

Improvement of Promoted Vanadyl Phosphate Catalyst Properties in *n*-Butane Oxidation to Maleic Anhydride by Barothermal and Mechanochemical Treatment

Valery A. Zazhigalov¹; Vsevolod E. Yaremenko¹; Ibrar Ayub²; Dangsheng Su²; Marc Willinger²; Alexey Kharlamov³; Leonid Ushkalov³; Robert Schlögl²

¹ *Ukrainian-Polish Laboratory of Catalysis, Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, ul. Naumova 13, 03164, Kiev, Ukraine*

² *Fritz-Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany*

³ *Institute for Problems of Materials Science, NAS of Ukraine, Kiev, Ukraine*

More than twenty years ago the process of *n*-butane oxidation to maleic anhydride was realized in industry. The yield of maleic anhydride on used VPO catalysts was equal 53-55 mol. %. Any progress in maleic anhydride manufacture on VPO catalysts for passed time obtained. The mechanism of *n*-butane oxidation proposed in [1-2] predicted that the maleic anhydride selectivity and yield could be improve by active cluster (6-8 paired vanadyl group) isolation by means of phosphorus surplus introduction on surface or amorphous zone around active groups creation. For realization of these assumptions in this investigation two method were used: barothermal treatment of VPO-Bi catalyst by phosphorus acid and phosphorus oxide vapour and its tribochemical treatment.

The barothermal treatment was realized in stainless autoclave equipped with a Teflon inner tube. The VPO-Bi precursor was introduced in Teflon tube and phosphorus compounds were loaded between autoclave and tube walls, and then autoclave was heated at 473-623 K for 6-24 h. The tribochemical treatment was effectuated in planetary ball mill (3000 rpm) in different medium (ethanol, water and dry milling) for several times (2-60 min).

The obtained catalysts were characterized by means of different techniques such as SEM, TEM, EELS, XPS, BET and XRD. The acidic properties of the catalysts were studied by means of TPD NH₃, pyridine and dimethylpyridine adsorption and 2-methyl-3-butin-2-ol transformation.

The barothermal treatment of VPO-Bi sample leads to increase of the relative ratio of (001) plane of precursor without changes of the phase composition. The P/V surface ratio increases more than two time and the phosphorus surplus forms the islands on catalyst surface which decrease the size of available active surface fragments. The change of Bronsted/Lewis acidity ratio of surface as result of treatment also was observed. The activity of the catalyst in *n*-butane oxidation less changes up to several value of P/V ratio and decreases with its growth. The selectivity to maleic anhydride increases (more than 10 mol.%) practically in all interval of the P/V ratio changes. Well correlation was observed between the selectivity to maleic anhydride and Bronsted acidity of the catalysts.

SEM and TEM show that the particles size becomes smaller with short milling time and agglomeration occurs as milling time increase. Samples, which had been mechanochemical treated all showed more rounded particles with homogeneous dispersion of BiPO₄ compared with precursor. The change of phase composition of the sample after tribochemical treatment also was observed. XRD reveals that milling in air for 28 minutes resulted in an amorphous phase but the increase the time treatment up to 30 min converted sample to (VO)₂P₂O₇. In contrast milling in ethanol for 30 minutes did not induce any phase change but after 60 min treatment the vanadyl pyrophosphate and amorphous component were formed. XRD also reveals that milling in water for just 2 minutes hydrates VOHPO₄·0.5H₂O to VOHPO₄·4H₂O and transforms its to initial phase with time treatment rise.

The mechanochemical treatment catalyst shows an enhancement of *n*-butane conversion and an improvement in maleic anhydride selectivity and yield. The sample milled in water exhibits an rise in conversion to 91 % but selectivity increases only some percents. The maximal increase of the selectivity after treatment in ethanol (more than at 15 mol. %) and growth of activity (but only 5-6 %) was observed. The correlation between the changes of selectivity and Bronsted acidity was established.

DGMK-Conference “C₄/C₅-Hydrocarbons: Routes to higher value-added products”, Munich, 2004

1. V.A.Zazhigalov. Selective oxidations in petrochemistry. DGMK Conference, 1998, p. 249.
2. V.A.Zazhigalov. Teor. And Experim. Chem., 35 (1999) 265.