

Synthesis of Vinyl acetate over Pd-Cu/ZrO₂ nanostructured based catalysts

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Abstract:

Catalytic oxidation is considered as a suitable route for the production of oxygenated compounds from lignocellulose biomass. The development of routes to convert green ethylene from renewable sources, have been motivating other possible applications like green monomers, fuels, and fine chemicals. In this research work we prepared Pd-Cu catalysts over ZrO₂ mixed oxides. The catalysts were characterized by following methods XRD-in situ, BET, H₂ chemisorption and High-Resolution Transmission Electron Microscopy (HRTEM). Catalytic tests were performed through experimental planning. Statistical analyses allowed finding the main correlations of the products. The Vinyl acetate monomer formation was influenced by the AcOH and O₂ consumption at low ethylene coverage. Acetaldehyde appeared as an important intermediate for Vinyl acetate monomer synthesis. XRD results showed that the Pd-Cu catalyst exhibit tetragonal/orthorhombic nature with differences in the lattice position. The presence of Cu⁺² in the lattice describes the promotion of Vinyl acetate monomer formation due to acetaldehyde formation, AcOH hydrogenation and posterior H₂ spillover, releasing the hydroxyl groups during Vinyl acetate monomer dehydrogenation from the active site. A microkinetical model was achieved from directions of fluctuations, indicating ethylene coupling and AcOH hydrogenation to produce Vinyl Acetate Monomer (VAM). ZrO₂ supports with different properties were prepared, and the hydrogenation of aqueous nitrate catalyzed by ZrO₂ supported Pd-Cu bimetallic catalysts were investigated. The results showed that ZrO₂ support calcined at 573 K was unstable during the preparation of the bimetallic catalyst. Increasing calcination temperature led to the increase of particle size of ZrO₂ support. In addition, using ZrO₂ calcined at 973 K as the support resulted in the increase of metal particle sizes and the increased content of bimetallic ensembles at the expense of monometallic Pd. The bimetallic catalyst with ZrO₂ calcined at 773 K as the support exhibited higher catalytic activity and N₂ selectivity for the reduction of aqueous nitrate as compared to the bimetallic catalyst with ZrO₂ calcined at 573 or 973 K as the support. The activity and selectivity of ZrO₂ supported bimetallic catalysts for nitrate reduction also depended on the Pd/Cu ratio. Decreasing Pd/Cu ratio led to the decrease of the amount of monometallic Pd sites and to the increase of the content of Pd-Cu ensembles. The bimetallic catalyst with Pd/Cu ratio of 4/1 showed the optimum activity and

N₂ selectivity for the reduction of aqueous nitrate. The focus of this study was to develop high performance catalysts for the synthesis of vinyl acetate monomer (VAM). By systematic variation of different preparation parameters a multitude of shell catalysts consisting of PdAu nanoparticles supported on a bentonite carrier was explored. In order to investigate the influence of these alterations on catalytic performance, a catalyst classification was accomplished in a high-throughput Temkin test unit by comparison with a highly efficient commercial benchmark, referred to as B. Due to the applied Temkin reactor concept efficient heat and mass transport was ensured. Thus, the prepared catalysts could be clearly distinguished with regard to their selectivity (± 0.25 %) and space time yield (± 5 %) within a wide range of values. Catalyst performances for the selective oxidation of ethylene and acetic acid to VAM revealed that samples synthesized in this study are able to compete with this state-of-the-art plant catalyst. Concerning the selectivity meaningful improvements of almost 3 % were achieved by catalysts based on different KA-Zr carriers (Zr doped bentonite). Gas phase reduction (GPR) at various temperatures was also identified as a promising synthesis step. Although catalysts produced by liquid phase reduction (LPR) achieved on average about 11 % higher activity (STY) than the internal standard, outstanding enhancements of up to approximately 40 % were attained via forming gas reduction. A challenging aim of this thesis can be attributed to the characterization of VAM catalysts. In view of the fact that the most significant differentiation in performance was observed between catalysts prepared using LPR and GPR, samples from each reduction medium were chosen for a detailed characterisation using XRD, TEM and EXAFS. However, high amounts of carrier components compared to low metal concentrations of approximately 1-2 wt % rendered analysis of VAM catalysts with well-established techniques such as XRD and EDX difficult. Valuable information about the local Pd and Au distribution was provided by EXAFS. In agreement with TEM characterisation and Pd dispersion measurements, larger particle sizes were found for the liquid phase reduced catalyst B compared to GPR samples processed at 150 °C and 250 °C, respectively. Furthermore, TEM analysis showed that nanoparticles of LPR tend to agglomerate to chain-like framework structures, whereas a distribution of small and isolated particles dominates the GPR catalysts, correlating with the observed higher activity.