b) CH_4:N_2O:O_2=30:10:1; (c) CH_4:N_2O:O_2=30:10:5 (vol.%).

Thus, molecular oxygen suppresses the route of formation of O_2 during N_2O decomposition and does not influence N_2O decomposition with the formation of desirable oxygen species. The almost constant rate of C_2H_6 formation (Fig. 2) is assumed to prove this suggestion.

To explain the unusual behaviour of SrO in N_2O decomposition with and without methane it was of particular interest to study the surface and bulk intermediates over catalysts after the treatment by reaction mixtures. We used IR-spectroscopy for these purposes. Fig. 3(a) and Fig. 4(a) show the infrared spectra of SrO after the treatment by CH_4:N_2O= 30:10 vol.% reaction mixture. In the spectra of samples treated without oxygen we observed a strong absorption band near 3600 cm^{-1} and a broad band near 3500 cm^{-1}, assigned to the vibrations of O–H bonds. In the range 400–1700 cm^{-1} we observed a band at 1460 cm^{-1} assigned to CO_3^{2-} groups [16,17]. The narrow bands at 860 and 687 cm^{-1} may not be

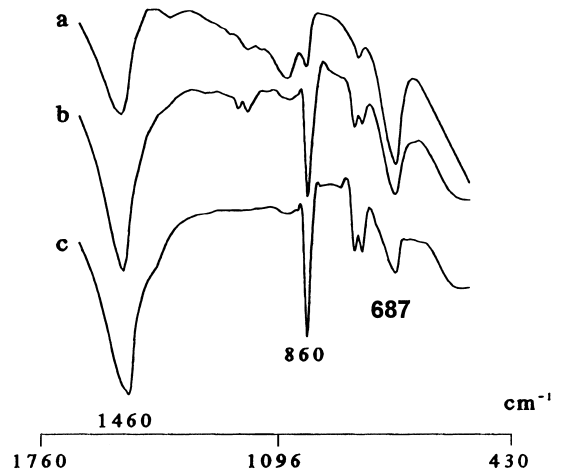

Fig. 4. IR absorption spectra of steady state SrO (1023 K) in the CO_3^{2-} band region after treatment in the reaction mixture: a) CH_4:N_2O=30:10; b) CH_4:N_2O:O_2=30:10:1; c) CH_4:N_2O:O_2=30:10:5 (vol.%).

classified as carbonate groups, because they are very sharp. Such narrow bands may correspond to formate-like groups, which were found earlier [18] by EPR-spectroscopy. So, three types of intermediates were found: OH^-, $CO_3^{2}-$ and formate-like groups. Fig. 3(b and c) and Fig. 4(b and c) show the infrared spectra of SrO after the treatment by CH_4:N_2O:O_2= 30:10:1 vol.% and CH_4:N_2O:O_2=30:10:5 vol.% reaction mixtures, respectively. One can see that the intensities of bands in the OH region decrease but intensities of bands in CO_3^{2-} region and at 860 and 687 cm^{-1} rose with increasing oxygen in CH_4–N_2O–O_2 reaction mixture. For all reaction mixtures studied we found that the concentration of the above mentioned bands are strongly oxygen dependent.

It should be noted that the concentration of the supposed formate-like species increased approximately three times with increasing O_2 concentration in reaction mixture up to 5 vol.%. Similar behaviour has been observed for the formate-like species observed by EPR-spectroscopy [18]. This fact is supposed to prove the evidence of formate-like species, observed by IR-spectroscopy.

Thus, according to the IR-spectroscopy data the hydroxyl, carbonate and formate-like groups are formed in SrO under the reaction conditions, with concentration of these groups depending on concentration of O_2 in CH_4–N_2O–O_2 reaction mixture.

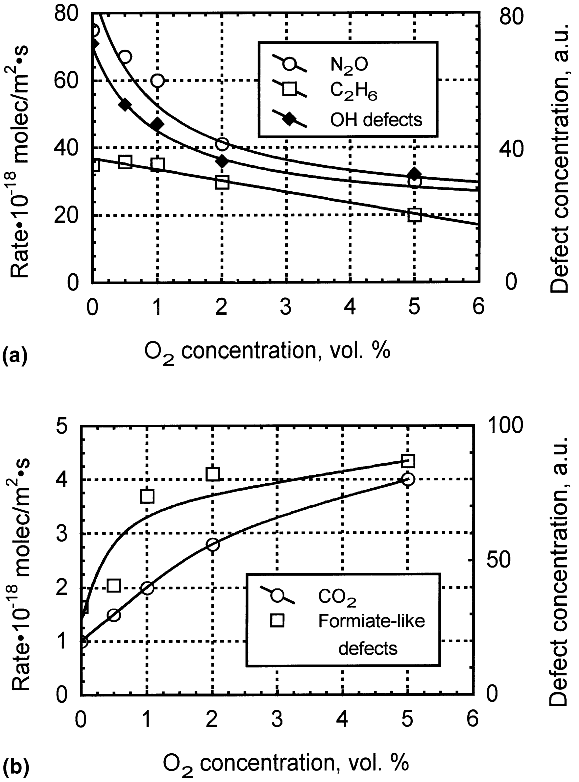

Fig. 5. (a) The rates of N_2O decomposition, C_2H_6 formation and concentration of OH defects with ν=3627 and 3507 cm^{-1} versus oxygen concentration over SrO catalysts. (CH_4:N_2O:O_2=30:10:X, vol.%, where X=0–5).(b) The rates of CO_2 formation and concentration of formate-like defects with ν=860 cm^{-1} versus oxygen concentration over SrO catalysts. (CH_4:N_2O:O_2=30:10:X, vol.%, where X=0–5) T=1023 K.

To elucidate the role of defects formed under OCM conditions, the data from the catalytic experiments and IR spectroscopy were compared. We found that the rates of N_2O decomposition per OH^- defect did not depend on the molecular oxygen concentration in CH_4–N_2O–O_2 reaction mixture (Fig. 5(a)). It can be expected that hydroxyl defects take part in the activation of N_2O. It is known [19] that the decomposition of these centres in CaO at T>800 K is accompanied by the formation of anion vacancies according to the following:

$$([OH]^-)_s + ([OH]^-)_s \rightarrow (O_2^{2-})_s + H_2 \quad (5)$$

$$(O_2^{2-})_s \rightarrow O + (O^{2-})_s + ([\,])_s \quad (6)$$

where subscript ‘s’ is the surface and [ ], the anion vacancy.

So, OH^--defects are, probably, intermediates for peroxide ions. When peroxide ions interact with methane, anion pair centres are released and may be filled by molecular oxygen. So, the increasing O_2 concentration in the reaction mixture leads to the decrease of OH concentration due to this phenomenon. In other words, molecular oxygen suppresses the formation of OH groups in the SrO structure.

When peroxide ions decompose according to Eq. (6), single oxygen vacancies are formed. On such centres N_2O decomposes with formation of atomic oxygen species. So, some fraction of OH defects may serve as a precursor for the activation centres of O_2, and another fraction is required for N_2O decomposition. That is why, a constant specific rate of C_2H_6 formation per OH defect has not been observed (Fig. 5(a)).

Absorption intensity of bands in CO_3^{2-} region at 860 and 687 cm^{-1} increased when partial pressure of O_2 in CH_4–N_2O–O_2 reaction mixture was increased (Fig. 4 (b and c). It should be noted the specific rate of CO_2 formation per one formate-like defect is approximately constant for all CH_4–N_2O–O_2 reaction mixtures (Fig. 5(b)). This means that the formate-like defects may be an intermediate species of gas-phase CO_2.

Thus, the composition of defects over SrO under reaction conditions may explain the peculiarities in catalytic behaviour of SrO in the reaction of N_2O decomposition with and without methane and prove our suggestion on the nature of active sites for oxidants.

4. Conclusions

The influence of molecular oxygen on N_2O decomposition over SrO and Li/Bi_2O_3 catalysts was studied under conditions of oxidative coupling of methane and of simple reaction without methane. It was found that the rate of N_2O decomposition over all the catalysts studied decreased when partial pressure of O_2 in CH_4–N_2O–O_2 reaction mixture increased. This effect may be explained by a competition of N_2O and O_2 for active catalysts sites. Molecular oxygen did not inhibit the decomposition of nitrous oxide over SrO when reaction mixtures without methane were used. In contrast, over Li/Bi_2O_3 catalyst the poisoning effect of molecular oxygen on N_2O decomposition without methane was observed. The IR-spectroscopy study of the SrO structure after treatment in reaction mixtures was carried out to elucidate the unusual behaviour of SrO. Three types of intermediates were found: OH^-, CO_3^{2-} and formate-like groups. The concentration of all intermediates is strongly oxygen-dependent. It has been shown that OH^- defects are probably responsible for N_2O decomposition and for O_2 activation, while formate-like defects are precursors of CO_2. Oxygen vacancies are assumed to be the activation sites for both oxidants over all the catalysts studied, but different abilities to form the desirable oxygen species cause the peculiarities in catalytic behaviour of SrO and Bi-containing catalysts.

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