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ROLE OF DEFECT STRUCTURE OF ACTIVE OXIDES IN OXIDATIVE COUPLING OF METHANE

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A new approach to the choice of catalysts for oxidative coupling of methane based on the determination of the defect degree is suggested. For the most active catalysts (oxides of rare earth elements (REE), alkaline earth metals (AEM), manganese, lead), it is shown that oxygen defectness is of great importance in this process.

Based on the structural approach Bi_2O_3-containing catalytic systems have been suggested. They have C_2-hydrocarbon formation activity and selectivity to be comparable with those ones for most active catalysts as REE oxides.

1. Introduction

The conception of heterogeneous-homogeneous nature of methane oxidative coupling reaction is now beyond any doubt. Different viewpoints concerning the reaction mechanism are centered mainly on the participation of different oxygen species in this process. These active oxygen species may be: (i) molecular species such as O_2^- [1], O_2^{2-} [2] for lanthanoide oxides; (ii) dissociated species such as O^- [3] or nucleophile ions O^{2-} of the catalyst lattice [4] for AEM-oxides. Previously we have suggested [5] that dissociated oxygen species with the features of atomic oxygen can take part in this process. This oxygen form can be produced at the disproportionation of peroxide ions on structural defects of the oxide catalyst.

Recent results have shown that oxide catalysts on the base oxides REE. AEM, manganese, lead, possess high efficiency in the production of C_2-hydrocarbons from methane. Sesquioxides of REE from the beginning of lanthanoide series (La_2O_3, Nd_2O_3, Sm_2O_3) are most active in C_2-hydrocarbon formation [6–8]. Nevertheless, both activity and selectivity of these oxides strongly change depending on the lattice type of the oxide. Thus, according to the data [8] Sm_2O_3 cubic modification is more active and selective for C_2-product formation than Sm_2O_3 monoclinic phase, though both phases have the same basicity.

In this work we discuss catalytic properties of known oxide systems and suggest new effective catalysts from the viewpoint of structural peculiarities and defect degree of the oxide structure.

2. Experimental

Catalysts were prepared through impregnating of bismuth oxide (III) by hydroxide or nitrate solutions of promoters (Li, Na, Er) with the subsequent drying and calcinating in air at 1023 K for 3 hours. The purity of initial reagents was 99.99%. The concentration of the promoter was chosen at the range of solid solution formation and controlled using atomic absorption analysis. The phase composition was determined by XRD. Bi_2GeO_5 catalyst was prepared from the melt [9].

To perform the catalytic experiment a microcatalytic flow reactor described in [5] and a reaction mixture composition $CH_4 : O_2 = 85 : 15$ vol.% were used.

3. Results and discussion

STRUCTURAL PECULIARITIES OF ACTIVE CATALYSTS IN OXIDATIVE COUPLING OF METHANE

The type of the crystalline lattice and of intrinsic and/or impure defects for most active catalysts are shown in table 1 and the comparison is made with less active catalysts for C_2-product formation. Table 1 shows that high efficient catalysts such as Sm_2O_3, Nd_2O_3, Mn_2O_3 under the reaction conditions have the similar structure type (cubic C-form of Ln_2O_3) which is close to the fluorite structure (fig. 1a), but in contrast it has 25% vacancies in the oxygen sublattice (fig. 1b) [10]. They are so-called structures with ordered oxygen vacancies to be determined initially by the crystal structure.

Oxides having an ideal fluorite structure such as CeO_2 possess low selectivity of C_2-hydrocarbon formation of the total high CH_4 conversion rate [6,7,11] (table 1). The catalyst activity in the methane coupling increases with the oxygen defectness. It can be observed using Pr_6O_{11} and Tb_4O_7 [11] which in contrast to CeO_2 can produce some of C_2-products. Oxides Pr_6O_{11} ($PrO_{1.818}$) and Tb_4O_7 ($TbO_{1.75}$) are the phases to be in the equilibrium with air.

The introduction of monovalent additive into these oxides can result in the following processes:

$$\underset{(\rightarrow Tb_4O_7)}{\tfrac{3}{2}Na_2O} \rightleftarrows 2Na_{Tb}^{iii} + Na_{Tb}^{ii} + 4V_O^{\bullet\bullet} + \tfrac{3}{2}O_O^{\times} \qquad (1)$$

where symbols ^{i}, $^{\bullet}$, $^{\times}$ denote efficient unit charges: negative, positive and neutral,

Table 1
Structural and catalytic oxide properties in oxidative coupling of methane

Catalyst composition (wt.%)	Crystalline lattice type [10]	Intrinsic or impure defects type [12,13]	Process conditions			$W_{C_2}\cdot 10^{-17}$ $\left(\frac{\text{molec.}CH_4}{m^2\cdot s}\right)$	ΣS_{C_2} (%)	Ref.
			T (K)	P_{O_2}	CH_4/O_2			
Sm_2O_3	C-Ln_2O_3	[a] $O_i^{ii} + V_O^{\cdot\cdot}$ [b] $O_i^{ii} + 2h^{\cdot}$	1023	14.5	6	13800	64	[33]
Nd_2O_3	C-Ln_2O_3	[a] $O_i^{ii} + V_O^{\cdot\cdot}$	973	3	12	150	63	[7]
at $T > 973$–1073 →	A-Ln_2O_3	[b] $O_i^{ii} + 2h^{\cdot}$						
La_2O_3	A-Ln_2O_3	[a] $O_i^{ii} + V_O^{\cdot\cdot}$	973	3	12	80	50	[7]
1%Sr/La_2O_3	A-Ln_2O_3	[a] $2Sr_{La}^{i} + V_O^{\cdot\cdot}$	973	5	10	586	62	[31]
	A-Ln_2O_3	[b] $2Sr_{La}^{i} + h^{\cdot}$	1023	5	10	1340	72	[31]
CeO_2	fluorite	[b] Ce_i^{iii}	1043	9	2.7	0	0	[17]
5%Na/CeO_2	defect fluorite	[a] $2Na^{iii} + 3V_O^{\cdot\cdot}$	1043	9	2.7	13 [c]	59	[17]
4%Na/CeO_2	fluorite	[b] $Na_{Ce}^{iii} + 3h^{\cdot}$	1048	redox. regime		0.2	48	[11]
Pr_6O_{11}	fluorite		1048	redox. regime			2	[11]
4%Na/Pr_6O_{11}	fluorite	[a] $2Na_{Pr}^{iii} + 3V_O^{\cdot\cdot}$	1048	redox. regime		11	70	[11]
	fluorite	[b] $2Na_{Pr}^{iii} + 6h^{\cdot}$	1048	10	5	9	51	[11]
Tb_4O_7	fluorite		1048	redox. regime			2	[11]
4%Na/Tb_4O_7	fluorite	[b] $Na_{Tb}^{iii} + 3h^{\cdot}$	1048	redox. regime		6	59	[11]
Li/Mn_2O_3	C-Ln_2O_3	[a] $Li_{Mn}^{ii} + V_O^{\cdot\cdot}$	1023	28.5	2	45 [c]	43	[33]
40%PbO/Al_2O_3	rhomb.		973		1.5	67	68	[32]
MgO	NaCl	[a] $V_{Mg}^{ii} + V_O^{\cdot\cdot}$	1023	15	2	0.2	20	[26]
Li/MgO	NaCl	[a] $2Li_{Mg}^{i} + V_O^{\cdot\cdot}$	1023	15	2	1.6	56	[26]
CaO	NaCl	[b] $O_i^{ii} + 2h^{\cdot}$	1023	15	2	0.9	12	[26]
Li/CaO	NaCl	[b] $Li_{Ca}^{i} + h^{\cdot}$	1023	15	2	19.0	68	[26]

[a] $P_{O_2} < 0.1$ kPa,
[b] $P_{O_2} > 0.1$ kPa,
[c] $W_{C_2}\cdot 10^{-17}$ molec.CH_4/g·s.

respectively; V_O-oxygen vacancy having the efficient charge +2 (the lack of two electrons);

$$4Tb^{3+} + Na_2O \rightleftarrows 2Na_{Tb}^{+} + 4Tb^{4+} + O^{2-} \tag{2}$$

$$4Me_{Tb}^{2+} + Na_2O \rightleftharpoons 2Na_{Tb}^{+} + 4Me_{Tb}^{3+} + O^{2-} \tag{3}$$

where Me^{2+}-ion the transition metal (TM) that is present in REE-oxides as accompanying impures.

That is, by doping with low valence ions, compensation of the charge can occur as a result of: (i) formation of oxygen vacancies; (ii) oxidation of host ions ($Tb^{3+} \rightarrow Tb^{4+}$): (iii) oxidation of impure TM-ions ($Me^{2+} \rightarrow Me^{3+}$). It has been shown [12,13] for the oxides PrO_x and TbO_x, that one of the processes (1), (2) and (3) will be preferred depending on the partial oxygen pressure and temperature.

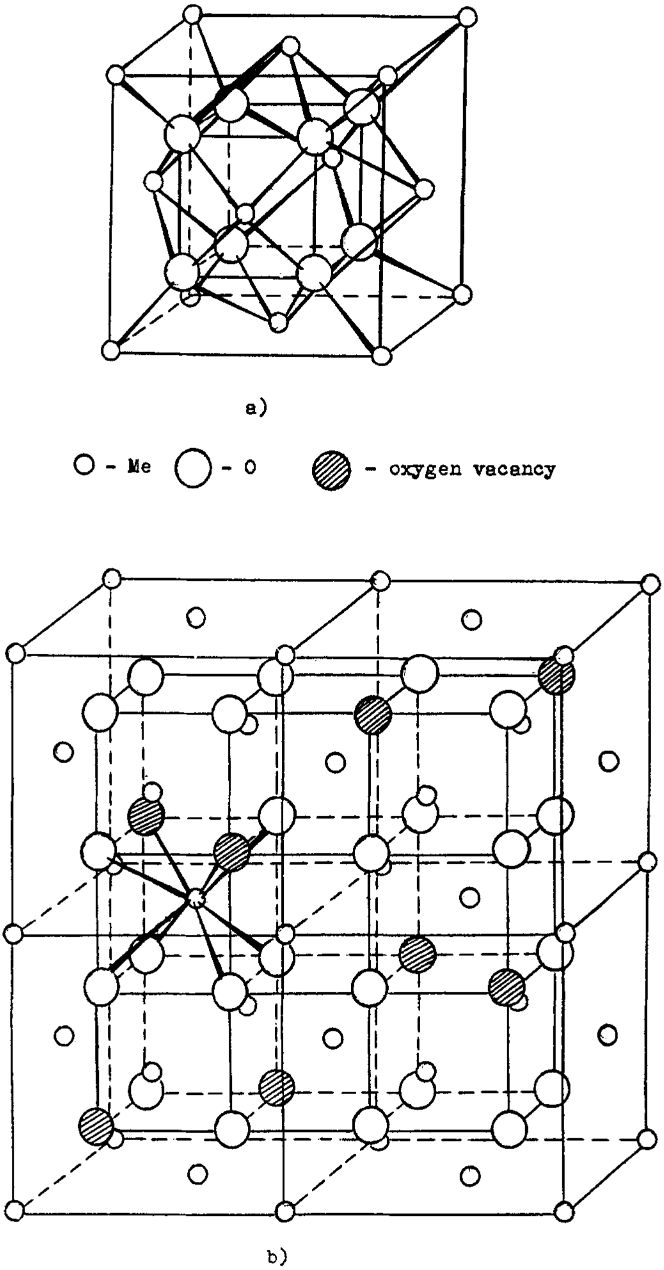

Fig. 1. Crystal structure of fluorite (a) and C-phase Ln_2O_3 (b) [10].

The value "x" is reduced with the temperature increase and P_{O_2} pressure drop. At $T > 873$ K and $P_{O_2} < 21$ kPa the process from eq. (1) predominates. Thus, at doping the oxide TbO_x by lower valence additive (Y) at $T = 1173$ K in air the value "x" is 1.5 practically at the whole range of TbO_x-Y_2O_3 solid solution formation [14]. The tendency for PrO_x is the same [12].

With the increase of P_{O_2} these oxides can add gaseous oxygen and become the p-type semiconductor [15]:

$$V_O + 2\bar{e} + O_{2(g)} \rightleftarrows O_2^{2-}(\text{ads}) \rightleftarrows 2O^- + 2h \tag{4}$$

where h is an electron hole.

The electron concentration required for the oxygen activation according to the eq. (4) in oxides PrO_x, TbO_x can be determined by the redox potential of both hosts (Tb^{3+}/Tb^{4+}) and impure TM-ions.

It has been shown [12], that the p-type semiconductivity for PrO_x and TbO_x is remained to the value $x = 1.75$. At $x > 1.75$ these oxides are n-semiconductors, i.e. here the process which is reverse to (4) dominates. And the oxides with $x > 1.75$ are less capable to active oxygen with the formation of peroxide ions. CeO_2 is also the n-type semiconductor at $P_{O_2} < 101.3$ kPa [16].

Oxides with low oxygen defectness (CeO_2, Pr_6O_{11}, Tb_4O_7) should be noted to produce a small amount of CH_3-radicals [17]. The radical conversion to CO_2 over them is very high. The introduction of alkali promoters into these oxides increases their capability to generate CH_3-radicals. Simultaneously, the deep oxidation reaction is inhibited (table 1) and oxygen conversion decreases [17].

Sesquioxides of REE are p-type semiconductors [13]. The lattice is extremely open for oxygen and the excess oxygen enters the vacancies of the C-phase lattice. Here, the electric conduction of Ln_2O_3 is decreased from La to Lu, i.e. the oxygen activation capability is decreased. Simultaneously, both C_2-formation activity and selectivity in the series of REE-oxides is also decreased [6–8].

In contrast to Ln_2O_3, pure oxides MgO, CaO (NaCl-type structure) without "biographic" vacancies are characterized by the low intrinsic disorder (Schottky type defects) and, therefore have rather low C_2-formation activity and selectivity (table 1). When the alkali additive is introduced into AEM-oxides at low oxygen pressure ($P_{O_2} < 0.1$ kPa) the process of oxygen vacancy formation takes place [12] (table 1). Under the reaction conditions ($P_{O_2} > 0.1$ kPa) MgO, CaO doped with low valence elements have the p-type conductivity [18]. The more defective lattice of these oxides becomes capable to add excess oxygen with the formation of peroxide ions (eq. (4)).

However, neither Ln_2O_3 (except Ce, Pr and Tb) nor AEM-oxides can change the valence state of host ions to activate molecular oxygen. Thus, the process in these oxides takes place due to oxidation of TM impure ions.

Thus, ion stabilization of transition metals (Ni, Cr, Pd) to the higher oxidation state was observed in [15] when surface of REE-sesquioxides were oxidized. If it was reduced by CO or H_2, the reverse process occurred. Previously, it has been suggested [19] that oxygen activation process on Ln_2O_3 proceeds with the formation of peroxide ions:

$$O_{2(g)} + Ni^+ \rightleftarrows O_{2(\text{ads})}^{-2} + Ni^{3+}. \tag{5}$$

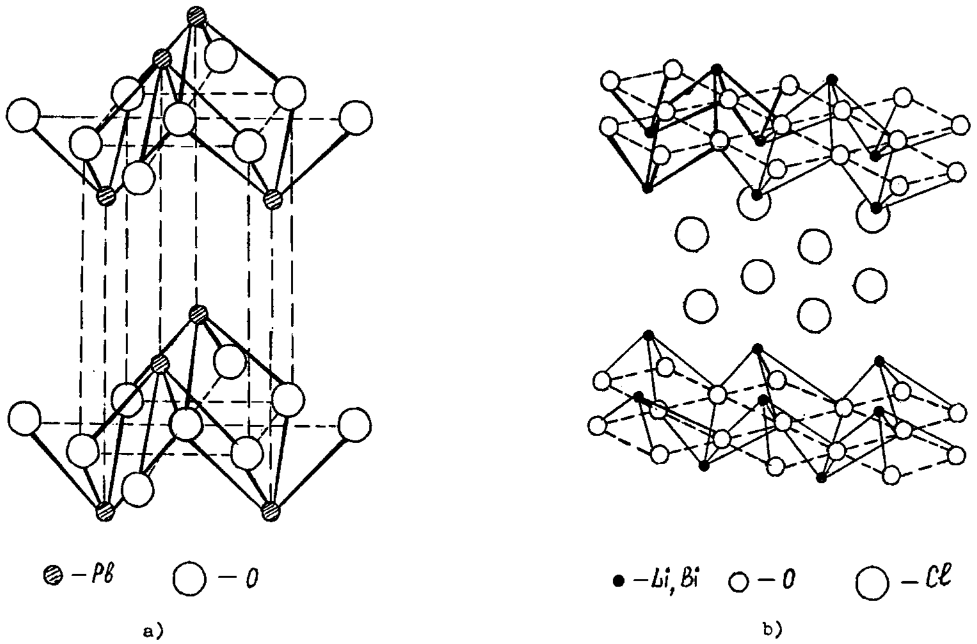

Fig. 2. Crystal structure of PbO (a) [10] and Aurivillius phases (b) [30].

We showed [20] that on Li/MgO and Li/CaO the formation of sites $[Li^+O^-]$ with simultaneous oxidation of Fe^{2+} to Fe^{3+} takes place at $P_{O_2} > 0.1$ kPa.

The formation of ion-radicals O_s^- is not the only way to dissociate peroxide ions. Thus, on pure MgO at $T > 873$ K peroxide ions start to disproportionate to atomic oxygen, that was observed in [21]. The possibility to carry out oxidative coupling of methane in the presence of atomic oxygen has been proved experimentally [22] using the silver membrane process.

One of the active catalysts–PbO has the layer rhombic lattice under the reaction conditions (fig. 2a). The layers consist of tetragonal pyramids at the base of which there is a rhombus from oxygen ions. Due to a large distance between the layers, the PbO lattice is extremely open for oxygen, i.e. the concentration of oxygen vacancies is high and PbO is p-semiconductor at $P_{O_2} > 0.1$ kPa [13]. Oxyhalide Bi-containing compounds, the so called Aurivillius phases, have similar structures (fig. 2b). They also have high activity and selectivity for C_2-hydrocarbon formation from methane [23].

Thus, it is obvious that the structural peculiarities of oxides determine their catalytic properties. All catalyst compositions discussed are effective coupling of methane and have oxygen defectness at $P_{O_2} < 0.1$ kPa. At the higher P_{O_2} values (table 1) they possess closer oxygen affinity, i.e. they are more capable to activate oxygen.

The present structural approach allows one to determine the basic criteria to choose active catalysts for oxidative coupling of methane: (i) The catalyst lattice structure must have oxygen defectness and must be able to add excess oxygen at vacant anion sites. At the same time the catalyst must also be able to activate oxygen to peroxide ions. In most cases, the former and latter condition may be fulfilled by the introduction of alkali and alkaline earth additives. (ii) To activate molecular oxygen the presence of donor ions (host or impure) is required. However, the concentration of these ions must be low (at the doping level). Otherwise, the excess of donor ions results in the significant acceleration of the oxidation process [15].

It is obvious from the present approach that efficiency of alkali additive introduction will be observed only in the case when ion radius (r_i) of the doping component is lower than (or equal to) r_i of the host ion. Thus, maximum C_2-product yields for AEM-oxides have been observed over systems Li/MgO, Na/CaO. At the same time, the promotion by alkali metal ions of the bigger size than that of the host ions causes the decrease of activity and selectivity (Na/MgO, K/CaO) or leads mainly to deep oxidation (K/MgO) [24]. However, the system Na/MgO is observed to be more effective than Li/MgO [25]. This phenomenon may occur due to the different techniques of catalyst preparation. It has been shown [25] that at high temperature calcination the Na-phase segregation is observed. This process promotes the formation of Na_2CO_3 and its participation in oxidative coupling of methane similar to the Li/CaO system with the high Li content [26].

The approach described based on the structural peculiarities of oxide catalysts allows to propose a new catalytic system for oxidative coupling of methane.

CATALYTIC PROPERTIES OF Bi_2O_3-BASED SYSTEMS

The selection of Bi(III) oxide as the base is stipulated by the fact that the high temperature δ-phase of Bi_2O_3 (phase transition $\alpha \rightarrow \delta$ at $T = 1000$ K) has C-type structure of Ln_2O_3 [10]. This is characteristic for most active REE-oxide catalysts. The catalytic properties of some Bi_2O_3-based systems are shown in table 2.

Table 2
Catalytic properties of Bi-containing oxide system
($T = 1053$ K, $CH_4 : O_2 = 85 : 15$ vol.%, $m_{cat.} = 0.1–0.3$ g, flow rate = 10–20 ml/min)

Catalyst composition	S (m^2/g)	$W \cdot 10^{-17}$ ($molec.CH_4/m^2 \cdot s$)			Selectivity (%)	
		C_2H_6	C_2H_4	CO_2	ΣC_2	CO_2
1. Bi_2O_3	0.5	2.0	0.2	1.0	68.5	31.5
2. 1.4%Li/Bi_2O_3	< 0.1	25.3	5.3	7.4	80.4	19.6
3. 1.1%Na/Bi_2O_3	< 0.1	36.4	7.6	17.1	72.1	27.9
4. 1.5%Er/Bi_2O_3	0.2	42.3	14.8	62.7	48.4	51.6
5. 20%Er/Bi_2O_3	0.2	44.0	6.7	80.5	38.7	61.3
6. Bi_2GeO_5	< 0.1	126.9	42.7	72.2	70.2	29.8

As indicated in table 2, Bi_2O_3 is not very active in C_2-hydrocarbon formation as compared to REE-oxides. Activity may occur due to the low capability of Bi_2O_3 to produce peroxide ions. To increase the oxygen defectness and capability to activate oxygen for production of peroxide ions, Bi_2O_3 solid solution with alkali (Na, Li) additives (to 1.5 at.%) were prepared. Besides, the alkali additive introduction is likely to promote the increase of donor capabilities for both host ($Bi^{3+} \rightarrow Bi^{5+}$) and impure TM ions according to eqs. (2) and (3).

Table 2 shows that activity of Bi-oxide doped by Li, Na increases by an order of magnitude with some increase of C_2-formation selectivity. All catalysts studied have been mentioned above to be solid solution.

To elucidate the role of oxygen vacancies Bi_2O_3-Er_2O_3 systems have been chosen. Er additive to Bi_2O_3 favours the increase of oxygen-ion conductivity [27]. The oxygen-ion conductivity and oxygen vacancy concentration are correlated values. Oxygen vacancies promote to increase electric conductivity stipulated by oxygen ions [28]. As the consequence of the increase of oxygen vacancy concentration, the activity growth in C_2-hydrocarbon formation for Er-doped systems has been observed. The solid solution of 20 mol.% Er_2O_3 in Bi_2O_3 is known to have the highest oxygen conductivity among all the Bi-containing oxide systems studied [27]. However, extremely high mobility of lattice oxygen causes the essential activity increase for deep oxidation reaction.The results obtained are in agreement with the ones reported in [29] where it was shown that the increase of oxygen mobility leads to the deep oxidation of methane over Ce-containing catalysts.

Another system to be chosen according to the suggested requirements for active catalysts is the Bi_2GeO_5 compound. It has a structure similar to the Aurivillius phase (fig. 2b). The only difference is that there are tetrahedrons (GeO_4) with common (with Bi-layers) oxygen atoms between bismuth-oxygen layers [Bi_2O_2] [30]. Depending on the P_{O_2}, this structure can have high oxygen defectness since it has a broad homogeneous area, up to 15 mol.% GeO_2 at $T = 973$ K in air [9]. This catalyst is seen from table 2 to be the most effective of all the Bi-containing systems investigated.

4. Conclusions

Based on the comparison of catalytic and structural properties of oxide catalysts it was concluded that the increase of intrinsic or impure defectness results in the growth of the C_2-formation activity. Oxygen defects are believed to play an important role since the activation of gas phase oxygen may occur on them.

Based on the structural approach, Bi_2O_3-containing catalytic systems have been suggested. They have C_2-hydrocarbon formation activity and selectivity to be comparable with those ones for most active catalysts such as REE-oxides.

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