Nanocomposites and nanomaterials

Nanosized titanium phosphate as catalyst of aldol condensation

V.Sydorchuk[1], V.Ivasiv[2], S.Khalameida[1], R.Nebesnyi[2], J.Skubiszewska-Zięba[3], Iu.Dmytruk[2], N.Lapychak[2]

[1] *Institute for Sorption and Problems of Endoecology of NAS of Ukraine, 13 Naumova st., 03164, Kyiv, Ukraine. E-mail: svkhal@ukr.net*

[2]*Institute of Chemistry and Chemical Technologies, L'viv National Polytechnic University,12 S.Bandera Str., 79013, L'viv, Ukraine*

[3]*Faculty of Chemistry, Maria* Curie-Skłodowska *University, 3* Maria Curie-Skłodowska *Sq., 20 031, Lublin, Poland*

It is known that amorphous and crystalline titanium hydrophosphate (TiP) is typical acid catalyst. We modified of its properties via hydrothermal, microwave and mechanochemical treatments (HTT, MWT and MChT, respectively) for use as a catalyst of aldol condensation reactions, namely acetic and propionic acids (AcA and PA) with formaldehyde. Initial precipitated $Ti(HPO_4)_2$ is X-ray amorphous with particles size of 16 nm which are consolidated into porous granules. At the same time, TiP undergoes crystallization with formation of $Ti(HPO_4)_2$ and TiP_2O_7 nanocrystals (11-18 nm), as a result of all kinds of modification, especially HTT and MWT. Initial and all modified TiP samples possess developed hierarchical meso-macroporous structure. Besides, HTT and MWT leads to decrease of total surface acidity compared with initial (unmodified) TiP.

Initial sample possessing maximal acidity is non-active and non-selective in the target process but catalyzes formation of acetone. However, HTT, MWT and MChT promote improvement of its catalytic properties. Thus, dry MChT as well as HTT and MWT cause increase of activity i.e. reagents conversion. The last two types of processing result in the growth of selectivity to acrylic acid AA (about 70-80 mol.%). Therefore, the yield of AA reaches 38-45 mol.% at 380ºC. One can believe that samples with minimal values of specific surface area, low acidity and having crystal structure ($Ti(HPO_4)_2$ and TiP_2O_7 phases) exhibit the highest catalytic performances. XRD data shows no changes of phase composition for spent catalysts. There are also catalysts coking (minimal for the most active catalysts) that can be seen from the results of DTA-TG. Some reduction of specific surface area and pore volume is a consequence of this process.

The same modified samples were also investigated in process of condensation of propionic acid with formaldehyde to form methacrylic acid MAA. However, selectivity and yield of MAA do not exceed 51 and 12 mol%, respectively. The latter results can be associated with steric hindrance, namely with less accessibility of larger molecules of reagents and reaction products to active surface.