

Doping vanadyl pyrophosphate with Nb^V: improved efficiency of the catalyst for *n*-butane oxidation to maleic anhydride

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Introduction

Vanadyl pyrophosphate 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 δ -VOPO₄ on the vanadyl pyrophosphate surface, and that the generation of this V^V phosphate is favoured in the presence of the forementioned 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 δ -VOPO₄ compound.

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 NbCl₅ to the slurry containing V₂O₅, H₃PO₄ and isobutanol, raw materials for the the synthesis of the vanadyl pyrophosphate precursor. Catalysts were prepared with atomic V/Nb ratio equal to 44. Catalysts were characterized by means of X-ray Diffraction, Raman Spectroscopy and UV-Vis Diffuse Reflectance. Catalytic experiments were carried out in a continuous flow reactor; different inlet feed compositions were used, either *n*-butane lean (1% *n*-butane, 17% oxygen, remainder He), or *n*-butane-rich (10% *n*-butane, 17% oxygen, remainder He).

Results/Discussion

Doping the V/P/O catalyst with Nb had important implications on the catalytic behavior. Under hydrocarbon-lean conditions, e.g., with 1.7% *n*-butane in feed, the improvement was that of an increase of *n*-butane conversion, with respect to the undoped system. Since the selectivity to maleic anhydride did not decrease, the activity increase led to an higher yield to the desired compound. Even more remarkable was the effect of Nb doping under hydrocarbon-rich

conditions, i.e., with 10% *n*-butane and 17% oxygen in feed. As shown in Figure 1 (left), there was only a minor effect on *n*-butane conversion, but the yield to maleic anhydride was higher with the Nb-doped system, especially at temperatures higher than 400°C. The higher selectivity did correspond to the decrease of selectivity to both CO_x and phthalic anhydride. It is worth noting that the formation of phthalic anhydride, a minor compound under hydrocarbon-lean conditions, but an important one at hydrocarbon-rich conditions, derives from the Diels-Alder type reaction between maleic anhydride and butadiene, the latter being an intermediate compound in *n*-butane oxidation.

In order to explain the better efficiency of the Nb-doped catalyst in maleic anhydride formation, we carried out *in-situ* Raman experiments on the V/P/O catalysts. We found that the Nb-doped VPP developed the desired δ -VOPO₄ during heating in air at 380°C (Figure 1, right); on the opposite, the undoped VPP developed the desired oxidized phase only after treatment in an air/steam flow, an environment that favoured the transformation of the VPP to δ -VOPO₄ via hydrolysis to VOPO₄·2H₂O. We concluded that the enhanced formation of the desired δ -VOPO₄ was the reason for the better selectivity shown by the Nb-doped catalyst; in fact, the transformation of the intermediately formed butadiene into maleic anhydride turned out to be more favoured, because of the higher concentration of the selective δ -VOPO₄ compound.

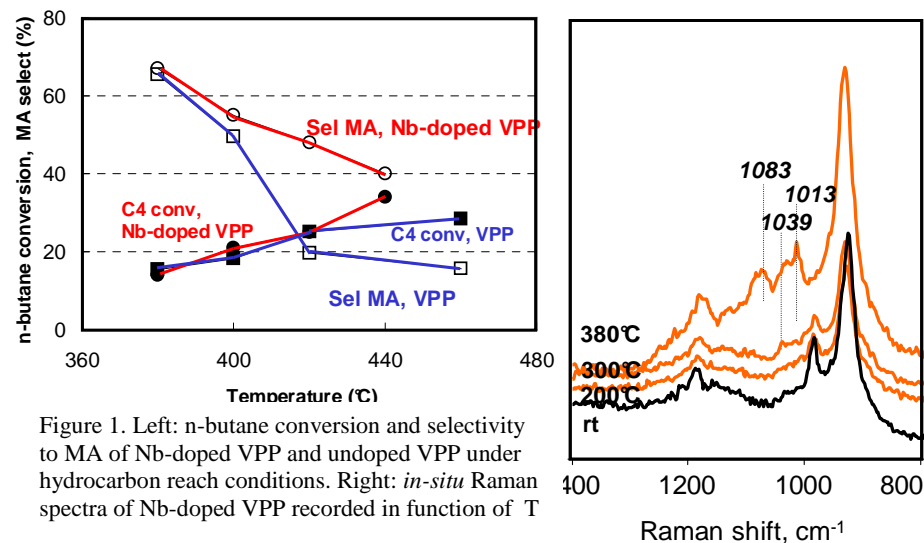


Figure 1. Left: *n*-butane conversion and selectivity to MA of Nb-doped VPP and undoped VPP under hydrocarbon rich conditions. Right: *in-situ* Raman spectra of Nb-doped VPP recorded in function of T

References

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