Improved catalysts for \( n \)-butane oxidation to maleic anhydride

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**Introduction**

Vanadyl pyrophosphate \((\text{VO})_2\text{P}_2\text{O}_7\) is the main component of the industrial catalyst for the selective oxidation of \( n \)-butane to maleic anhydride. Various structural and morphological characteristics affect the catalytic behavior of the V/P/O system, but the most important one is the presence of a slight excess P with respect to the stoichiometric amount required for the vanadyl pyrophosphate formation. In this regard, we recently reported that the key point to obtain a moderately active but highly selective catalyst is the in-situ generation, under reaction conditions, of discrete amounts of \( \delta \)-\( \text{VOPO}_4 \) on the vanadyl pyrophosphate surface, and that the generation of this \( \text{V}^\circ \) phosphate is favored in the presence of the abovementioned P excess [1,2]. In order to further improve the catalytic performance of the industrial catalyst, we doped the vanadyl pyrophosphate with controlled amounts of a Nb\(^V\) compound, precursor for the generation of Nb or mixed Nb/V\(^V\) phosphate [3]. The latter compound might facilitate the generation of the desired \( \delta \)-\( \text{VOPO}_4 \) compound. Raman in situ treatments with equilibrated vanadyl pyrophosphate catalyst (P/V>1), showed the transformation of the hydrated oxidized phase into \( \delta \)-\( \text{VOPO}_4 \) over the catalyst surface, under oxidizing atmosphere [1].

**Experimental**

The V/P/O catalyst was prepared according to the procedure described in refs [1,2]; the Nb-doped V/P/O were prepared by adding the desired amount of Nb\(^V\) salt to the slurry containing \( \text{V}_2\text{O}_5 \), \( \text{H}_3\text{PO}_4 \) and isobutanol. We also prepared a sample using NbCl\(_5\) as the Nb source and using a mixture of solvents (20% v/v of 1,4-butane diol and 80% v/v of isobutanol). Catalysts were prepared varying the V/Nb molar ratio (\( \infty \), 150, 80, 46, 17). Catalysts were characterized by means of X-Ray Diffraction, Raman and UV-Vis Diffuse Reflectance Spectroscopy. Catalytic experiments were carried out in a continuous flow reactor, under \( n \)-butane lean reactive mixture (1.7% \( n \)-butane, 17% oxygen, remainder He). Raman characterizations and in-situ tests were carried out using a Renishaw 1000 instrument equipped with a commercial Raman cell (Linkam Instruments TS1500).

**Results and discussion**

Catalytic results (figure 1, left) evidenced that the effect of Nb dopant, a promoter for both activity and selectivity to maleic anhydride (MA), was not simply proportional to its concentration: different factors, regarding the preparation method of catalyst precursor, may influence it. Best performance was obtained with the sample prepared using 1,4-butane diol (O80Cl): this catalyst showed higher activity, and higher MA yield as well; this effect was interpreted as being due to the retention of organic molecules between precursor layers, which caused the development of a peculiar morphology [4]. The results indicated that an increase of Nb content (V/Nb = \( \infty \)-80), led to a better selectivity to MA at low reaction temperature (<400°C), whereas at higher temperature (440°C) a positive effect of Nb was observed only for very low Nb concentration (V/Nb = 150). In fact, Nb favored the development of oxidized \( \text{VOPO}_4 \) compounds (especially of the desired \( \delta \)-\( \text{VOPO}_4 \)), but under more oxidizing reaction conditions the amount of the latter was excessive, finally leading to a worse selectivity to MA. In fact, the catalyst containing the greater amount of Nb (V/Nb = 46) gave

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a worse selectivity at both low and high temperature, being it already largely oxidized. Thus, we demonstrated that the optimal amount of Nb was a function of reaction conditions (temperature, inlet composition). Characterization of fresh and used catalysts showed that the increasing quantity of Nb not only favored the formation of \( \delta-\text{VOPO}_4 \), but also stabilized it. This effect was not always beneficial for catalyst performances: an excessive amount of the oxidized compound led to over-oxidation of reactants and product, lowering MA yield.

The formation of \( \delta-\text{VOPO}_4 \), which is supposed to be involved in the surface redox mechanism with \((\text{VO})_2\text{P}_2\text{O}_7\) (but only when the former is present in small amount, dispersed over the latter), was further investigated by carrying out in-situ Raman experiments, feeding either air or the reactive mixture, and also varying the percentage of the reactants in the inlet feed (n-butane and oxygen). We found that i) Nb favored the formation and the stabilization of \( \delta-\text{VOPO}_4 \) patches over catalyst surface (figure 1, right), and ii) Nb rendered the re-oxidation of superficial vanadyl pyrophosphate easier, finally improving MA selectivity. An important remark is that heterogeneity of the catalyst surface has to be taken into account when in-situ experiments are carried out using Raman spectroscopy.

Figure 1. Left: MA selectivity as a function of n-butane conversion for Nb doped samples (V/Nb=\( \infty \), 150, 80, 46) and 100% isobutanol) and O80Cl (V/Nb=80, using 20% v/v 1,4-butanediol and 80% v/v isobutanol). Right: in-situ Raman spectra of Nb-doped sample (V/Nb=46) recorded during isothermal step (air, 380°C); symbols: *\((\text{VO})_2\text{P}_2\text{O}_7\); \( \delta=\delta-\text{VOPO}_4 \).

References


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