

INVESTIGATION OF THE INDIVIDUAL, BINARY AND TERNARY CATALYTIC SYSTEMS IN OXIDATION OF 4-METHYLPYRIDINE

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We report here the investigation of the individual V_2O_5 , binary $V_2O_5-SnO_2$, $V_2O_5-TiO_2$, and ternary $V_2O_5-TiO_2-SnO_2$ catalysts in oxidation of 4-methylpyridine (4-MP) to isonicotinic acid (INA). The experimental results were interpreted by the quantum chemical computation (Gaussian 09 W). We studied the influence of oxide-modifiers on the nucleophilic properties of vanadyl oxygen and also on the deprotonation enthalpy of methyl group of chemisorbed substrate.

According to experimental data, conversion of 4-MP increases in the following row of the catalysts: $V_2O_5 < V_2O_5-SnO_2 < V_2O_5-TiO_2$. In the same row, reactivity of the methyl substituent was increasing, indicated by the position of maximum yield of pyridine-4-aldehyde and INA at variation of the reaction temperature. Thereby, it shows that modification of V_2O_5 with dioxides of tin and titanium brings to increasing the catalytic activity.

The activity of the ternary $V_2O_5-TiO_2-SnO_2$ catalytic system is possible to estimate by the shifting of maximum yield of pyridine-4-aldehyde and INA to the low-temperature area, and also by decreasing in temperature at which aldehyde intermediate disappears as a product of the reaction.

It is known, that SnO_2 may increase mobility of the $V=O$ bond in the V_2O_5 lattice, thus contributing to the intensification of its dissociation and reduction to VO_2 . One may consider that in the vanadium-titanium catalysts with SnO_2 addition, this function of tin dioxide has not manifested itself, because an extent of V_2O_5 reduction in the three-component $V_2O_5-TiO_2-SnO_2$ system has been approximately the same, and even less, than that in the two-component $V_2O_5-TiO_2$ catalysts without SnO_2 additions. Probably it depends on the fact that SnO_2 may play a role of an oxidizer in relation to the low vanadium oxides. Due to this function of SnO_2 in the VO_2-SnO_2 system an oxygen rearrangement was observed: SnO_2 was reduced to SnO , giving off its oxygen for oxidation of VO_2 into V_2O_5 , and the formed SnO was easily and rapidly oxidized by the air oxygen again to SnO_2 . Hence, it follows that SnO_2 may stabilize the structure of the three-component $V_2O_5-SnO_2-TiO_2$ system, giving off its oxygen to vanadium and facilitating reoxidation of the catalyst by the gas phase oxygen.

The obtained results demonstrate that TiO_2 gives to V_2O_5 new catalytic properties in an oxidizing process. Increasing activity of the vanadium oxide catalyst under the influence of TiO_2 additives, in our opinion, is associated with the change of chemical and phase composition of the catalyst during its preparation. This change influences on the reactionary ability of V_2O_5 oxygen. Titan dioxide, apparently, weakens the $V=O$ bond in the lattice of V_2O_5 and promotes both acceleration of V_2O_5 transformation to VO_2 , and formation the new active centers on the surface of the catalyst, increasing its oxidizing and selective ability.

Modifying V_2O_5 with simultaneous addition of SnO_2 and TiO_2 leads to an increase in activity of the ternary catalytic system in the oxidation reaction of 4-MP in comparison with binary contacts.