

**Enhanced Catalytic Activity by Tribomechanical Activation Treatment on Bi-promoted Vanadyl phosphate Systems**

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**Abstract**

Vanadium phosphate (VPP) compounds are important industrial catalysts used in the conversion of *n*-butane to maleic anhydride [1, 2]. The catalysts are produced by activating the hemi-hydrate,  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  (VHP), in an *n*-butane/air gas mixture at about 400 °C for an extended time period. The resultant catalyst often consists of a complex mixture of vanadium phosphorus oxide phases (i.e.  $(\text{VO})_2\text{P}_2\text{O}_7$ ,  $\alpha_1\text{-VOPO}_4$ ,  $\alpha_{II}\text{-VOPO}_4$ ,  $\gamma\text{-VOPO}_4$ ,  $\delta\text{-VOPO}_4$ , and  $\text{VO}(\text{PO}_3)_2$ ) [3]. Some researchers [4, 5] favour a single  $\text{V}^{4+}$  compound,  $(\text{VO})_2\text{P}_2\text{O}_7$  (VPP), while others [6, 7] suggest that the combinations of some  $\text{V}^{5+}$  phases ( $\alpha_{II}\text{-}$  and  $\delta\text{-VOPO}_4$ ) and a  $\text{V}^{4+}$  phase ( $(\text{VO})_2\text{P}_2\text{O}_7$ ) are a necessary requirement if the catalyst is to simultaneously exhibit good activity and selectivity.

Mechanical treatment of VPO catalysts is a method to influence the solid-state properties and indirectly the catalytic function. Mechanochemical treatment of the VHP precursor imparts a specific real structure that enhances the catalytic properties of the final catalyst [8].

$\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  (VHP) was mechanotreated in ethanol, water and air for several times and the morphology was studied by several characterisation techniques such as SEM,

TEM, EELS, XPS, BET and XRD. SEM shows that the initial sample consists mainly of flat smooth needles, that form a blossom secondary morphology. Under mechanochemical treatment the secondary morphology is lost and packages form with coin-shape particles. XRD reveals that milling in air for 28 minutes resulted in an amorphous phase. Milling for 30 minutes in air converted VHP to VPP. In contrast to milling in ethanol for 30 minutes did not show any phase change. XRD also reveals that at milling in water for just 2 minutes hydrates VHP. In contrast milling in ethanol for 10 minutes is required to hydrate VHP, but milling for longer dehydrates the sample back to VHP.

Catalytic activities of the mechano-activated samples are compared with the conventional thermal-activated VPP. The mechanotreated samples show an enhancement of *n*-butane conversion and an improvement in maleic anhydride selectivity and yield. The sample milled in water for just 2 minutes exhibits an increase in conversion to 91 %. The aim of this work is not only the microstructure, but it is also important to know how different milling environments change the catalytic properties, how important this method is in catalysis.

**Keywords:** amorphous and crystalline VPO, mechanochemical treatment, *n*-butane oxidation to maleic anhydride, electron microscopy

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- [1] G. Centi, Catal. Today, **16** (1993), 1.
- [2] M. Gasior and T. Machej, J. Catal., **83** (1983), 472.
- [3] C.J. Kiely, A. Burrows, G.J. Hutchings, K.E. Bere, J.C. Volta, A. Tuel and M. Abon, Faraday Discuss., **105** (1996), 103.
- [4] J.R. Ebner and M.R. Thompson, Catal. Today, **16** (1993), 51.
- [5] V.V. Gulians, J.B. Benziger, S. Sundaresan, N. Yao and I.E. Wachs, Catal. Lett., **32** (1995), 379.
- [6] G.J. Hutchings, A. Desmartin-Chomel, R. Olier and J.C. Volta, Nature, **368** (1994), 41.
- [7] G.W. Coulston, S.R. Bare, H. Kung, K. Birkeland, G.K. Bethke, R. Harlow, N. Herron and P.L. Lee, Science, **275** (1997), 191.
- [8] M. Fait, B. Kubias, H.J. Eberle, M. Estenfelder, U. Steinike and M. Schneider, Catal. Lett., **68** (2000), 13.