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Competition between molecular and anionic diffusion of oxygen in a catalytic membrane reactor for oxidation reaction

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Abstract

A microreactor with two chambers separated by a disc of catalyst has been made and included in a catalytic test with on-line analysis by gas chromatography. The oxidative dimerization of propene in benzene and hexadiene has been studied using a disc of Bi–La–O catalyst. The results show that conversion of propene is higher (45–70 mol.-%) than in conventional reactors with co-fed oxygen. The selectivity in 1,5-hexadiene and benzene is also higher because of a lower amount of CO_2. The deactivation of the catalyst is examined.

1. Introduction

Membrane reactors provide the possibility of coupling reaction and separation. Several applications are known, and restricting to gas–solid reactions a pioneering work has been made by Gryaznov et al. [1]. When selectivity towards a given product is an important factor, as in mild oxidation of hydrocarbons (C–H), an improvement of the catalyst performance can be obtained by avoiding contact between reactants. Co-fed oxygen can indeed react with C–H in the homogeneous phase and/or be responsible for unselective processes. It has recently been demonstrated that, when n-butane oxidation is carried out in a circulating fluid bed reactor, the selectivity to maleic anhydride is higher than with conventional co-feed (butane and air) reactors [2,3]. Recently, several research teams have used catalytic membrane reactors (CMR), made with two chambers separated by a porous ceramic support on which is deposited a catalytic layer of oxide. They have shown that the catalytic performance is improved in several cases [4–7]. However, this CMR concept can be explored in another way which is to use the active phase itself as a 'membrane'. This has been understood by Di Cosimo et al. [8], who were the first to experiment with a CMR in an oxidation reaction. They used bismuth oxide-based solids, which are known to catalyze the oxidative dimerization of propene in usual reactors, but also to deactivate quickly [9–13]. After having built the reactor and included it in a catalytic test [14] we have examined the feasibility of this reaction on lanthanum-doped bismuth oxide, and tried to determine the role of diffusion of oxygen species.

2. Experimental

The microreactor (inconel) was made of two chambers (I) and (II), separated by the catalytic

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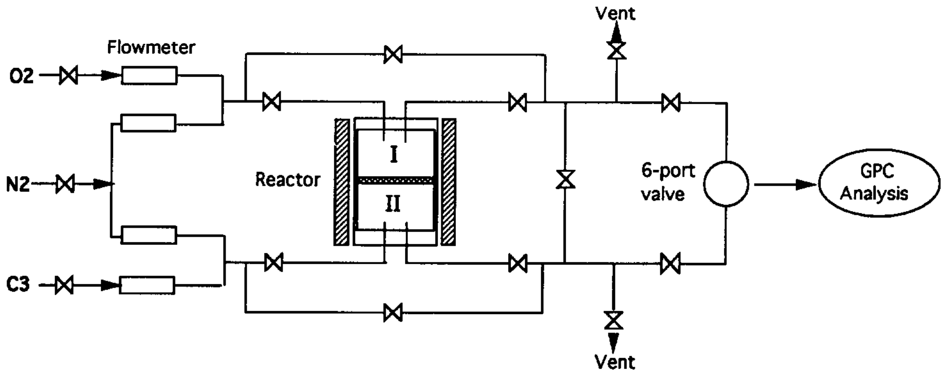

Fig. 1. Catalytic test with the catalytic membrane microreactor and analysis of feed and effluents by on-line gas chromatography.

disc displayed in an insert, and which were fed respectively, by (I) O_2+N_2 and (II) propene $+N_2$. The disc was sealed in the insert with a sealing glass, and two nickel gaskets ensured the tightness of the insert in the chambers. The reactor was heated by an electric furnace regulated at 0.5°C. The rates were controlled by mass flow meters. Two gas circuits allowed to analyze the feed entering and leaving each chamber of the reactor by on-line gas chromatography, using a 6-port gas sampling valve (Fig. 1). The experimental procedure was as follows: one chamber, e.g. (II), was fed with the mixture C_3/N_2 and analysis was performed on the other side (I) of the disc in order to detect any leak. The effluent leaving the other chamber was similarly analyzed. In this way no compound like, e.g., C_3 or N_2, has been detected on side (I). The reactor was then heated at 500°C and maintained at this temperature for at least 2 h before the experiments were carried out [14]. The feed rates were 0.21 l/h, with $C_3/N_2=20/80$ and variable O_2/N_2 (0–80%). A new catalytic disc was used for each new value of O_2/N_2. Contact times were between 1 and 10 s, and pressure close to 1 atm.

The catalyst $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ (BiLaO) was prepared in three steps [8]. A solution of bismuth and lanthanum nitrates first acidified by 10% of HNO_3 was heated with stirring at 80°C. NH_4OH was added dropwise so that the pH increased from 1 to 4. The white precursor precipitated and was filtered after concentration of the mixture, washed with distilled water and dried in an oven (110°C, 12 h). The solid residue was calcined up to 290°C (4 h) and to 425°C (16 h). The manually ground powder was calcined at 800°C during 16 h and ground again after cooling ($\varnothing < 45$ μm). At this stage the solid solution was obtained, as checked by XRD. The powder was then pressed into disks ($\varnothing$ 13 mm, thickness 2 mm) under 9 tons/cm^2, and then sintered at 800°C (16 h) in a furnace in air. The mean mass of solid used was 1.7 g and surface area measured by BET method was 0.2 m^2/g after sintering. Solids were analyzed before and after the catalytic test by several methods (X-ray diffraction, infrared spectroscopy and scanning electron microscopy coupled with X-emission spectroscopy).

3. Results

3.1. *Catalytic results*

The operating conditions were 500°C, O_2/N_2 variable in (I) and $C_3/N_2=20/80$ in (II). The contact time was fixed at 5 s. The main products obtained in side (II) were benzene and 1,3-hexadiene (called C_6-dimers), and CO_2. Very low amounts of acetic acid, acrolein and CO were detected (< 1 mol.-%).

The variation of conversion of propene and selectivity in C_6-dimers with time is shown Fig. 2 ($O_2/N_2=1/1$). Initially, the conversion of pro-

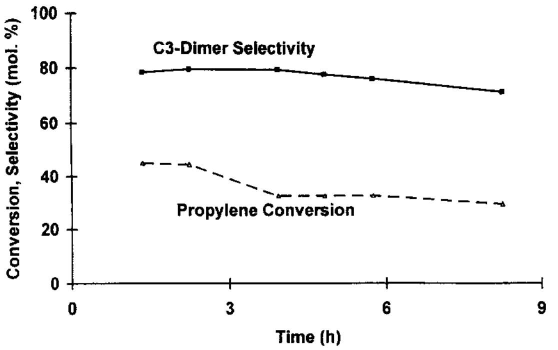

Fig. 2. Conversion of propene and selectivity in C_6-dimers vs. time with BiLaO catalyst (500°C, $O_2/N_2=50\%$, $C_3/N_2=20/80$, $\tau=5$ s).

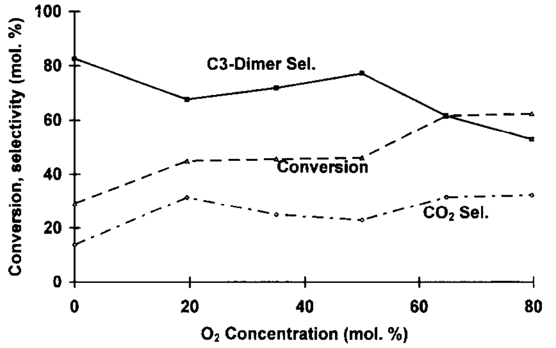

Fig. 3. Conversion of propene and selectivities in C_6-dimers and CO_2 vs. O_2/N_2 (mol.-%) (other conditions as in Fig. 1).

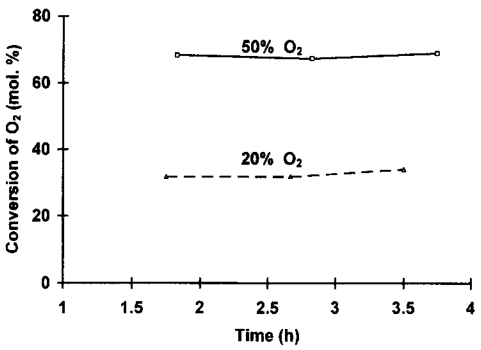

Fig. 4. Conversion of molecular oxygen on side (I) for $O_2/N_2=20$ and 50 mol.-% vs. time (other conditions as in Fig. 1).

pene is 45 mol.-%, and then it decreases slightly with time on stream. The selectivity in C_6-dimers stays at a high value (79 mol.-%) and then begins to decrease. The trend, a slight decrease with time, followed by conversion and selectivities vs. time is very similar for various values of O_2/N_2. In absence of oxygen feeding in (I) the selectivity in C_6-dimers is high ($S_{\mathrm{dim}}=82$ mol.-%) but the conversion of propene is lower (28 mol.-%) (Fig. 3), and the catalyst deactivates quickly. The catalytic behavior depends on the range of O_2 concentration when O_2/N_2 is varied. With a composition close to that of air ($O_2/N_2=21/79$) the conversion of propene is higher than without oxygen ($C=43$ mol.-%), and S_{dim} is close to 70 mol.-%. At 20–50% of O_2, selectivity increases slightly up to the optimum value ($S_{\mathrm{dim}}=79\%$ for $O_2/N_2=1/1$). Higher O_2 concentrations lead to a decrease of S_{dim} (Fig. 3). During experiments with $O_2/N_2=20$–50% the oxygen is not totally converted (Fig. 4), and when plotted against time its conversion is constant. It could mean either that short-circuit exists (that is all oxygen is not used by the solid nor transferred to the other side), and/or that sites able to convert gas oxygen to bulk oxygen are not numerous enough.

3.2. *Catalyst characterization and ageing*

After preparation and calcination, the solid solution BiLaO was identified by comparison of its XRD pattern with ASTM file no. 40-321. Its IR spectrum is very close to that of δ-Bi_2O_3, in accordance with the hypothesis of a solid solution of this type. SEM pictures show that the surface of the pressed disc is smooth at first and has a glassy aspect. At higher magnification however several pores are seen, with mean dimensions $\varnothing=1$–7 μm (Fig. 5a,b).

After catalytic experiments (20 h) several changes in the samples are noted by various methods (Table 1). The color changes from yellow to brown (I) or black (II). More pores and cracks are observed by SEM. Metallic bismuth is detected by XRD (ASTM file no. 5-519), and its lines are superimposed to those of the solid solution BiLaO and of La_2O_3 (in small amount). No difference is seen whatever the side (I) or (II) of the disc observed, which is due to the fact that XRD is a bulk method of identification. SEM pic-

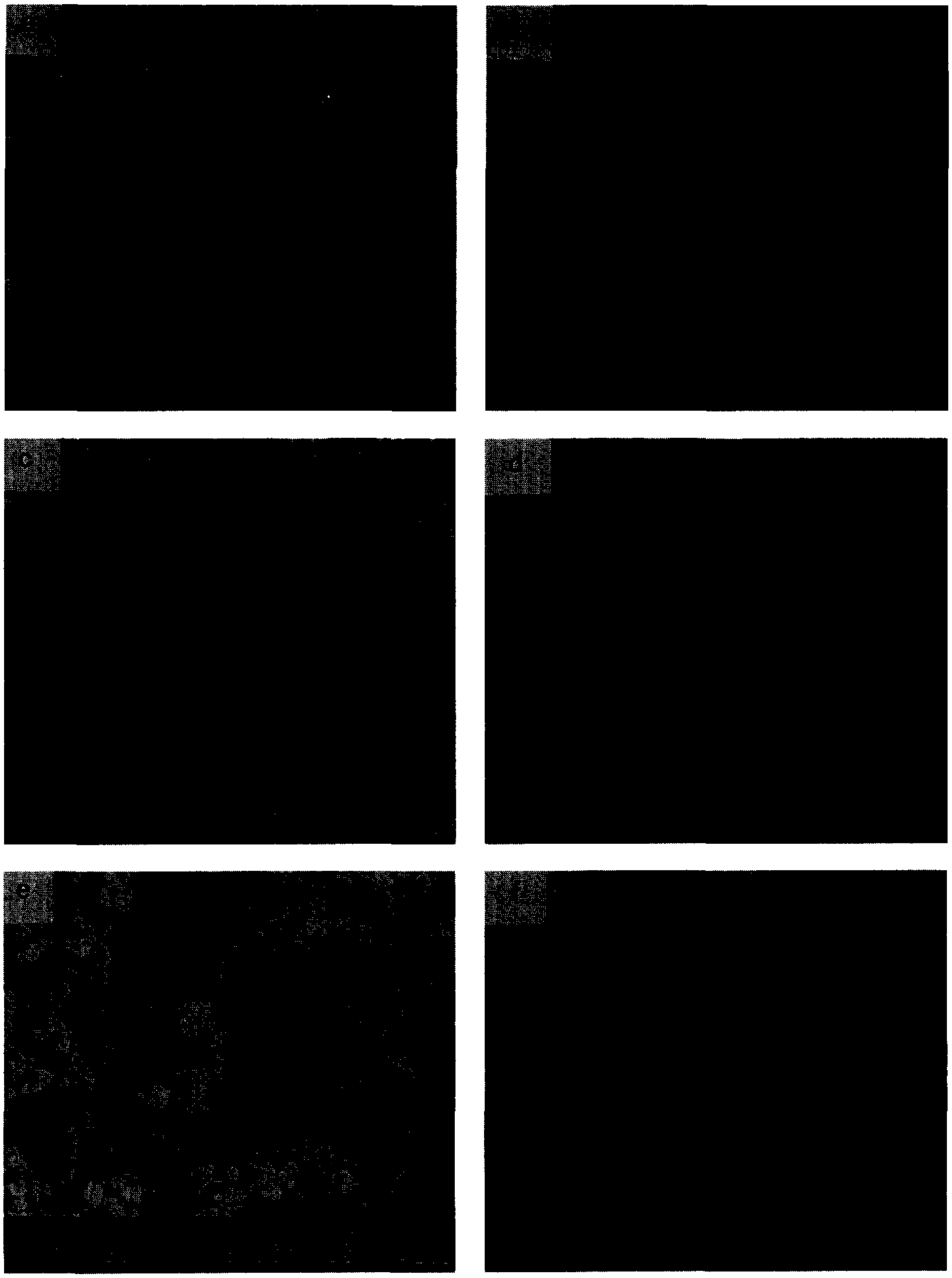

Fig. 5. SEM pictures showing several aspects of BiLaO. Before catalytic experiments (a,b), after catalytic experiments (c–f); on oxidation side (I) (c,d) and on reaction side (II) (e,f).

tures of reaction side (II) show that Bi^0 develops as spheres of mean diameter $\varnothing = 1$–4 μm (Fig. 5c,d). Crystal plates are distinctly seen on the oxidation side (I) and the glassy aspect before test has now disappeared (Fig. 5e). Few spheres are also observed, but of smaller size ($\varnothing \approx 0.5$–1.5 μm) than on (II). Some needles are seen growing from them (Fig. 5f). These needles could come from the reoxidation of metallic Bi but there is no experimental evidence, like XRD lines of a bismuth oxide, to confirm this point.

Table 1
Characterization of the catalyst on the two sides (reaction and oxidation)

	Before reaction	After reaction	
		Reaction side	Oxidation side
Colour	Yellow	Black–brown	Brown
XRD	Solid solution: $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$	Solid solution + Bi^0 (+ La_2O_3)	
SEM	Smooth, no cracks, pores (∅ < 4 μm)	Cracks, Bi spheres (∅ < 5 μm)	Plates, Bi spheres, with growing needles

4. Discussion

It can be said, at least in first approximation, that catalysts of selective oxidation are anionic conductors by oxygen (O^{2-}). In that sense bulk (and not only surface) lattice oxygens are involved in the reaction as selective species. Moreover, they necessarily possess semiconducting properties to allow the ionization of molecular oxygen. The δ form of Bi_2O_3 (fluorite type) chosen for the present experiments exhibits mainly ionic conductivity, which is enhanced by lanthanides. Adding Ln = Y, La, Gd, Dy, Er, Tm, Yb leads also to its stabilization [15–17].

Inside the CMR, oxygen vacancies are created on reaction side (II) by the conversion of propene molecules into water and, e.g., benzene. If oxygen is fed on side (I) in the same time, the supply of O^{2-} by means of anionic diffusion through the bulk is supposed to replenish surface vacancies in (II). At the steady state, a dynamic equilibrium between the supply of active oxygens from side (II) to the surface of (I) and their removal by reaction must be settled. Without oxygen in (I) and when time of reaction increases, the propagation of more and more vacancies through the bulk would result in the reduction $Bi^{3+} \rightarrow Bi^0$. Similarly metallic bismuth will occur if in (I) the activation of molecular oxygen, or the anionic diffusion of O^{2-}, are inefficient processes. The structural characteristics of the aged BiLaO catalysts show that Bi^0 is indeed present. This means that the catalyst deactivates by reduction, although at a lower rate than in conventional fixed bed reactors [9–13].

It is interesting to compare our catalytic results with those given in [8]. The selectivity in C_6-dimers is comparable since it reaches values close to 80 mol.-%. On the contrary, although the operating conditions were chosen similar, the conversion of propene, and so the yield in C_6-dimers, is by far higher: the best conversion of propene is 45 mol.-% at 500°C instead of 3.2 mol.-% at 600°C [8]. These promising results could mean that many active and selective sites were present on (II), although the surface area is low. Similarly, one could think that the rate of anionic diffusion of O^{2-} through the bulk after activation of O_2 on side (I) is fast enough to ensure the replenishment of vacancies by selective bulk oxygens. However, considering the physicochemical characteristics of the solid after testing led us to modify these explanations. First, the presence of metallic bismuth on aged catalysts shows that the production of vacancies on (II) is not balanced by the rate of O^{2-} diffusion from (I). Moreover, the conversion of oxygen on side (II) is not complete, which means that sites for activation of oxygen are not numerous (and/or active) enough. Second, the presence of several cracks in the solid discs (SEM) after test could account for molecular diffusion (O_2) instead of anionic diffusion (O^{2-}). However, O_2 has never been detected on side (II) and the selectivity in CO_2 is always low. In a co-fed regime the production of carbon dioxide is generally attributed to the formation of unselective species like O^- or O_{2-} due to activation of O_2 on surface vacancies. For the present case the supply of O_2 to side (II) could be controlled by diffusion through the cracks. The result would be a kind of 'on request' distribution of O^{2-} after activation of O_2 by the surface.

Acknowledgements

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