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DEEP OXIDATION OF ETHANOL OVER SiO_2-SUPPORTED HETEROPOLY ACIDS MODIFIED WITH PALLADIUM

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The purpose of this study was to investigate the effect of silica-supported 12-phosphomolybdic acids in which molybdenum is partially substituted for vanadium on deep oxidation of ethanol and the effect of introduction of palladium to the catalysts on their activity and selectivity in total ethanol oxidation.

$H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$, and $H_5PMo_{10}V_2O_{40}$ heteropoly acids (HPA) were used for the impregnation of SiO_2 support. The prepared catalysts were subsequently impregnated with $Pd(NO_3)_2$ aqueous solution. The catalysts were characterized by elemental analysis MP-AES, nitrogen physisorption, FTIR, DR UV-vis, EPR, and X-ray photoelectron spectroscopies, H_2-TPR, and NH_3-TPD.

The non-modified Mo (MoV)/Si catalysts containing 5-8 wt. % of Mo introduced from heteropoly acids and silica-supported (Pd/Si) catalyst with 0.8 wt. % of Pd showed lower catalytic activity in ethanol oxidation than the Pd-modified silica-supported molybdenum catalysts. Replacement of one Mo atom in the Keggin unit of heteropoly acid for V caused an increase in oxidation of ethanol. Increasing number of vanadium atoms introduced into the anion of molybdenum heteropoly acid caused gradual decrease in the total amount of strong acidic sites, portion of acidic sites of medium strength increased. The activity order of the calcined MoV heteropoly compounds in ethanol oxidation correlated well with the total amount of acidic sites. Acidic sites of medium strength seem to be the most suitable for ethanol oxidation to CO_2.

Modification of Mo (MoV)/Si catalysts by palladium caused slight decrease in the amount of acidic sites, but in spite of this, their activity in ethanol oxidation increased. It was demonstrated that presence of Pd in the catalysts caused faster oxidation of reaction intermediates (acetaldehyde, CO) to demanded final oxidation product – CO_2.

The results obtained from IR, H_2-TPR, NH_3-TPD, DR-UV-vis, EPR, and XPS experiments and catalytic activity studies confirmed the complex effect of individual introduced components and showed direct connection of oxidation activity of the catalysts in ethanol oxidation with their acidity.

Therefore, the MoV mixed heteropoly acids can be used as interesting precursors of oxidation catalysts. After calcination, resulting $Pd/HPA/SiO_2$ materials are promising catalysts for deep alcohol oxidation due to their high acidity and redox power.

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