Oxidative dimerisation of propene to 1,5-hexadiene on Bi–Zn–O catalysts

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The oxidative dimerisation of propene to 1,5-hexadiene has been investigated on Bi–Zn–O catalysts. The $Bi_{48}ZnO_{73}$ phase, observed in the catalysts calcined at 700°C is an active and selective catalyst for the formation of 1,5-hexadiene. The best catalytic performance (1,5-hexadiene selectivity $\approx 64\%$) has been obtained at 525°C, with a propene to oxygen ratio of 26, on a catalyst formed by $Bi_{48}ZnO_{73}$ with a small excess of ZnO.

Keywords: Oxidative propene dimerisation; 1,5-hexadiene; Bi–Zn–O; $Bi_{48}ZnO_{73}$; kinetic behaviour

1. Introduction

The catalytic mild oxidation of propene to acrolein or acrylic acid has been extensively investigated in the past decades [1,2] since these products are of great interest for chemical industry. The catalysts used were mainly molybdenum oxide based. Studies have shown that the reaction proceeds in two different steps [1,2]. The first step, which is generally expected to be rate controlling [1–4], consists of the abstraction of one allylic hydrogen from the propene molecule. The resulting intermediate has been identified to be an allyl radical [4–7] which can desorb in the gas phase or migrate on the surface [7,8]. The second step, which strongly depends on the nature of the catalytic sites, can lead to the formation of acrolein or to a deeper oxidized product such as allylic acid or carbon oxides. A Lewis acid site is needed to stabilize the allyl radical through the π-electron of the C=C double bond [9]. In the absence of such sites,

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the allyl radical can either desorb in the gas phase to form the 1,5-hexadiene by coupling with another radical [7] or react with molecular oxygen, to form the carbon oxides in the gas through an allyl peroxy radical intermediate [10]. Consecutive secondary reactions can also occur by the cyclization of 1,5-hexadiene to form 1,3-cyclohexadiene which leads to the formation of benzene by dehydrogenation.

The catalysts able to perform this reaction have been reviewed by Mamedov [11]. Bismuth oxide based catalysts appear to be the most interesting [3,12–15]. According to the previous mechanism, two different reaction modes have been used to produce 1,5-hexadiene: (i) cofeed mode, i.e. continuous flow of propene and oxygen [3,14], (ii) redox mode: sequential flow of propene (catalyst reduction) and oxygen (catalyst reoxidation) [14–16]. The first mode seems to be industrially more attractive (fixed bed catalyst, continuous flow), but the main problem is the low selectivity obtained when oxygen is present in the gas phase.

In this paper, we have investigated the possibility of forming 1,5-hexadiene by oxidative dimerisation of propene on bismuth oxide based catalysts using the cofeed mode.

2. Experimental

The catalysts were prepared by either impregnation or coprecipitation (samples hereafter referred to as I or C respectively). The impregnated samples were prepared by the incipient wetness method with an aqueous nitrate solution acidified by HNO_3 to pH 1 (to solubilize the nitrate). Various supports have been used, including Sm_2O_3 (Aldrich), MgO (Aldrich), ZnO (Aldrich), SiO_2 (Aerosil 200, Degussa), α-Al_2O_3 and γ-Al_2O_3 (both supplied by Rhône-Poulenc). After impregnation, the wet solid was then dried in air at 80°C for 2 h and finally calcined overnight in air at 500 or 700°C to produce samples I-500 and I-700 respectively.

The coprecipitated samples were prepared from an aqueous mixture of bismuth and zinc nitrates acidified to pH 1 by HNO_3. The precipitation was performed by addition of ammonia in concentrated aqueous solution (26 N) to pH 8. The precipitate was separated by filtration, then dried 2 h at 80°C and finally calcined overnight in air at 500 or 700°C to give samples C-500 and C-700 respectively. In addition, unsupported bismuth oxide (α-Bi_2O_3) was prepared by a calcination overnight of hydrated bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) in air at 600°C. The bismuth content was expressed as an atomic percentage: $100 \times Bi/(Bi + Zn)$ calculated from the chemical weight composition by assuming that bismuth and zinc are engaged in their respective oxides Bi_2O_3 and ZnO.

The X-ray diffraction patterns were recorded with an automatic diffractometer (Siemens D 500) using the Cu $K\alpha_1$ radiation.

The catalytic measurements were performed in a fixed bed continuous flow reactor working in isothermal conditions. The composition and the flow rate of the reactant mixture (He, O_2 and propene) were obtained by adjusting the flow rate of each component with mass flow controllers (RDM 280–Alphagaz–Air Liquide). A computerized gas chromatographic system built in the laboratory was used to analyze the reaction products. The catalytic results are expressed relatively to the consumption of propene.

The BET surface area (measured by N_2 adsorption) of the samples calcined at 700°C, was always found in the 1 ± 0.5 m^2/g range. For these low values of the BET surface area, the systematic error due to the apparatus can be estimated to be of the same order of magnitude as the differences between the catalysts. By consequence, the rates of products formation are expressed in mmol per hour and per gram of catalyst (mmol/h/g).

3. Results

3.1. CATALYTIC BEHAVIOUR OF BISMUTH OXIDE UNSUPPORTED OR SUPPORTED ON VARIOUS SUPPORTS

The supported samples first investigated were prepared by impregnation and were calcined at 500°C. They contain 2.5 at% of bismuth. The catalytic experiments were performed at 400°C ($C_3H_6/O_2/He = 21/3/76$ mol%). The catalytic behaviour is characterized by a poor selectivity in 1,5-hexadiene ($< 2\%$) for the supports alone (Sm_2O_3, MgO, ZnO, γ-Al_2O_3, SiO_2, Bi_2O_3) except for the pure bismuth oxide (9%). Bismuth oxide supported on zinc oxide shows the best selectivity (12.4%) amongst the catalysts studied. These preliminary results point out the ability of the Bi_2O_3–ZnO catalysts for the oxidative dimerisation of propene to 1,5-hexadiene. The catalytic study of this system is presented above.

3.2. INFLUENCE OF THE PREPARATION METHOD FOR ZINC CONTAINING CATALYSTS

The catalytic results are gathered in table 1 for the samples containing 9.7 at% of bismuth. The preparation method (impregnation or coprecipitation) seems to play only a minor role, compared to the calcination temperature, on the catalytic behaviour. Whatever the preparation method (I or C), the best selectivities in 1,5-hexadiene are obtained after the 700°C calcination.

It must be noticed that the samples calcined at 500°C, and especially the impregnated ones, are rapidly deactivated with a strong decrease in 1,5-hexadiene selectivity. By contrast, neither deactivation nor selectivity variation are observed for the samples calcined at 700°C. However, the initial catalytic

Table 1
Influence of the preparation method and the reaction temperature (T_R) on the catalytic behaviour of the 9.7 at% Bi/ZnO catalyst. $He/O_2/C_3H_6 = 76.6/2.7/20.7$ (mol%)

Catalyst	T_R (°C)	Selectivity (%)			
		1,5-hexa.	1,3-cyclohexa. + benzene	total ODP	carbon oxides
I-500	450	22.0	6.0	28.0	68.8
	475	25.9	7.0	32.9	62.2
I-700	450	30.9	1.1	32.0	62.7
	475	33.0	5.6	38.6	54.5
	525	27.7	6.9	34.6	50.8
C-500	450	18.9	6.1	25.0	72.0
I-700	450	27.8	1.1	28.9	66.1
	475	29.1	3.2	32.3	62.1
	525	30.1	8.3	38.4	49.4
	575	15.1	3.2	18.3	52.5

behaviour of the catalysts calcined at 500°C can be regenerated by a 2 h treatment in oxygen at 450°C.

The data of table 1 were measured after about 30 min on stream.

The X-ray diffraction patterns of the catalysts show the superposition of the α-Bi_2O_3 and ZnO patterns for the samples calcined at 500°C. The samples calcined at 700°C exhibit a totally different pattern. The diffraction lines of α-Bi_2O_3 have disappeared and a new pattern, assigned to the compound $Bi_{48}ZnO_{73}$ [17], is visible in addition to that assigned to ZnO (fig. 1).

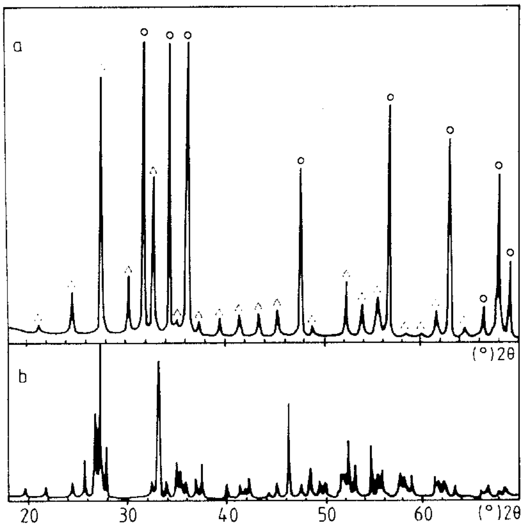

Fig. 1. XRD patterns of (a) 5.7 at% Bi/ZnO catalyst (C-700), (△) $Bi_{48}ZnO_{73}$; (○) ZnO; (b) α-Bi_2O_3.

Table 2
Influence of the sum of the partial pressures of propene and oxygen and of the propene to oxygen ratio on the catalytic behaviour in the oxidative dimerisation of propene. $T_R = 525°C$

Catalyst	$P_{C_3H_6}+P_{O_2}$ (atm)	$P_{C_3H_6}/P_{O_2}$	Selectivity (%)				$S_{1,5\text{-hexa.}}/S_{1,3\text{-cyclohexa.+benzene}}$
			1,5-hexa.	1,3-cyclohexa. +benzene	total ODP	CO_x	
C-700							
Bi = 9.7 at%	0.24	7.7	30.1	8.3	38.4	49.4	3.6
I-700	0.24	7.7	27.7	6.9	34.6	50.8	4.0
Bi = 9.7 at%	0.24	3.3	19.6	8.8	28.4	60.2	2.2
	0.24	1.0	12.0	5.1	17.1	75.0	2.3
C-700	0.44	28	45.0	4.7	49.7	43.2	9.6
Bi = 13.1 at%	0.58	18	34.0	7.5	41.5	47.9	4.5
C-700	0.44	28	51.4	1.9	53.3	35.7	27
Bi = 89 at%	0.22	26	63.6	2.3	65.9	25.6	28

3.3. KINETIC STUDY

We have studied the influence of the reaction temperature (table 1), the propene to oxygen ratio, and the partial pressure of reactants on the catalytic behaviour of the Bi/ZnO catalysts calcined at 700°C (table 2). For both kinds of catalysts (I and C), the selectivity in 1,5-hexadiene strongly depends on the reaction temperature and passes through a maximum in the 475–525°C temperature range. The secondary reactions, which tend to decrease the 1,5-hexadiene selectivity, seem to be favored by the increase of the reaction temperature. However, the selectivity for the total coupling products (1,5-hexadiene + 1,3-cyclohexadiene + benzene), which gathers all the products obtained from the oxidative dimerisation of propene (total ODP), is maximum in the same temperature range.

At 525°C, the 1,5-hexadiene selectivity increases with the propene to oxygen ratio. In the same time, a low partial pressure of both reactants favors the 1,5-hexadiene selectivity. For the highest values of the propene to oxygen ratio (large excess of propene), we have observed the total consumption of oxygen. In this case, the conversion of propene is managed by the initial quantity of oxygen in the reactants. The relative importance of the secondary reactions to the primary 1,5-hexadiene formation can be estimated by the ratio of the 1,5-hexadiene selectivity to the sum of the selectivities for the products resulting from the cyclization of 1,5-hexadiene, i.e. 1,3-cyclohexadiene and benzene. We have observed that this ratio increases with the propene to oxygen ratio. By contrast, the value of the total partial pressure of the reactants does not seem to change the 1,5-hexadiene to the cyclization products ratio.

3.4. INFLUENCE OF THE COMPOSITION

The influence of the catalyst composition was systematically studied ($T = 525°C$, $C_3H_6/O_2/He = 41.5/1.5/57$ mol%, $C_3H_6/O_2 = 28$) for the samples C-700 to optimize the 1,5-hexadiene production. As mentioned above, the XRD analysis has shown the presence of two distinct crystalline phases (ZnO and $Bi_{48}ZnO_{73}$) for bismuth contents less than 95 at%. In the 95–98 at% range, only $Bi_{48}ZnO_{73}$ can be detected by XRD and for higher bismuth content, only α-Bi_2O_3 is detected. Surprisingly, a small excess of bismuth seems to transform the $Bi_{48}ZnO_{73}$ phase into α-Bi_2O_3. The ZnO phase is no longer visible by XRD in these catalysts since the quantity present is too small to be detected.

The catalytic results are shown in fig. 2. The 1,5-hexadiene selectivity rapidly increases with the bismuth content until about 20 at%, and then increases slower until the $Bi_{48}ZnO_{73}$ composition (90–95 at%). A small excess of bismuth further, this composition dramatically decreases the selectivity down to that obtained for unsupported bismuth oxide. The selectivity for the cyclic products follows a different trend, passing through a maximum in the 15–25 at% range. By consequence, the evolution of the selectivity for the total ODP (1,5-

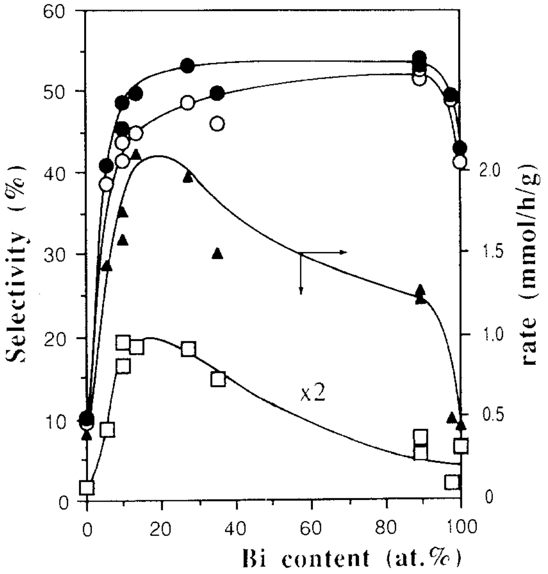

Fig. 2. Variations of the selectivities and the 1,5-hexadiene formation rate in the oxidative dimerisation of propene (ODP) on Bi–Zn–O catalysts, as function of the bismuth content, for the C-700 catalysts. $T = 525°C$, $C_3H_6/O_2/He = 41.5/1.5/57$ (mol%). (○) 1,5-hexadiene, (□) 1,3-cyclohexadiene + benzene, (●) total ODP, (▲) 1,5-hexadiene formation rate.

hexadiene + 1,3-cyclohexadiene + benzene) is slightly different from that of 1,5-hexadiene. After the rapid increase until 20 at%, the selectivity reaches a plateau which falls down beyond 95 at% when the XRD pattern of $Bi_{48}ZnO_{73}$ disappears to the benefit of the α-Bi_2O_3 one.

The maximum rate of formation of 1,5-hexadiene is obtained for 15–25 at% Bi, and then decreases slowly with the bismuth content until the $Bi_{48}ZnO_{73}$ composition, which appears as a limit. A small excess of bismuth drastically changes the catalytic properties by decreasing together activity and selectivity.

4. Discussion

It appears from these catalytic results that the $Bi_{48}ZnO_{73}$ phase seems to be a selective catalyst for the oxidative dimerisation of propene to 1,5-hexadiene, since the best selectivities in 1,5-hexadiene are obtained for the samples where the $Bi_{48}ZnO_{73}$ is observed alone and a small further increase in the bismuth content of this composition leads to both a decrease in the selectivity and a change in the XRD pattern from $Bi_{48}ZnO_{73}$ to α-Bi_2O_3.

The large domain where the ODP selectivity is maximum (20–95 at%) indicates that the $Bi_{48}ZnO_{73}$ phase is likely located at the surface of the catalyst particles which can be considered, in this composition domain, as $Bi_{48}ZnO_{73}$ supported on ZnO. This hypothesis is consistent with the data of table 1, which show a slightly higher 1,5-hexadiene selectivity for the I-700 catalyst where the bismuth containing phase must be essentially located at the surface of the catalyst particles after the impregnation procedure. However, the secondary reactions of cyclization which conduct to the formation of 1,3-cyclohexadiene and benzene, seem to be favored by the simultaneous presence of ZnO and $Bi_{48}ZnO_{73}$. By consequence, the highest selectivity in 1,5-hexadiene requires the smallest quantity of ZnO excess which is needed to completely engage the bismuth into the $Bi_{48}ZnO_{73}$ phase, since a small excess of bismuth leads to the formation of only unselective α-Bi_2O_3.

The crystalline structure of the $Bi_{48}ZnO_{73}$ phase is close to the high temperature β form of Bi_2O_3, which is stable at temperatures above 735°C. It can be easily obtained by heating α-Bi_2O_3 above this temperature [17], but cooling below 735°C, reversibly transforms it into α-Bi_2O_3 again.

In the $Bi_{48}ZnO_{73}$ oxide, the role of the Zn atoms seems to be maintaining of the β-structure of bismuth oxide at temperatures lower than 735°C. This possibility has been already mentioned by doping α-Bi_2O_3 with small quantities of cations such as V, Al, or Pb [18]. The dramatic decrease of 1,5-hexadiene selectivity within a small range of excess bismuth, suggests that the catalyst should not contain any traces of free α-Bi_2O_3 to be selective and that the best selectivity requires a small excess of Zn to transform all the bismuth oxide into $Bi_{48}ZnO_{73}$.

5. Conclusion

We have shown that the compound $Bi_{48}ZnO_{73}$ is an active and selective catalyst for the oxidative dimerisation of propene to 1,5-hexadiene. The crystalline structure of this phase is close to the high temperature β form of Bi_2O_3, which is unstable in the reaction conditions. The role of zinc is probably to stabilize the β form at lower temperature. The best catalytic performances have been obtained for a reaction temperature in the range 500–550°C with a propene to oxygen ratio of 26.

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