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Lamellar perovskites $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ catalysts for oxidative coupling of methane

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The oxidative coupling of methane has been studied in the presence of lamellar perovskites $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ belonging to Aurivillius phases. These materials are selective and stable in the OCM reaction. Moreover, their substitution in perovskite (A) or octahedral (B) sites leads to significant changes of the C_{2+} selectivity or yield which are attributed to modifications of the basicity of A–O or B–O bonds.

Keywords: Methane; oxidative coupling; lamellar perovskites; Aurivillius phases

1. Introduction

From the pioneer work done by Keller and Bhasin [1] numerous solids have been used in the oxidative coupling of methane as reported in recent reviews by Pitchai and Klier [2] and Amenomiya [3]. All the results show that there are difficulties in the direct conversion, mainly due to the high stability of the methane molecule and to the thermodynamic disadvantage which can be overcome by introducing an oxidant. Nevertheless, mechanistic or kinetic constraints place an upper bound on yield, independent of catalyst [4,5], which is very close or under the target values [6]. Our main objective in this field is to find trends between catalyst composition and activity–selectivity in OCM, which is one of the reasons for studying perovskite-like materials. Perovskites are well known catalysts for total oxidation of various hydrocarbons, but recently some of these solids have also been used in selective oxidation [7].

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At the origin of our study is a new family of solids composed of exchangeable lamellar perovskites $M^I(A_{n-1}B_nO_{3n+1})$ prepared for the first time by three of us [8]. These solids can be substituted in different sites (interlamellar (M), perovskite (A) or octahedral (B)) and we have studied the influence of such substitutions on their catalytic properties [9,10]. Nevertheless, we evidenced that there were some limitations for the substitution of these solids while keeping the same structure. In order to overcome the limitations, we decided to extend our investigation to some Aurivillius phases of general formula $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ [11]. These compounds have also a lamellar character, the M^I cations being replaced by $(Bi_2O_2)^{2+}$ sheets. The A or B elements can be easily substituted. Recently, Thomas and co-workers have studied related solids such as layered bismuth oxyhalides, $MBi_3O_4X_2$ ($M = Na, K, \ldots, X = F, Cl, Br$), which seem promising catalysts in hydrocarbon oxidation [12,13].

In the present paper, we report (i) the preparation of some of these phases and (ii) the first catalytic results in OCM.

2. Experimental

2.1. SYNTHESIS AND CRYSTALLOGRAPHICAL CHARACTERIZATION OF THE LAMELLAR $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ COMPOUNDS

This structural family with the general formula $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ belongs to the well known Aurivillius phase type [11] where a Bi_2O_2-layer is intercalated between $A_{n-1}B_nO_{3n+1}$ perovskite-like sheets with a thickness of n sharing corner octahedra. The relative disposition of these perovskite blocks is similar to that observed in the β $NaCa_2Nb_3O_{10}$ [14]. The relative shift between two adjacent layers is $ap/\sqrt{2}$ along the [110] axis. The texturing Bi_2O_2-layer is built up from BiO_4 square pyramids pointing alternatively along [001] and $[00\bar{1}]$ and sharing all their oxygenated vertices. The $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ network is schematically presented in fig. 1.

These bismuth compounds are synthesized in air, using a platinum crucible, from stoichiometric mixtures of Bi_2O_3, alkaline and alkaline-earth carbonates and transition metal oxide, at temperatures ranging from 1223 to 1423 K. It can be outlined that these bismuth phases are easy to prepare because it is not necessary to use an excess of one of the reagents as for $M^I(A_{n-1}B_nO_{3n+1})$ compounds. Furthermore, the reaction time can be reduced. Sixteen compounds, involving $n = 2$, 3 and 4 terms have been prepared. Other modifications involving changes of the A subarray (Ca, Sr, Ba) or changes of the Bi_2O_2-layer of Bi(III) by lone pair cations (Pb^{II}) and also in the thickness together with the chemical nature of the transition metal or the perovskite blocks have been carried out. As an example, substitution of tantalum for niobium decreases the covalency inside the MO_6 octahedra.

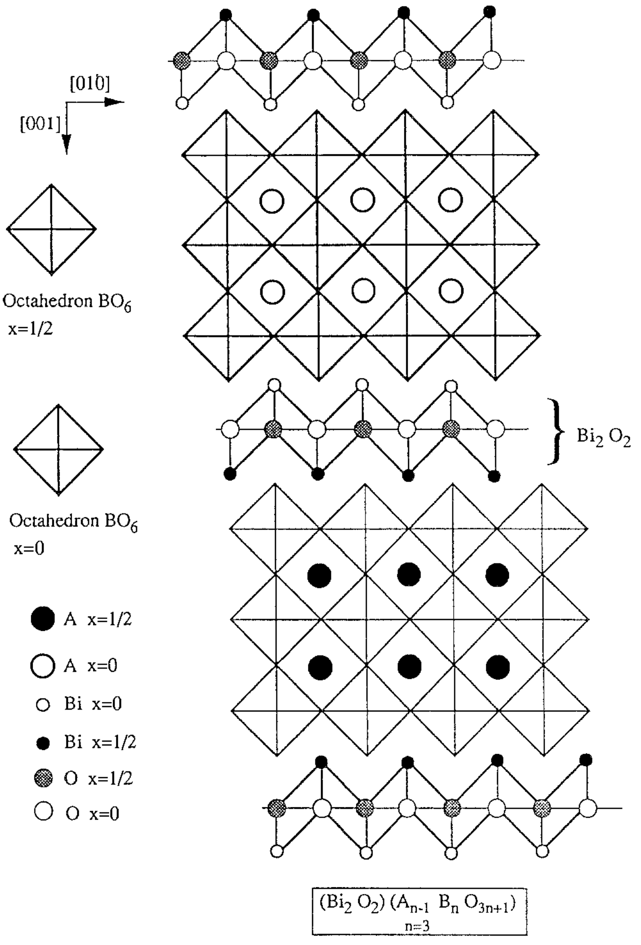


Fig. 1. Network of $Bi_2O_2(A_{n-1}B_nO_{3n+1})$ Aurivillius phases.

Furthermore, in order to check the specific area influence, one part of each preparation was finely ground. After this mechanical treatment, a slight broadening of the lines in the X-ray pattern was observed for some compounds. Cell parameters were determined from Guinier camera data recorded at room temperature. For some phases, the symmetry seems to be but is not tetragonal, whereas it appears orthorhombic for others. Indeed all the synthesized compounds were ferroelectric at room temperature, their symmetry is effectively orthorhombic. Cell parameters are given in table 1 together with the Curie temperatures [15] corresponding to the orthorhombic tetragonal phase transition.

2.2. OCM REACTION

The reaction has been carried out in conditions similar to those defined for $M^1(A_{n-1}B_nO_{3n+1})$ lamellar perovskites [9,10]. The reactant mixture of methane,

Table 1
Cell parameters of Aurivillius phase

Compounds	Pseudotetragonal symmetry		
	a (Å)	c (Å)	T_c (K)
$SrBi_2Nb_2O_9$	3.897(1)	25.085(2)	713
$SrBi_2Ta_2O_9$	3.908(1)	25.002(3)	608
$BaBi_2Nb_2O_9$	3.935(1)	25.613(3)	473
$BaBi_2Ta_2O_9$	3.930(1)	25.499(2)	383
$PbBi_2Ta_2O_9$	3.887(1)	25.368(2)	703
$SrBi_3Ti_2NbO_{12}$	3.863(1)	33.125(4)	≈ 473
$PbBi_3Ti_2NbO_{12}$	3.861(1)	33.459(5)	≈ 573
$SrBi_4Ti_4O_{15}$	3.849(1)	40.978(10)	803

Compounds	Orthorhombic symmetry			
	a (Å)	b (Å)	c (Å)	T_c (K)
Bi_3TiNbO_9	5.398(1)	5.440(1)	25.116(4)	≈ 1173
Bi_3TiTaO_9	5.400(1)	5.433(1)	25.177(3)	≈ 1123
$PbBi_2Nb_2O_9$	5.487(1)	5.503(1)	25.551(3)	833
$CaBi_2Nb_2O_9$	5.435(1)	5.482(1)	24.885(4)	≈ 873
$Bi_4Ti_3O_{12}$	5.408(1)	5.448(1)	32.826(6)	948
$CaBi_4Ti_4O_{15}$	5.412(1)	5.432(1)	40.716(6)	≈ 873
$PbBi_4Ti_4O_{15}$	5.431(1)	5.454(1)	41.384(6)	843
$Bi_5TiNbWO_{15}$	5.415(1)	5.410(1)	20.890(3)	

oxygen and helium (total flow rate: 25–100 ml/min, $CH_4/O_2 = 5$, $CH_4/He \approx 1$) was continuously introduced in a quartz fixed-bed reactor containing 0.5–1 g of catalyst. The temperature ranged from 773 to 1073 K and the total pressure was 0.1 MPa. The reaction effluents were analyzed on line with TCD and FID chromatographs.

3. Results

3.1. $Bi_2O_2(AB_2O_7)$ COMPOUNDS ($n = 2$)

3.1.1. Influence of the substitution in perovskites sites of $Bi_2O_2(ANb_2O_7)$ (A = Ca, Sr, Ba, Pb)

The results presented in table 2 show that the activity of compounds containing an A alkaline-earth element was quite similar. In addition, we notice that these materials are more active than the $M^I(A_{n-1}B_nO_{3n+1})$ phases [9,10]. When Pb occupy A sites, the activity is significantly decreased. Moreover, the selectivity in coupling increases particularly when Ba or Pb occupy the A position. With regard to the A cation size, the selectivity gradually increases from Ca phase to

Table 2
OCM in the presence of $Bi_2O_2(ANb_2O_7)$ and $Bi_2O_2(BaB_2O_7)$ Aurivillius phases. Conditions: $CH_4/O_2/He = 20/4/26$ ml/min, $P = 0.1$ MPa, $W_{catal} = 0.5$ g, $T = 1023$ K, (a) $T = 1073$ K

Catalysts	BET surface area (m^2/g)	Time (h)	Conversion (%)		Selectivity (%)				
			CH_4	O_2	C_2H_6	C_2H_4	C_3	CO	CO_2
$Bi_2O_2(CaNb_2O_7)$	5.5	4	14.5	83.4	30.9	14.5	–	–	54.6
	1.2	20	14.2	81.3	31.7	17.0	–	–	51.2
$Bi_2O_2(SrNb_2O_7)$	5.8	4	13.9	82.7	29.1	16.2	–	–	54.6
	1.3	20	13.6	75.3	30.5	17.7	–	–	51.8
$Bi_2O_2(BaNb_2O_7)$	3.7	4	14.1	75.1	36.8	18.3	1.1	0.2	43.6
	0.4	20	13.4	67.0	37.4	20.1	1.2	0.3	41.0
		(a)	14.0	100.0	23.0	17.0	1.2	0.7	58.1
$Bi_2O_2(PbNb_2O_7)$	7.3	4	9.6	57.4	36.0	18.7	–	0.2	45.0
	1.2	20	9.1	50.2	36.2	19.0	–	–	44.8
$Bi_2O_2(BaTa_2O_7)$	3.9	4	13.4	93.1	26.7	9.4	–	–	63.9
	1.2	20	14.5	89.0	28.6	12.2	–	–	59.2
		(a)	14.5	100	18.6	16.6	1.1	0.9	62.7

Ba phase, that is to say with the A ionic radius (r (Å): $Ca^{2+} = 0.99$, $Sr^{2+} = 1.12$, $Pb^{2+} = 1.20$, $Ba^{2+} = 1.34$). Lastly in spite of some changes in the CH_4 or O_2 conversion and in the selectivity at the beginning of the reaction, these catalysts (as for example $Bi_2O_3(BaNb_2O_7)$) have a rather good stability. The results in fig. 2 even show that the C_{2+} selectivity increases with time on stream.

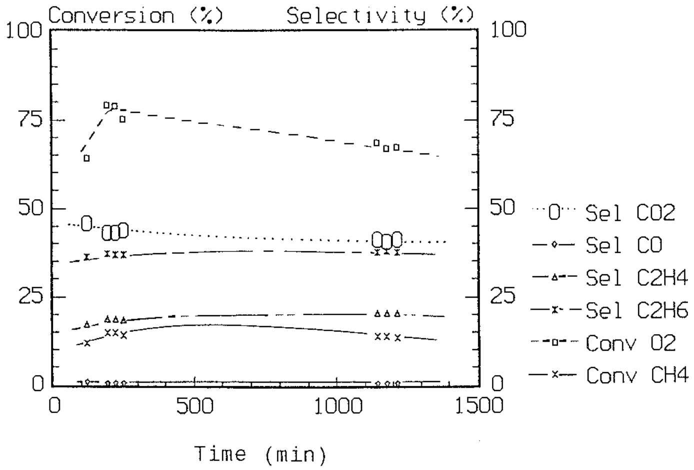


Fig. 2. Oxidative coupling of methane in presence of $Bi_2O_2(BaNb_2O_7)$. Reaction conditions: $T = 1023$ K, $CH_4/O_2/He = 20/4/26$ ml/min, $P = 0.1$ MPa, $W_{catal} = 0.5$ g.

Table 3
OCM in presence of Aurivillius phases. Effect of n and properties of mixed phases. Reaction conditions (see table 2). (a) $T = 1073$ K

Catalysts	n	Conversion (%)		Selectivity (%)				
		CH_4	O_2	C_2H_6	C_2H_4	C_3	CO	CO_2
$Bi_2O_2(Bi_2Ti_3O_{10})$	3	9.8	25.8	38.9	28.4	2.6	2.7	27.4
	(a)	17.5	76.8	21.5	37.6	4.9	5.8	30.1
$Bi_2O_2(BiSrTi_2NbO_{10})$	3	11.2	78.5	27.9	12.9	–	–	59.2
$Bi_2O_2(Bi_2PbTi_4O_{13})$	4	5.7	46.1	28.4	13.1	–	2.1	56.4
$Bi_2O_2(Bi_2SrTi_4O_{13})$	4	11.9	68.9	24.9	14.5	–	0.2	60.4
$Bi_3TiNbWO_{15}$	$n = 2$	6.3	32.1	40.5	23.4	1.9	4.2	29.9
	$m = 1$	6.7	22.2	37.4	22.9	2.0	5.3	32.4
	(a)	15.2	70.8	23.0	35.4	5.0	9.3	27.3

3.1.2. Influence of the substitution in octahedral sites of $Bi_2O_2(BaB_2O_7)$ ($B =$ Nb, Ta)

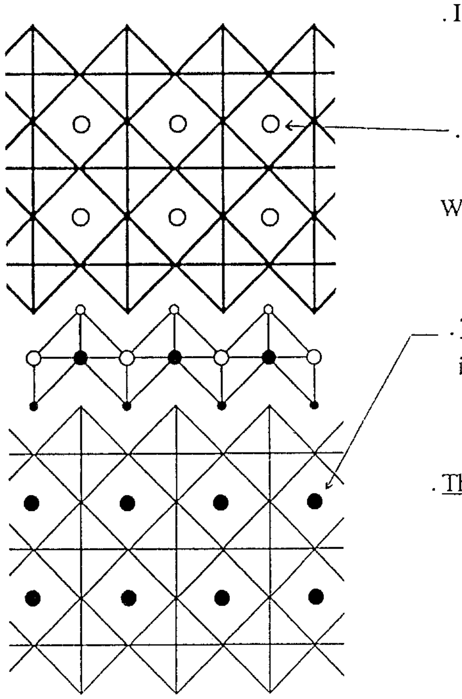
When tantalum is substituted for niobium, there is an increase of total oxidation reactions (table 2) and this selectivity change can result from the decrease of the covalency of the sheet containing Ta.

3.2. $Bi_2O_2(A_2B_3O_{10})$ COMPOUNDS; $n = 3$. EFFECT OF A DOUBLE SUBSTITUTION IN PEROVSKITE AND OCTAHEDRAL SITES

The Aurivillius phase $Bi_2O_2(Bi_2Ti_3O_{10})$ has a lower activity than the $n = 2$ term but the coupling of methane is greater (70%) than that obtained with $Bi_2O_2(BaNb_2O_7)$ (57.5%) (table 3). Because of this particularly high selectivity we have characterized these materials before and after OCM reaction. XRD and ESCA results do not evidence significant modifications of this solid during the reaction when the temperature is less than 1073 K. On the other hand if the reaction (or the pretreatment) temperature is increased up to 1273 K, the sample is sintered without any change in its chemical composition but, however, both the activity and the C_{2+} productivity are decreased.

3.3. $Bi_2O_2(A_3B_4O_{13})$ COMPOUNDS; $n = 4$

As for the ($n = 3$) phases presented above there is a diminution both of CH_4 conversion and of C_2 selectivity when Sr is replaced by Pb (table 3). Moreover, if we compare all the results describing the effect of n it seems that both the activity and the selectivity changes are rather similar to those obtained with lamellar perovskites $M^I(A_{n-1}B_nO_{3n+1})$; the increase of n favours the oxidation into carbon oxides [9,10].



. In usual conditions, methane conversion and selectivity lead too significant C_2 yield, especially with $Bi_4Ti_3O_{12}$.

. The substitution in perovskite sites (A) (n = 2 term)
With the increase of cation size A there is an increase of C_2 selectivity without change in the activity (except for Pb^{2+})

. The substitution in octahedral sites (B), if it induces an increase of sheet ionicity favours the total oxidation of CH_4 into carbon oxides.

. The double substitution in perovskite (A) and octahedral (B) sites (n = 3 ; Bi ---> Sr and Ti ---> Nb) increases both the activity and carbon oxides production.

Scheme 1.

3.4. $Bi_2O_2(A_{n-1}B_nO_{3n+1})$–$Bi_2O_2(A_{m-1}B_mO_{3m+1})$ MIXED COMPOUNDS. EXAMPLE $n = 2$, $m = 1$: $Bi_2O_2(BiTiNbO_7)$–$Bi_2O_2(WO_4)$

From results reported in table 3, the catalytic properties of $Bi_4Ti_3O_{12}$ and $Bi_3TiNbWO_{15}$ are rather similar except for the lower activity of the second sample.

4. Conclusions

Aurivilius phases $Bi_2O_2(A_{n-1}B_nO_{3n+1})$, with a structure similar to that of $M^I(A_{n-1}B_nO_{3n+1})$ [9,10] are easy to prepare and to modify. The catalytic results obtained in oxidative coupling of methane lead to the conclusions of scheme 1.

At first sight the last result (double substitution) could seem contradictory to the other conclusions. However, in that particular case, one may suppose that substitutions are statistical and produce some structural disorder. It results in an increase of the anionic mobility and an increase of total oxidation. Therefore the selective oxidation of methane into ethane and ethylene is sensitive to the substitution effects in perovskite or in octahedral sites. These results can be interpreted by changes of the basicity of the A–O or the B–O bonds; their increase favours the oxidative coupling of methane. But with such covalent materials it seems difficult to propose reaction steps occurring on very localized ionic species (A or B) especially at so high temperatures. We rather suspect that the active center could be a polaron in relation to a surface defect structure.

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