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"Methanol synthesis over copper - palladium supported ($\text{CeO}_2 - \text{Al}_2\text{O}_3$, $\text{ZrO}_2 - \text{Al}_2\text{O}_3$) catalysts"

Methanol is industrially used as a solvent and a raw material required to obtain a wide range of chemicals, such as: formaldehyde, acetic acid, methyl methacrylate and fuel additives which increase the octane number (e.g. Methyl tert-butyl ether). Methanol due to the high of carbon to hydrogen ratio in the molecule is an excellent source of hydrogen used to power fuel cells. Methyl alcohol is synthesized via catalytic hydrogenation of carbon oxides. This reaction is carried out at a temperature of 250 °C in the pressure range of 4-10 MPa on a copper catalyst ($\text{Cu-Zn-Al}_2\text{O}_3$). The recent attention has been focused on the attempt to develop new efficient methanol synthesis catalysts, which will allow decrease of the reaction temperature and pressure, while maintaining an acceptable yield of methanol synthesis reaction.

This doctoral thesis presents the physicochemical and catalytic results of Cu and Pd-Cu catalysts supported on $\text{ZrO}_2:\text{Al}_2\text{O}_3$, $\text{CeO}_2:\text{Al}_2\text{O}_3$ and $\text{ZnO}:\text{Al}_2\text{O}_3$ binary oxide systems used for the methanol synthesis reaction. The main goal of this work is to determine the nature and chemical state of the catalysts surface, as well as to explain the effect of the active phase composition and metal-metal and metal-support interactions on the catalytic properties of bimetallic catalysts in the methanol synthesis reaction.

The theoretical part of the work contains important information regarding the methanol synthesis process, including reaction conditions, the probable reaction mechanism and the commonly used catalysts. The experimental part describes the results of the physicochemical and catalytic properties of the copper and palladium-copper supported catalysts.

The catalytic supports were prepared by co-precipitation of hydroxides from the appropriate nitrates using ammonia as a precipitating agent. The deposition of metal nanoparticles onto the surface of obtained binary oxides was performed by the conventional

wet impregnation method. The physicochemical properties of the catalysts were studied using BET, TPR-H₂, TPD-NH₃, XRD, SEM-EDS and FT-IR techniques. The catalytic activity tests in methanol synthesis from carbon dioxide and hydrogen were carried out using gradientless reactor at 220 °C under pressure of 3.5 MPa.

The BET results showed that the addition of copper and palladium oxides onto support surface results in decrease of the specific surface area of the investigated catalysts. The reducibility measurements carried out for catalytic materials confirmed an interaction between copper (II) oxide and palladium what is connected with the shifts of the observed reduction effects visible on the TPR profiles recorded for Pd-Cu/support catalysts towards lower temperature range. A simultaneous presence of palladium and copper oxide in the same place on the surface was confirmed by SEM-EDS technique. EDS spectra of bimetallic catalysts after reduction at 300 °C indicated inhomogeneous distribution of elements on the surface. Therefore, it was concluded that the catalyst surface is not homogeneous. XRD measurements recorded for the reduced catalysts at 300 °C showed the presence of the following crystallographic phases: Cu, ZnAl₂O₄, CeO₂, ZrO₂, Al₂O₃ phases. In addition, in the case of bimetallic catalysts, PdCu phase was also observed. The presence of PdCu alloy phase confirm the interaction between Pd and CuO during the reduction process and explain the shifts of reduction profiles of palladium-copper catalysts toward lower temperature range (the alloying can take place only in the case of the simultaneous presence in the same place of palladium and copper oxide). The acidity measurements showed that the total acidity of the copper catalysts decreases with increasing of the active metal on the support surface. The introduction of palladium onto the copper supported catalysts surface results in increased of their total acidity. The results of FTIR measurements performed for mono- and bimetallic catalysts supported on CeO₂:Al₂O₃ binary oxide in CO₂ hydrogenation have proven the presence of surface groups of HCO₂⁻, CH₃O⁻ on the surface of the support. The presence of these species confirmed that CO₂ is adsorbed on the catalyst support, which is hydrogenated into intermediates in subsequent stages of the reaction, which further react with surface hydrogen and create methanol. The promotion effect of palladium on the catalytic activity of the copper supported catalyst in methanol synthesis reaction was proven. The improvement of the activity of bimetallic Pd-Cu catalyst in methanol synthesis reaction was explained by the PdCu alloy formation. The PdCu alloy formed during the activation process of the catalysts prior to the activity tests is a factor determining the activity and selectivity of the methanol synthesis reaction.

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