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Catalytic behaviour of BIMEVOX powders in the oxidative dehydrodimerisation of propene

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Abstract

Ionic oxide conductors of the BIMEVOX family are potentially interesting catalysts for selective oxidation of hydrocarbons in which the migration of lattice oxygen plays an important role. The catalytic performance in fixed bed reactor of $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ (BICUVOX) and $Bi_2Co_{0.1}V_{0.9}O_{5.35}$ (BICOVOX) in the oxidative dehydrodimerisation of propene has been studied. BICOVOX is more active and more selective to 1,5-hexadiene than BICUVOX but hexadiene is found at high temperature only. The characterisation of the catalysts before and after catalysis by XRD, TPD and TGA shows that this particular catalytic behaviour is related to their partial reduction.

Keywords: BIMEVOX; Ion oxide conductivity; Oxidative dehydrodimerisation of propene; 1,5-Hexadiene

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1. Introduction

Catalysts used in heterogeneous oxidation of hydrocarbons exhibit redox properties and their lattice oxygen mobility is a key parameter for activity as well as for selectivity. Ion oxide conductors may be good candidates to examine the influence of this parameter. A high oxygen ionic conductivity at moderate temperature (ca. 600 °C) is characteristic of a family of oxides referred to as BIMEVOX, which are derived from bismuth vanadate $Bi_4V_2O_{11}$ by partial substitution of vanadium with other ME metals [1,2]. Their structure can be described as alternated $(Bi_2O_2)^{2+}$ layers and $(VO_{3.5}\square_{0.5})^{2+}$ ($\square$ = oxygen vacancy) perovskite-like sheets, the high oxide ion conductivity found in the γ-polymorph being associated with these oxygen vacancies. Much work has concentrated on the BICUVOX system, the maximum conductivity being reached with $Bi_2Cu_{0.1}V_{0.9}O_{5.35}$, which was examined as a catalyst in the oxidative coupling of methane and oxidative dehydrogenation of propane [3].

In a former paper [4] we have presented a study of the oxidative dehydrodimerisation (ODD) of propene to 1,5-hexadiene (HXD) on BICUVOX and BICOVOX showing that the formation of HXD is related to the partial reduction of the solids, in accordance with results obtained by EPR spectroscopy and TPD experiments. This study is completed here by the influence of other operating parameters on the reaction regimes, and more details are given on their solid-state behaviour (XRD before and after treatment under reaction mixture, TPD before and after propene adsorption, and TGA in redox conditions). The same samples with low surface area ($0.2\,m^2/g$) have been used because of their behaviour as dense membranes which is examined in a parallel study carried out in a catalytic dense membrane reactor [5].

2. Experimental

The catalytic experiments were carried out in the conventional flow set-up using stainless-steel fixed bed reactor and on-line analysis with a gas chromatograph as described previously [4]. The volume of the catalyst bed was 1 ml and contact times were varied between 0.5 and 6 s at 1 bar with gas mixtures of $O_2/C_3H_6/N_2 = 7.5/22.5/70\text{-}15/15/70$. The conversion of reactants and the selectivity to products were determined in the temperature range 300–550 °C. Powders of BIMEVOX (Me = Cu, Co) were prepared by conventional solid-state synthesis from oxides at 600 °C and

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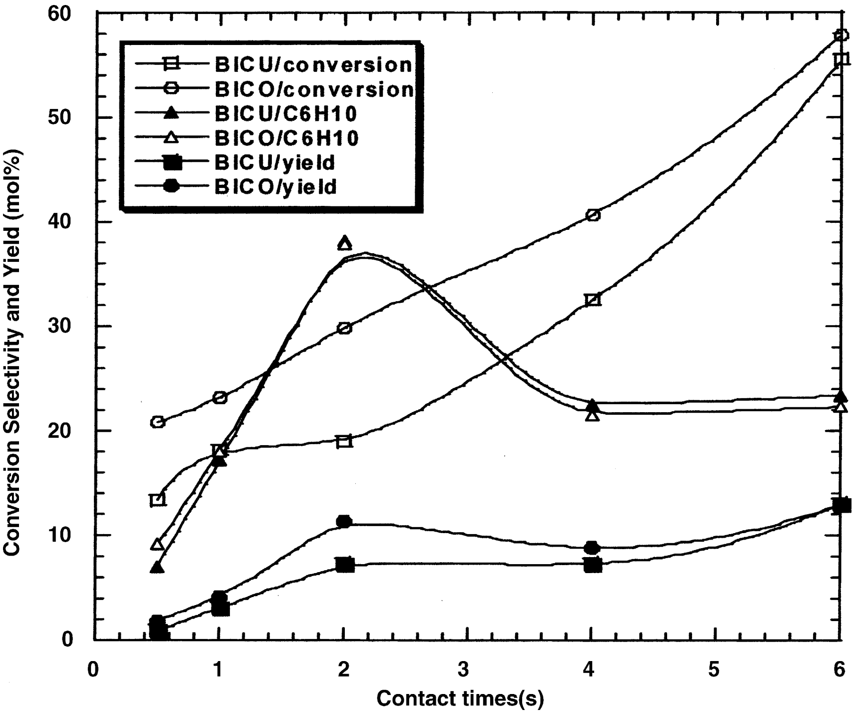

Fig. 1. Influence of contact time τ at 550 °C on propene conversion, selectivity and yield to HXD on BICUVOX and BICOVOX ($O_2/C_3H_6 = 1/2$).

then at 850 °C as previously described [4]. The morphology and composition of fresh and used catalysts was examined by SEM equipped with X-emission spectrometer. Thermogravimetric analyses (TGA) were carried out in redox conditions by heating fresh catalysts up to 500 °C at 3 °C/min and then in isothermal conditions at 500 °C, under 0.1 l/h of reducing (N_2:C_3H_6 = 90:10), followed by oxidising (0.1 l/h of N_2:O_2 = 90:10) gaseous mixture. For temperature programmed desorption (TPD) of specie, fresh catalyst samples were heated at 10 °C/min after 1 h degassing at 300 °C and then treated in N_2:C_3H_6 = 90:10 (0.1 l/h) at two different temperatures (100 and 300 °C). The desorbed specie were

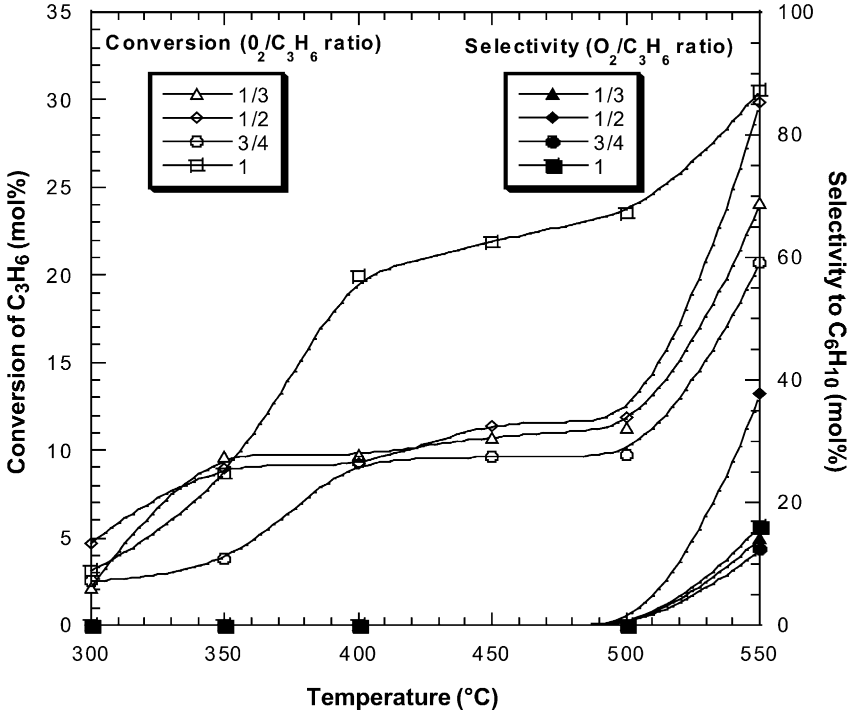

Fig. 2. Influence of the initial O_2/C_3H_6 ratio on propene conversion and selectivity to HXD vs. temperature (τ = 2 s); case of BICOVOX.

analysed by a quadripole mass spectrometer. X-ray diffraction (XRD) diffractogramms of fresh and used catalysts were obtained using Cu Kα radiation, and high temperature XRD was performed on used catalysts in oxygen flow (1 l/h) up to 600 °C at 0.2 °C/s (Cu Kα).

3. Results

3.1. Catalytic reaction

The conversion of propene, the selectivity and yields to 1,5-hexadiene versus contact time τ at 550 °C are shown in Fig. 1 for BICOVOX and BICUVOX catalysts. Their surface area which is 0.2 m^2/g does not change after catalysis. The complement to 100 mol% is mainly due to CO_2 ($CO_2/CO \approx 10/1$). The conversion of propene increases continuously with contact time while the selectivity to HXD passes through a maximum at $\tau = 2$ s. The decreasing selectivity when τ increases is probably due to HXD degradation to CO_x at high contact time ($\tau \geq 4$ s). BICUVOX is less active, and less selective to HXD than BICOVOX at the same conversion. For example, at $C = 30$ mol%, $S_{HXD} = 36$ and 24 mol%, respectively; yields to HXD are higher with BICOVOX than with BICUVOX at all contact times.

The influence of O_2/C_3H_6 on the conversion of propene and selectivity to HXD was examined versus temperature for various O_2/C_3H_6 ratios at the optimal contact time (2 s). In the case of BICOVOX (Fig. 2), two main domains are seen: (i) the propene conversion increases and then is constant between 350 and 500 °C, and CO_2 is mainly produced ($S_{CO_2} \approx 100$–92 mol%), (ii) the conversion increases sharply above 500 °C and selectivity to HXD increases while that to CO_2 decreases. The selectivity to CO remains low and approximately constant at all temperatures, and when HXD is formed methane is also produced but in very small amounts [4]. The conversion of oxygen increases with T, up to 100 mol% when $T \approx 400$ °C, whatever the O_2/C_3H_6 ratio. This two regimes trend does not vary much with O_2/C_3H_6 ratio in the examined 0.33–1/1 range (Fig. 2) and it is also observed when using BICUVOX. Again, BICOVOX is more selective (38 mol%) and give higher yields (11.3 mol%) of HXD than BICUVOX.

3.2. Temperature programmed desorption

TPD experiments were performed on fresh BICUVOX and after adsorption of propene at 100 or 300 °C. A small amount of oxygen begins to escape from the fresh sample above 570 °C (Fig. 3a). After adsorption of C_3H_6, the amount of desorbed oxygen and its desorption rate increase with the temperature of adsorption. Therefore, the lattice oxygen mobility depends on the reduction degree and, as expected, the diffusion of bulk oxygen becomes faster after adsorption at 300 °C. CO_2 desorbs from the fresh catalyst ca. 515 °C (Fig. 3b) and, as in the case of oxygen, its amount increases with the temperature of propene adsorption. Weakly bound CO_2 specie are desorbing between 220 and 500 °C but the main peak is located at 515 °C. Therefore, the amount of CO_2 which evolves from the fresh sample is greater when propene has been adsorbed. The desorption of HXD is not observed on fresh sample nor when propene has been adsorbed at 100 °C and the latter simply desorbs at high temperature. HXD desorbs at 670 °C but only after treatment by propene at 300 °C (Fig. 3c). Summarising these TPD results, all the adsorbed propene is converted into CO_2, but also into C_6H_{10} after adsorption of propene at 300 °C, that is when the lattice oxygen becomes more mobile (in vacuum). In interrelationship with the fact that, at this temperature, V^{5+} are reduced into V^{4+} as seen by TGA, we suppose that this V^{5+}/V^{4+} couple plays a role in the ODD of propene.

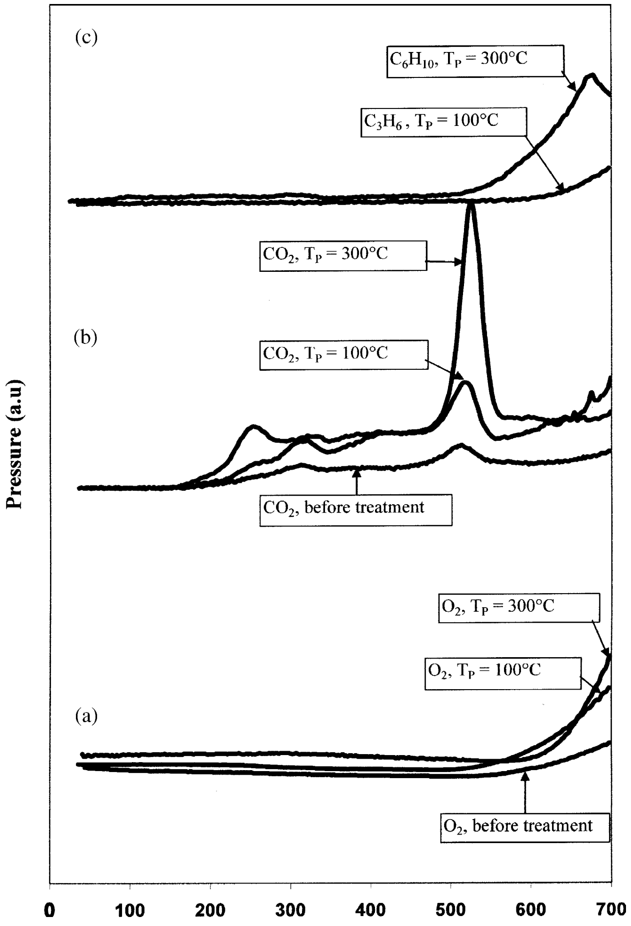

Fig. 3. TPD curves before and after treatment by propene at $T_P = 100$ and 300 °C: (a) oxygen desorption, (b) carbon dioxide desorption, (c) HXD and propene desorption; case of BICUVOX.

3.3. Characterisation by XRD and SEM

XRD patterns of fresh samples confirm the formation of the expected γ-$Bi_2Cu_{0.1}V_{0.9}O_{5.35}$ and γ-$Bi_2Co_{0.1}V_{0.9}O_{5.35}$ phases. After a whole set of catalytic experiments (e.g.

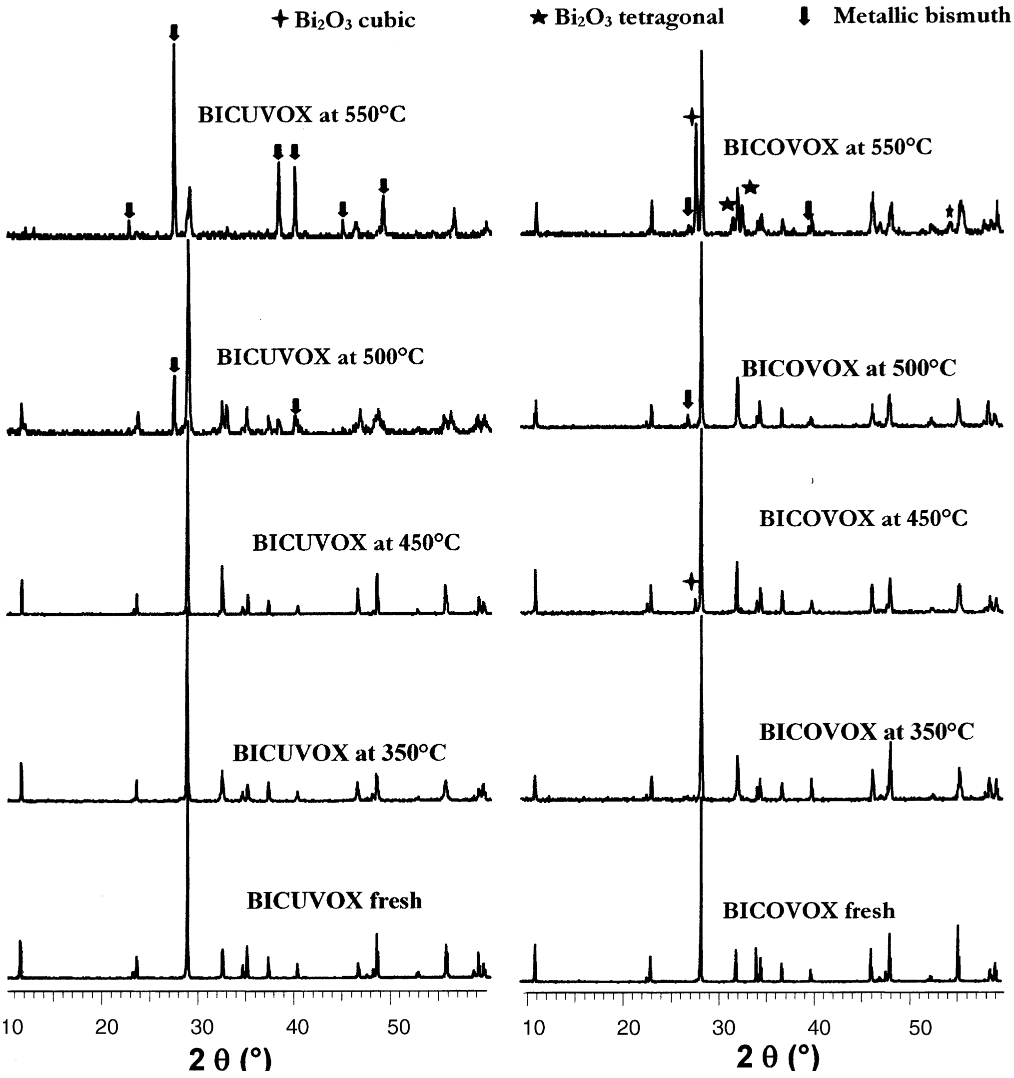

Fig. 4. HT-XRD diffractogramms before and after catalytic treatment at $T_T = 350$–$550\,^{\circ}$C: (left) BICUVOX, (right) BICOVOX.

variation of τ or O_2/C_3H_6) performed on the same sample, the colour initially orange of BIMEVOX darkens only (ME = Co) or becomes black (ME = Cu). On SEM images of used BICUVOX catalysts are observed small spheres (Ø ≈ 1 μm) which are characteristic of metallic bismuth, as confirmed by XRD [4,6,7]. Another set of samples was also examined by XRD: the solids were treated for 20 mn in the reactor in the optimum catalytic conditions ($\tau = 2$ s, C_3H_6:O_2:N_2 = 20:10:70) at given treatment temperatures: T_T = 350, 450, 500 and 550 °C (Fig. 4). Lines of metallic bismuth occur clearly besides BICUVOX lines when $T_T \geq 500\,^{\circ}$C. In the case of BICOVOX samples treated at the same respective T_T only BICOVOX lines were observed up to 500 °C. Weak lines of metallic Bi occur only at $T_T = 550\,^{\circ}$C, besides few weak lines belonging to cubic and to tetragonal Bi_2O_3. The occurrence of bismuth oxide lines means probably that some metallic Bi was formed temporarily but that, in the catalytic operating conditions, enough oxygen was present to reoxidise it as bismuth oxide.

The re-oxidation of BICOVOX samples used in a whole set of catalytic experiments was followed by HT-XRD in pure oxygen. Interestingly, mainly the lines of BICOVOX appear (besides weak lines of $Bi_8V_2O_{17}$ phase), which means that used BICOVOX can be regenerated in oxygen. Similar work is in progress with BICUVOX.

3.4. Thermogravimetric analysis

In reducing conditions, BICOVOX loses only 0.8% and its weight is stable for 2.5 h at 500 °C. The re-oxidation starts at very low temperature (ca. 60 °C) but it is not complete ($\Delta m/m \approx 0.65\%$ after 2 h at 500 °C). As the theoretical weight loss during reduction of all V^{5+} to V^{4+} is $\Delta m/m = 1.3\%$, the final formula after reduction in these conditions would be $Bi_2Co_{0.1}V^{5+}{}_{0.3}V^{4+}{}_{0.6}O_{5.05}$. On the contrary, the reduction of BICUVOX, which at first is smooth like that of BICOVOX (1.3% at 450 °C), becomes deeper (rate 0.25 wt.% per mn) and the final weight loss

(9.8%) is stabilised in 1.4 h at 500 °C. At this temperature the reduction of Cu^{2+} to Cu proceeds (theoretical $\Delta m/m = 0.29\%$ for $Cu^{2+} \rightarrow Cu$) as shown by EPR spectroscopy [4]. Therefore ca. 85% of Bi^{3+} are reduced to Bi^0 (reduction of all Bi^{3+} for $\Delta m/m = 8.6\%$). The re-oxidation begins at 200 °C and is not complete ($\Delta m/m = 5.8\%$). These experiments show that BICUVOX is reduced faster than BICOVOX and that not only vanadium is concerned as in the latter, but also copper and a part of Bi^{3+}.

4. Discussion

In selective oxidation of unsaturated hydrocarbons, it is rather unusual that by increasing temperature the deep oxidation precedes selective oxidation because most often the formation of CO_2 is the result of consecutive degradation of adsorbed intermediates. The two regimes are observed here when temperature varies in the examined conditions of O_2/C_3H_6 and contact times [4], and apart from the fact that higher yields of HXD are found with BICOVOX, the two catalysts behave similarly. In the literature, there is a general agreement on the role of Bi^{3+} which is to promote the abstraction of α-hydrogen of an alkene to produce an allylic intermediate [8]. This intermediate can be a substituted olefin, or it may dimerise to form, e.g., 1,5-hexadiene. Generally, cations with a saturated d electronic configuration like in Sn, Cd, Tl, Bi, In, Pb and Hg oxides are responsible for this abstraction, which is due to the optimum value of lattice oxygen nucleophilicity [8]. It was proven that propene dimerisation could process in the absence of oxygen but that the catalysts deteriorate quickly. Moreover, the decomposition of this intermediate is directed towards acrolein or hexadiene depending on the Lewis acidity of the transition metal cation when present in the catalyst, whereas the deep oxidation is mostly depending on the energy of oxygen on the surface [8]. When the temperature is low ($T_R \leq 450\,°C$) these weakly bound oxygens are present and deep oxidation proceeds as long as gas O_2 is fed. Indeed, as BIMEVOX are very poor electronic conductors, there are little available electrons to promote the full reduction up to O^{2-}, and then electrophilic specie are formed on catalysts. At these temperatures, even though HXD is formed as shown by TPD (after C_3H_6 adsorption or after catalytic reaction [4]), it is burnt by surface electrophilic specie. When T_R is higher, propene begins to reduce the solid and VO^{2+} appear as shown by EPR on catalysts at 500 or 550 °C [4]. The resulting oxygen vacancies can be replenished by diffusion of bulk O^{2-} and/or by gaseous oxygen. The latter process is often faster than the former, the more so when enough neighbouring V^{4+} are associated to vacancies, which is the case of reduced ($VO_{3.5-\delta}\square_{0.5-\delta}$) layers in BIMEVOX:

$$4V^{4+} + O_2 + 2\square \rightarrow 4V^{5+} + 2O^{2-}$$

However, if the ionic oxide conductivity is high enough, bulk diffusion is also fast and the two processes may occur in the same time. This is the case of BIMEVOX in which ion conductivity takes place in the two-dimensional perovskite layers while the oxygens of bismuth oxide layers are frozen and do not take part in the diffusion. The difficulty found with all bismuth-based oxides (except perhaps bismuth molybdates) is that bismuth can be reduced [4–8]. In the case of BICOVOX the reduction rate of Bi^{3+} is low, contrary to BICUVOX in which copper is also reduced. Finally, BICOVOX is more active (at all temperatures) than BICUVOX although its reduction is slower. The reason could be that, although poor, its electronic semi-conductivity is p while it is n-type for BICUVOX [9]. Therefore, if gaseous dioxygen is more easily converted to O^{2-} the turn-over on BICOVOX is increased, and higher HXD yields result.

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