Catalytic properties of bismuth vanadates based catalysts in oxidative coupling of methane and oxidative dehydrogenation of propane

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The oxidative coupling of methane (OCM) and the oxidative dehydrogenation of propane (ODHP) have been performed on new mixed Bi–V oxides having a γ-Bi_2MoO_6-like structure. The results yield a correlation between the methane conversion and the oxygen diffusivity. The introduction of metals (Fe, Cu, Sr with 10 mol%) improves the C_2 selectivity. The use of an oxide with a scheelite structure ($BiVO_4$) shows that, under catalytic conditions, this oxide has the same behaviour as the above solids.

Keywords: Oxidative coupling of methane; oxidative dehydrogenation of propane; ionic conductors; oxygen diffusivity

1. Introduction

The very large reserves of natural gas throughout the world have induced the researchers to utilize methane, the principal constituent of this gas, for the production of useful chemicals instead of burning it. One of the most interesting ways is the conversion into C_2-hydrocarbons, the so-called oxidative coupling of methane (OCM). Since the pioneering work of Keller and Bashin [1], many types of catalysts, essentially alkaline oxides, alkaline earth oxides and rare earth oxides based catalysts, have been tested [2]. Dubois and Cameron have recently summarized the conditions which must lead to a highly active and selective catalyst for the OCM reactions [3]. Among these conditions, the diffusivity of the lattice oxygen is not the least [4,5]. Indeed, the generally admitted mechanism is the abstraction of one hydrogen of the methane by a surface oxygen species which can be regenerated by subsurface and bulk oxygen [6]. Ovsitser et al. have studied the oxygen diffusion in MgO and have found good correlation between the oxygen diffusion rate at 750 K and the degree of surface reduction

[7]. On the other hand, the oxidative dehydrogenation of propane (ODHP) is assumed to start by the same kind of hydrogen abstraction, and generally this ODHP is performed on vanadium oxide based catalysts. This paper presents some results in OCM and ODHP over new mixed Bi–V oxides based catalysts, which have a γ-Bi_2MoO_6-like structure and exhibit good anionic conductivity [8]. The addition of metals, such as Fe, Cu, Sr, does not change the structure, and good conductivity is retained at low temperature [9]. We compare the behaviour of these solids with that of an oxide having a scheelite structure ($BiVO_4$).

2. Experimental

2.1. CATALYSTS

Samples were prepared by solid state techniques. The starting materials were metallic oxides or carbonate (Bi_2O_3, V_2O_5 and CuO from Aldrich Chemicals, Fe_2O_3 and $SrCO_3$ from Jonhson Mattey) with purity $\geqslant 99.9\%$. Bi_2O_3 was prefired for decarbonatation at 873 K in air before use. The desired proportions were weighed and thoroughly mixed in an agate mortar and the mixtures were then heated in a gold crucible in air at 873 K for 15 h, reground and fired at 1120 K for 15 h. Purity of the compounds was checked by X-ray powder analysis using CuKα radiation.

Additive-free bismuth vanadates $BiVO_4$ and $Bi_4V_2O_{11}$, and partly V substituted $Bi_4V_2O_{11}$ derivatives designated by the acronym BIMEVOX [8,9] were prepared: a BICUVOX, a BISRVOX and a BIFEVOX corresponding to the nominal compositions $Bi_2V_{0.9}Me_{0.1}O_y$ with Me = Cu, Sr, Fe respectively. The O content is obviously correlated to the valency states of the cations: for Bi^{3+}, V^{5+}, $y = 5.35$ when Me is Cu^{2+} or Sr^{2+}, and $y = 5.40$ when Me is Fe^{3+}. These substitutions (V/Me) lead to the stabilization at 298 K of a γ-$Bi_4V_2O_{11}$ phase but anyhow, during the catalytic tests, all the compounds are in their high temperature structural form: scheelite-type for $BiVO_4$ with space group I_{4_1}/a [10] and γ-$Bi_4V_2O_{11}$ type for the other samples with space group I_4/mmm [8]. This latter structure consists of alternating (Bi_2O_2) layers and lacunar ($V(Me)O_{y-2}$) layers containing perovskite-like corner-linked VO_6 octaedra, in a similar manner as in the γ-Bi_2MoO_6 phase [11]. The crystal structure of $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ at 298 K is represented in fig. 1.

2.2. CATALYTIC TESTS

For OCM, the catalytic tests were carried out in an alumina microreactor, at atmospheric pressure and in a co-feed mode. Flow rates of gas (CH_4, O_2 and He from Air Liquide) were adjusted using Brooks flowmeters. Reactants and products were analyzed in-line with a Delsi IGC 121 ML chromatograph

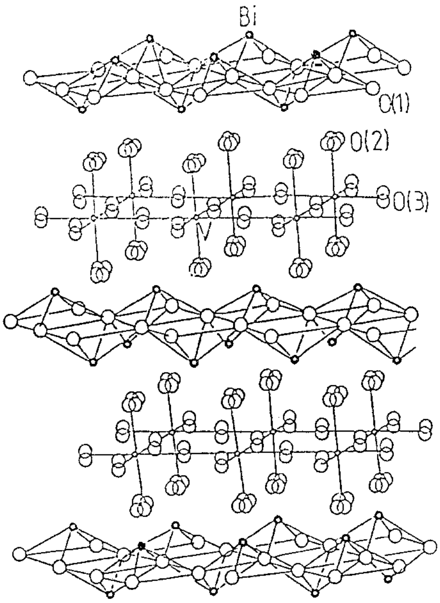

Fig. 1. Structure of $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$.

equipped with porapak and molecular sieve packed columns and a thermal conductivity detector. The partial pressure ratio of CH_4 to O_2 is 2, the total flow rate is 30 ml/min with 66% He and a mass of catalyst of 1 g. The temperatures used are 923 and 1023 K. For ODHP, the catalytic tests were performed in a stainless steel reactor, the $C_3H_8 : O_2 : N_2$ ratio is 5 : 15 : 80 and the total flow rate is 50 ml/min on 1 g of catalyst.

3. Results and discussion

The structure of γ-$Bi_4V_2O_{11}$ is the simplest example of an Aurivillius phase derivable from perovskite [12], and containing oxygen vacancies. Such an oxide can be implicated in the high mobility of lattice oxygen as previously described by Buttrey et al. [11]. This mobility is very important during the catalytic act of the OCM [13], and favoured by particular structures such as rock-salt, perovskite and pyrochlore types as demonstrated by Catlow et al. in computational studies [14]. The results obtained over $Bi_4V_2O_{11}$ for the OCM are summarized in table 1. The methane conversion is medium at 923 K (23%) and increases with the temperature. At 1023 K, the conversion is higher than over many pure basic oxides such as MgO or CaO [15], Sm_2O_3 [16] or La_2O_3 [17], comparable to the one obtained over some doped oxides [15,17], but remains lower than over some new solids which can lead up to 53% [18]. However, these high conversion values provide always a low C_2 selectivity, as predicted by Labinger and Ott who

Table 1
Oxidative coupling of methane over Bi–V–Me–O at various temperatures

Catalyst	CH_4 conversion (%)			C_2 selectivity (%)			C_2 yield (%)		
	923 K	973 K	1023 K	923 K	973 K	1023 K	923 K	973 K	1023 K
$BiVO_4$	8.5	26.5	35	11.5	18.5	19.8	1	5	7
$Bi_4V_2O_{11}$	23	29	37	20	21.6	22	4.6	6.3	8.1
$Bi_2V_{0.9}Fe_{0.1}O_{5.40}$	9.6	26.5	31.5	11.4	19.8	22.4	1.1	5.3	7.1
$Bi_2V_{0.9}Sr_{0.1}O_{5.35}$	9.6	26	32.6	16.9	23.1	24.8	1.6	6	8.1
$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$	17.8	33	39	15	23.6	28.2	2.7	7.8	11

forecast a C_2 yield limitation of about 25% [19,20]. So, at high CH_4 conversion, the production of CO_x is inevitable and the catalysts appear better described as total oxidation catalysts. Nevertheless, the C_2 yields obtained over $Bi_4V_2O_{11}$ are less than one third of the theoretical limit. Ito and Lunsford [21] have shown that the substitution of Mg^{2+} ions by Li^+ in the magnesium oxide crystal releases some electrons and, thus, increases its catalytic properties. We could then expect that the partial substitution of vanadium in the bismuth vanadate $Bi_4V_2O_{11}$ by cations of lower oxidation number will give rise to the same beneficial effect. We have previously shown that this substitution has an interesting influence on the structure. Indeed, on $Bi_4V_2O_{11}$, the disordered γ-form, which provides high anionic conductivity at high temperature, becomes ordered at low temperature (α and β forms) and the conductivity decreases drastically [8]. The partial substitution of vanadium by other metallic cations (Fe, Cu, Sr) stabilizes the high temperature disordered phase. As an example, the conductivity of BICUVOX reaches $1 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 510 K. Obviously, the numerous oxygen vacancies and the disordered character of this structural type are responsible for the high oxide ion conductivities [8,9].

Values of conductivity σ, deduced from complex impedence spectroscopy data, are reported in table 2 and were used combined with structural data [8] to calculate the corresponding oxygen diffusion coefficients D according to the Nernst–Einstein relation,

$$D = \sigma kT/Nq^2$$

with k the Boltzman constant, T the temperature (in K), N the concentration of

Table 2
Conductivity and diffusivity coefficient values of various solids

Compound	σ (Ω^{-1} cm^{-1})		$D \times 10^8$ (cm^2 s^{-1})	
	923 K	1023 K	923 K	1023 K
γ-$Bi_4V_2O_{11}$	0.186	0.224	82.47	110.08
$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$	0.144	0.2	66.70	102.68
$Bi_2V_{0.9}Fe_{0.1}O_{5.40}$	0.067	0.076	30.58	38.44
$Bi_2V_{0.9}Sr_{0.1}O_{5.35}$	0.012	0.038	5.56	19.51

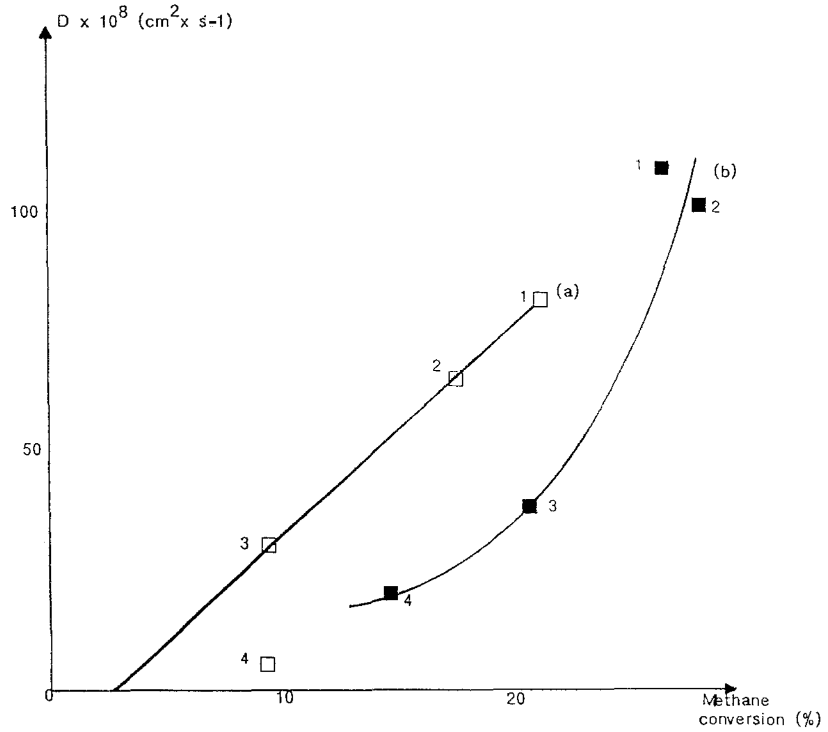

Fig. 2. Dependence of the diffusivity on the methane conversion at 923 K (a) and 1023 K (b) for (1) γ-$Bi_4V_2O_{11}$, (2) $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$, (3) $Bi_2V_{0.9}Fe_{0.1}O_{5.40}$, (4) $Bi_2V_{0.9}Sr_{0.1}O_{5.35}$.

the carriers (O(2) and O(3) oxygen as labelled in fig. 1) and q the charge of the carriers.

Methane activation needs much energy and, usually, a temperature range of 900–1000 K is used. At these temperatures, the oxygen diffusivity of $Bi_4V_2O_{11}$ is higher than those of BICUVOX (table 2). Nevertheless, the results obtained are very interesting as they show that the C_1 conversion varies linearly with the diffusivity coefficients (fig. 2). BISRVOX is a particular case and the solid probably undergoes a degradation during the catalytic test as proved by the change in the color. At temperature above 1000 K, the correlation is less linear probably because the total oxygen consumption makes the reaction limited. The curve of fig. 2 is in accordance with the importance of the diffusivity of lattice oxygen, and confirms that the layered structures facilitate the oxygen exchange as recently assumed by Dubois and Cameron [3]. The surface oxygen species probably lessen the charge difference with respect to the bulk species by giving their electrons to the superficial anionic vacancies which can react with the gaseous oxygen to create the reactive species oxanions. The oxygen transport number measurements performed on $BICUVOX_{0.10}$ and γ-$Bi_4V_2O_{11}$ have indicated that O^{2-} anions are the predominant charge carriers [9]. Movement of the oxygen species during the catalytic act has been evidenced by XPS. Indeed, the

Table 3
Reaction of propane over $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$

T (K)	Propane conversion (%)	Selectivity (%)		
		propene	CO_x	ethylene
723	2.6	42.2	58.4	–
773	6.5	26	75	2.5
823	11.7	24	68	17

results at room temperature show that the solid becomes a good conductor after test, unlike the initial solid. We have to notice, however, that the overall results of XPS and XRD do not reveal a new phase. That means the previous structure of these solids (γ-Bi_2MoO_6-like structure) is globally retained and the change which occurs during the catalytic act is the creation of vacancies probably by the help of migration of oxygen species. If the introduction of various cations into $Bi_4V_2O_{11}$ does not improve the C_1 conversion, it notably improves the C_2 selectivity. On $Bi_4V_2O_{11}$ the selectivity at 1023 K is twice the one at 923 K, whereas over BIMEVOX, it is five times as high. The present work does not yield a clear explanation of what precisely occurs. Surface potential measurements and the determination of the oxidation state of the cations (ESR and XPS techniques) will offer a better understanding.

It is generally admitted that the propane dehydrogenation mechanism starts in the same manner as that of methane. On the other hand, ODHP needs a much lower reaction temperature. So, we have tried to use BICUVOX (which has good conductivity at 700 K) as ODHP catalyst. Table 3 shows that, if the propene yield increases with the temperature, the CO_x remains the dominant product as on V_2O_5/TiO_2 (8% propene yield [22]) or V_2O_5/MgO (12% propene yield [23]), two well-known catalysts for the propane oxydehydrogenation. Probably, this can be explained by the easy abstraction of hydrogen (the first step in ODHP mechanism) in an allylic position in alkene, owing to the stable π complex intermediate proposed by Buttrey et al. [11] and Burrington et al. [24].

As a reference, $BiVO_4$ was also tested in the OCM reaction (table 1). Above 528 K, the transition temperature, this solid has a scheelite structure [9] and consists in regular Bi–O polyhedra and V–O tetrahedra. This oxide does not fill the structural demand as an oxygen ion conductor as previously said by Ueda et al. [25]. Yet, we can see from table 1 that pure $BiVO_4$ gives rise to about the same activity in OCM as the oxides with a layered-like structure. So, at high temperature, this oxide must present some mobility of lattice ions which occurs during the catalysis. This is reinforced by the work of Lu et al. who observed, with $BiVO_4$, good conductivity at high temperature [26]. This is not really surprising because our XRD analysis of $BiVO_4$ shows, after test, the simultaneous presence of the initial $BiVO_4$ and of a γ-$Bi_4V_2O_{11}$ phase. That means $BiVO_4$ has undergone some transformation which allows lattice oxide anion diffusion and explains that this oxide with an initial scheelite type structure at low temperature is a good catalyst for the oxidative coupling of methane at high temperature.

In conclusion, solid ionic conductors have an OCM activity which is depending on the diffusivity of lattice oxygen. This diffusivity is possible at high temperature with $Bi_4V_2O_{11}$ which has a layered structure similar to γ-Bi_2MoO_6, but also with $BiVO_4$ which presents some similarities. The introduction of copper, iron and strontium (10 mol% with respect to vanadium) improves the C_2 selectivity.

References

[1] G.E. Keller and M.M. Bashin, J. Catal. 73 (1982) 9.
[2] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuska and A.R. Sanger, Catal. Rev. Sci. Eng. 32 (1990) 163.
[3] J.L. Dubois and C.J. Cameron, Appl. Catal. 67 (1990) 49.
[4] G.W. Keulk, L.D. Krenzke and T.M. Noterman, Adv. Catal. 27 (1978) 183.
[5] V.D. Sokolovskii, React. Kinet. Catal. Lett. 35 (1987) 337.
[6] K.P. Peil, J.G. Goodwin Jr and G. Marcellin, J. Catal. 131 (1991) 143.
[7] O.Yu. Ovsitser, K.S. Guljaev and V.D. Sokolovskii, Catal. Lett. 8 (1991) 379.
[8] F. Abraham, M.F. Debreuille-Gresse, G. Mairesse and G. Nowogrocki, Solid State Ionics 28–30 (1988) 529; 40–41 (1990) 934.
[9] T. Iharada, A. Hammouche, J. Fouletier, M. Kleitz, J.C. Boivin and G. Mairesse, Solid State Ionics 48 (1991) 257.
[10] A.W. Sleight, H.Y. Chen and A. Ferretti, Mater. Res. Bull. 14 (1979) 1571.
[11] D.J. Buttrey, D.A. Jefferson and J.M. Thomas, Phil. Mag. 53 (1986) 897.
[12] B. Aurivillius, Ark. Kemi. 2 (1950) 519.
[13] E.S.R. Winter, J. Chem. Soc. A (1986) 2889.
[14] C.R.A. Catlow, R.A. Jackson and J.M. Thomas, J. Phys. Chem. 94 (1990) 7889.
[15] J.M. Deboy and R.F. Hicks, Ind. Eng. Chem. Res. 27 (1988) 1577.
[16] K.D. Campbell, H. Zhang and J.H. Lunsford, J. Phys. Chem. 92 (1988) 750.
[17] C.H. Lin, K.D. Campbell, J.X. Wang and J.H. Lunsford, J. Phys. Chem. 90 (1986) 534.
[18] J.L. Dubois, M. Baisiaux and C.J. Cameron, Chem. Lett. (1990) 967.
[19] J.A. Labinger and K.C. Ott, J. Phys. Chem. 91 (1987) 2682.
[20] J.A. Labinger, Catal. Lett. 1 (1988) 371.
[21] T. Ito and J.H. Lunsford, Nature 314 (1985) 721.
[22] A. Corma, J.M. Lopez-Nieto, N. Paredes, M. Pérez, Y. Shen, H. Cao and S.L. Suib, in: *New developments in Selective Oxidation*, Louvain 8–10/4/91, preprints.
[23] K.T. Nguyen and H.H. Kung, J. Catàl. 122 (1990) 415.
[24] J.D. Burrington, C.T. Kartisek and R.K. Grasselli, J. Catal. 81 (1983) 489.
[25] W. Ueda, K. Asakawa, C.L. Chen, Y. Moro-oka and T. Ikawa, J. Catal. 101 (1986) 360.
[26] T. Lu and B.C.H. Steele, Solid State Ionics 21 (1986) 339.