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The role of the defect structure of oxide catalysts for the oxidative coupling of methane. The activation of the oxidant

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Abstract

Based on analysis of the catalytic properties and defect structure of oxide catalysts, the new systematization of catalysts for the oxidative coupling of methane (OCM) reaction has been proposed. The oxygen defects (anion vacancies for SrO and Li/Bi_2O_3 (0.1 at.%)) and impurity defects (transition metal ions for Li/CaO, Na/CaO) was proposed to play the important role for the process of N_2O activation in OCM. The addition of O_2 in CH_4–N_2O reaction mixture decreased the rate of N_2O decomposition over SrO and Li/Bi_2O_3, while for M/CaO catalysts such effect was not observed. It was explained by the fact that the activation of O_2 and N_2O in OCM process occurs on the same centres for the first group of catalysts and different centres for the second group of catalysts. Two temperature ranges of proceeding of OCM reaction over SrO was established. The mechanism in which CO_2 is a poison for active oxygen species was proposed.

1. Introduction

Much of the research works on the oxidative coupling of methane (OCM) has dealt with development of suitable catalysts. General concepts, e.g. the effect of basicity and acidity on coupling selectivity [1,2], oxygen ion mobility [3,4], p-semiconductivity [5,6] and active oxygen species [7–9] have also been proposed and discussed. There are some suggestions concerning the nature of the active catalyst centres for OCM. In previous study [10] we have shown that it is necessary to distinguish the catalysts with high and low promoter content before the examination of active catalytic sites. The systems which are single phases on one hand and the catalysts being multiphase systems on the other, considerably differ by their catalytic performance [3, 11]. Therefore, active species for catalysis will be different on two groups of catalysts. These species are hard to be detected spectroscopically under the reaction condition because of high temperature and low surface concentration. In Ref. [6] it was concluded that the oxygen defects promote the catalyst performance for OCM reaction. This conclusion was made based on detailed analysis of defect structure for number of OCM catalysts, but not based on experimental data under OCM conditions. The study of the reaction of N_2O decomposition under the reaction condition is useful test on the nature of defects [12–15]. At present two simple equations (1,2) are used to describe the process of N_2O decomposition, with the ions of transitional metals [14, 15] [Eq. (1)] and anion vacancies [12, 13] [Eq. (2)] being active centres for N_2O decomposition.

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$$\frac{dN_2O}{dt} = -k \cdot P_{N_2O} \quad (1)$$

$$\frac{dN_2O}{dt} = -k \cdot P_{N_2O} \cdot P_{O_2}^{-0.5} \quad (2)$$

The present work is aimed at the further development of the concept concerning the important role of structural defects not only for OCM reaction, but for oxidant activation.

The detailed investigations of these aspects will allow to predict the catalytic properties essential for the formation of certain oxygen species which are responsible for the selective oxidation of methane. Besides, such approach may be useful for the study of the selective oxidation of other lower hydrocarbons.

2. Experimental

Catalysts were prepared from high purity grade CaO (Fe < 0.01, Mn < 0.001 at.%), $SrCO_3$ (Fe < 0.001, Mn < 0.0005), Bi_2O_3 (Fe < 0.003, Mn < 0.001), NaOH (impurity content: 0.0001–0.001 at.%), LiOH (impurity content: 0.0001–0.001 at.%). M/CaO and Li/Bi_2O_3 were prepared by impregnating the original oxides with sodium or lithium hydroxide followed by drying and calcination at the air for 3 h at 1273 K for M/CaO and at 1023 K for Li/Bi_2O_3. After calcination the actual alkali concentration was determined by atomic adsorption analysis on AAS-1 apparatus. We used M/CaO and Li/Bi_2O_3 catalysts with a low amount of alkali promoter (< 2 at.%) within the range of solid solution formation.

$SrCO_3$ was calcinated at 1523 K for 2 h in the flow of O_2 and was cooled at this atmosphere.

The BET method was utilized to determine the surface areas of the catalysts.

Catalytic activity was examined in a microcatalytic quartz fixed bed reactor using reaction mixtures: CH_4:O_2:He = 30:15:55 vol.% or CH_4:N_2O:He = 30:30:40 vol.%. 5–40 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 at 1 atm (= 101.325 kPa) pressure. A 'Biochrom-1' gas chromatograph was used to analyze the product stream. Separation of the various components was achieved using NaX zeolite and Porapak Q columns.

The N_2O decomposition was studied under the conditions of methane oxidation using the following mixtures: CH_4:N_2O:O_2:He = 30:10:X:(60 − X), where X = 0–15 vol.%.

The method of EPR spectroscopy was used to determine the Fe^{3+} ions concentration. Paramagnetic centres (pc/g) concentration was determined with reference to standards of $Cr_2(SO_4)_3$ and Cr/α-Al_2O_3.

3. Results and discussion

3.1. Structural systematization for OCM catalysts

The examination of number of oxide catalysts for the oxidative coupling of methane has allowed to pick out two large catalyst groups which differ by their properties (Table 1):

i) multiphase catalysts (with the high promoter content);

ii) single phase catalysts (individual compounds or solid solutions, as a rule with the low promoter content).

As for the first group the catalyst properties may be defined by the features of the compound of promoting element formed on the surface or of the compound formed between the promoter and support. For example, for catalyst 10 at.% Na/CaO the sodium carbonate was assumed to be served as active phase [11]. For the catalysts 20 mol.% Ba/CeO_2 the compound of promoter with support ($BaCeO_3$) was observed as active catalyst phase [16].

Catalytic properties of the second group have been found to stipulate by the availability of the defects of oxygen type – oxygen vacancies or interstitial oxygens (see Table 1) on which the formation of active catalytic species may occur. For rare earth oxides of the beginning of REE line

(La_2O_3, Nd_2O_3, Sm_2O_3) and for alkaline earth oxides (SrO, BaO) the oxygen defects (oxygen vacancies at oxygen pressure $P_{O2} < 0.1$ kPa and surplus (interstitial) oxygens at $P_{O2} > 0.1$ kPa) are intrinsic structural defects [17]. The oxidant activation of both molecular oxygen and N_2O is possible over such type defects.

It has been shown [10] that the formation of solid solutions is the simplest way to create the defects of the desirable type. For solid solutions based on alkaline earth oxides the incorporation of monovalent additive (Li, Na) into CaO lattice may result in the following processes [6]: i) formation of the oxygen vacancies and ii) oxidation of impurity ions of Fe^{2+} to Fe^{3+} and the stabilization of Fe^{3+} ions in cation positions to compensate for charges.

Earlier [18], we have shown that for Li/CaO and Na/CaO catalysts oxidation of Fe^{2+} to Fe^{3+} takes place. It was also established that the increased of Fe^{3+} ions concentration resulted in the growth of OCM activity and such correlation did not depend on type of alkali promoter (Li or Na).

Thus, it is obvious that the structural peculiarities of oxides determine their catalytic properties. The presented structural systematization has allowed us to propose the basic criteria for choosing active catalysts for OCM:

- the availability of oxygen defects in catalyst lattice;
- the ability for electron transfer which can be realized by oxidation of impurity ions of transition metals for irreducible oxides.

3.2. Catalytic properties

To verify proposition concerning the role of structural defects of OCM catalysts, the reaction

Table 1 Systematization of the OCM catalysts

Catalyst type	Active oxygen sites	Type of defects
I. Multiphase catalysts (with high promoter content)	a) surface promoter compound b) compound of promoter with oxide matrix	
II. Single phase catalysts 1. Individual compounds		
1.1. Rare earth oxides (except Pr, Ce, Tb oxides)	O_2^{2-} and/or O_2^-	$p < 0.1$ kPa-oxygen vacancies $p > 0.1$ kPa-interstitial oxygen O_i or formation of active oxygen
1.2. Alkaline earth oxides	O_2^{2-}, O^-, O^0 (uncharged form)	Oxygen vacancies or interstitial oxygen
2. Solid solutions on the based on alkaline earth oxides	O_2^{2-}, O^-, O^0 (uncharged form)	i). $p < 0.1$ kPa-oxygen vacancies ii). $p > 0.1$ kPa-formation of active oxygen iii). impurity ions of transition metals (it not depends on p_{O2})

of N_2O decomposition over alkali-earth metal oxides, Bi_2O_3 and CaO with a low content of alkali promoter (usually single phase samples) was studied under conditions of OCM. As follows from introduction, the influence of molecular oxygen on the rate of N_2O decomposition is the main test on the nature of defects, taking part in the decomposition of nitrous oxide. Experimental data on N_2O decomposition are given in Table 2. The increase of O_2 concentration is not seen to influence the decomposition rate of N_2O over Na/CaO and Li/CaO catalysts. This means that the different catalyst centres are necessary for activation of O_2 and N_2O. In contrast to these catalysts, for SrO and Li/Bi_2O_3 catalysts the rate of N_2O decomposition decreases with increase of concentration of molecular oxygen in CH_4–N_2O reaction mixture (Table 2). This observation may be explained by competition of O_2 and N_2O for the same active catalyst centres. Since the decomposition of N_2O under OCM condition over SrO, Li/Bi_2O_3 and Li/CaO, Na/CaO is different then distinctive active catalyst centres are responsible for the decomposition of nitrous oxide over catalysts studied here. In previous study of N_2O decomposition over numerous oxides, Winter [13] found the poison effect of O_2. He proposed that anion vacancies were active catalyst sites for N_2O decomposition. Hall et al. [14] and Panov et al. [15] established that decomposition of N_2O over Fe-containing zeolites did not depend on partial pressure of O_2. They proposed that ions of iron were active for N_2O decomposition. Earlier [18], we have found that impurity ions of Fe^{3+} were the main defects in Li/CaO and Na/CaO. Under conditions of our experiments the impurity Fe^{3+} ions in the CaO lattice seem to play important role for the activation of N_2O.

Thus, we believe that ions of Fe^{3+} and anion vacancies may be part of active centres for N_2O decomposition over Li/CaO, Na/CaO catalysts and SrO, Li/Bi_2O_3, respectively.

It is also necessary to note that the addition of O_2 in CH_4–N_2O reaction mixture influence not only the rate of N_2O decomposition but also the rates of formation products of OCM. So, the activity of C_2H_6 over Li/CaO, Na/CaO catalysts increases when partial pressure of O_2 in the CH_4–N_2O–O_2 reaction mixture raises (Table 2). The quite different situation is realized when SrO and Li/Bi_2O_3 catalysts are used. One can see that the rate of ethane formation is not practically changed (Table 2).

For CO_2, the addition of O_2 in CH_4–N_2O–O_2 reaction mixture influences the rate of CO_2 formation. So, the rate of CO_2 formation over Li/CaO and Na/CaO does not practically depend on the partial pressure of O_2 (Table 2), while over SrO and Li/Bi_2O_3, the rate of CO_2 raises with increasing concentration of molecular oxygen

Table 2

Rates of N_2O decomposition (N_2), C_2H_6 (C_2) and CO_2 formation, T=1023 K, CH_4:N_2O:O_2:He=30:10:X:(He-X) vol.%, for Li/Bi_2O_3 (0.1) T=1053 K.

X, vol.%	W, 10^{18} molecules CH_4*s^{-1}*m^{-2}											
	Na/CaO(0.1)			Li/CaO(0.1)			Li/Bi_2O_3(0.1)			SrO		
	N_2	C_2	CO_2	N_2	C_2	CO_2	N_2	C_2	CO_2	N_2	C_2	CO_2
0	6.6	2.4	0.2	9.4	5.3	0.3	4.2	1.5	0.1	75	35	1
1	6.4	3.0	0.2	7.2	6.2	0.3	2.8	1.2	0.2	60	37	2
5	6.0	3.4	0.3	9.4	6.9	0.4	2	1.7	0.6	39	20	4
15	6.2	4.1	0.4	9.2	9.4	0.5	1.8	1.5	0.9	18	22	6

(Table 2). Since the catalytic conditions were similar for all catalysts studied here, we may conclude that CO_2 does not come from gas-phase oxidation of methane and/or ethane. This means that appearance of O_2 in a gas mixture results in the formation of surface oxygen species over SrO and Li/Bi_2O_3 which reacts non-selectively with CH_4 or CH_3 radicals. For Li/CaO and Na/CaO, the results obtained may indicate the such forms of surface oxygen are not formed. Earlier, based on dependence of selectivity of product formation on methane conversion we have found, that CO_2 is formed from CH_4 over SrO [19] and Li/Bi_2O_3 [3] but over Li/CaO and Na/CaO [18], CO_2 is formed from CO, C_2H_6 and C_2H_4. Thus, surface reaction is assumed to be responsible for deep oxidation of methane over catalysts studied here, when O_2 is used as oxidant.

Based on experimental data obtained and data concerning the type of defects of catalysts studied here (Table 1) we may conclude that the distinctions between SrO, Li/Bi_2O_3 and Li/CaO, Na/CaO in the reaction of N_2O decomposition and OCM are basically caused by different defect structure of these catalysts.

3.3. Kinetics of OCM over SrO

Further, to elucidate the details of OCM mechanism and the role of anion vacancies the kinetic peculiarities of process of the OCM over SrO were studied, using N_2O as oxidant. Conversion and selectivity data were obtained for the N_2O decomposition and for the reaction of CH_4 with N_2O over the temperature range 923–1123 K. The conversion of methane was selected low and did not exceed 1%. CO_2 produced as a product of reaction was appeared only at high temperature (higher than 1023 K). The Arrhenius plot is shown in Fig. 1. One can see that over 923–1023 K temperature range of N_2O decomposition considerably exceeds the rate of C_2H_6 formation and E_a of C_2H_6 formation is 250 kJ/mol but E_a of N_2O decomposition is 67 kJ/mol. However, over 1023–1123 K temperature range, E_a of ethane formation is changed (138 kJ/mol) and the rates of C_2H_6 formation nd N_2O decomposition become close. This means that there are two temperature ranges of proceeding of OCM reaction.

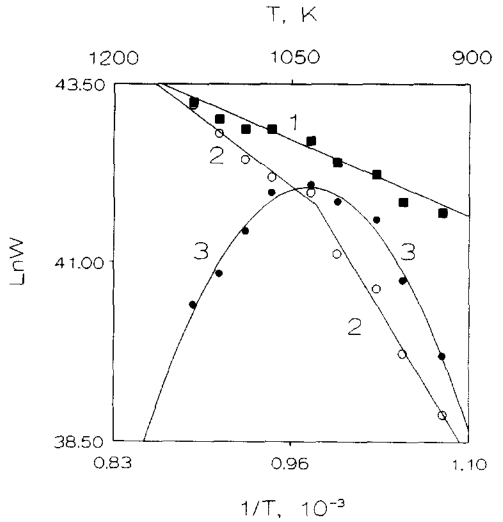

Fig. 1. Arrhenius relation of catalytic activity of SrO. 1 – N_2O; 2 – C_2H_6; 3 – O_2.

High activation energy for ethane formation and pronounced distinctions between the rate of ethane formation and the rate of N_2O decomposition are characteristic of low temperature range (923–1023 K). Also for these temperatures $W(N_2)-W(C_2H_6)>W(O_2)$, where $W(N_2)$ is the rate of N_2O decomposition, $W(C_2H_6)$ is the rate of ethane formation and $W(O_2)$ is the rate of O_2 formation from N_2O. This means that there is not a carbon balance between reactants and reaction products. These differences may be caused by suppressing the active oxygen species or active catalyst centres. Since SrO is well known to form stable $SrCO_3$ we can speculate that CO_2 inhibits this process.

$$W_{C_2H_6}=\frac{k\cdot f(P_{CH_4}\cdot P_{N_2O})}{1+K\cdot P_{CO_2}} \qquad (3)$$

This is the classic equation that one would obtain for a Rideal mechanism is which one of the products is a poison [20]. Examining the equation 3, we can see that measured E_a of ethane formation will depend on which of the two terms $(1+K\cdot P(CO_2))$ is predominant. We calculated equilibrium constant (K) for the reaction 4. This constant decreases when temperature increases. Over 923–1023 K temperature range, $K \cdot P(CO_2)) >> 1$ and $E_a = E_a + \Delta H$, where ΔH is enthalpy for reaction (4) and E_a is real activation energy for C_2H_6 formation.

$$SrO + CO_2 \rightleftharpoons SrCO_3 \qquad (4)$$

The increase of temperature results in the decrease of constant of reaction 4. Since K decreases but the absolute amount of CO_2 is small, $K \cdot P(CO_2) << 1$. It also is necessary to note that over 1023–1123 K temperature range $W(N_2)-W(C_2H_6) = W(O_2)$ and CO_2) was found as a reaction product. It is obvious that the poisoning effect of CO_2 drastically decreases. Therefore, the energy of activation of ethane formation is changed (Fig. 1). For these temperatures the amount of O_2 produced from N_2O decreases and the rate of ethane formation and the rate of N_2O decomposition become close (Fig. 1). This means that a low pressure of molecular oxygen favours the effective decomposition of N_2O and 100% selectivity of ethane formation may be achieved under these catalytic conditions. One can see (Table 1), the anion vacancies are formed into SrO when concentration of molecular oxygen is low ($P(O_2) < 0.1$ kPa). Therefore, the presence of anion vacancies into the lattice of SrO may be one of the important features which are necessary for oxidant activation.

Thus two temperature ranges of proceeding of OCM reaction over SrO was established. Over 923–1023 K temperature range, the mechanism in which CO_2 is a poison for active oxygen species was proposed to explain the kinetic peculiarities obtained. Over 1023–1123 K temperature range, the anion vacancies can play the important role for effective decomposition of N_2O and selective oxidation of methane.

4. Conclusions

1. Based on analysis of the catalytic properties and defect structure of oxide catalysts, the new systematization of catalysts for the OCM has been proposed.
2. It was obtained that the addition of O_2 in CH_4–N_2O reaction mixture decreased the rate of N_2O decomposition over SrO and Li/Bi_2O_3 (0.1 at.%), while for Li/CaO (0.1 at.%), Na/CaO (0.1 at.%) catalysts such effect was not observed. It may be explained by the fact that activation of O_2 and N_2O in OCM process occurs on the same centres for the first catalysts and different centres for second group of catalysts.
3. Two temperature ranges of proceeding of OCM reaction over SrO was established. To describe the OCM reaction over low temperature region (923–1023 K) the mechanism in which CO_2 is a poison for active oxygen species was proposed. Over 1023–1123 K temperature range, it was assumed that the presence of anion vacancies into the lattice of SrO may be one of the important features which are necessary for oxidant activation.

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