

Copper catalysts supported on porous ZrO₂ for ethanol dehydrogenation reaction

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Copper is a well-known catalyst for ethanol dehydrogenation with a high selectivity and relative low cost in comparison with others metals. However, the application of Cu catalysts is fated to deactivation through of sintering of the mass metallic copper, due the low melting point. This results in a loss of active sites due to the decrease of metal superficial area. The zirconium oxide has been described as support that prevents the sintering of metallic phase in reaction conditions by optimization of the interaction between support and metal clusters [1]. In this work, the ZrO₂ was obtained through sol-gel method by addition of the surfactants [Pluronic 127 and Sodium dodecyl sulfate (SDS)] to create ceramic supports with different porosities and thus, variable dispersion of copper. After that, Cu catalysts, containing 10 wt. %, were obtained by wetness impregnation using Cu(NO₃)₂ solution. The supports used are ZrO₂ with 10 wt. % of Pluronic (Cu/Zr-1); with 7 wt. % of Pluronic and 3 wt. % of SDS (Cu/Zr-2); without surfactant (Cu/Zr-3) and commercial ZrO₂ (Cu/Zr-4). The catalysts were characterized by different techniques and evaluated in ethanol dehydrogenation reaction. The catalysts were previous reduced at 250 °C (H₂/N₂) for 0.5 h and 6 ml/h ethanol was introduced on N₂ flow. The presence of pluronic and SDS promoted an increase of surface area values in relation to ZrO₂ carriers without surfactants. However, the support containing SDS showed pore shrinkage after calcination at 800 °C. From XRD, catalysts that have porous structure showed lower crystallinity in relation to sample obtained from commercial ZrO₂. The TPR results are in accordance with XRD, since the catalysts with porous structure presented an increase of superficial Cu species in relation to bulk species, probability due to higher copper dispersion. In Fig. 1, the catalysts with higher values of S_{BET} and porosity showed higher ethanol conversion and selectivity to ethyl acetate. In this case, the presence of Cu in the porous structure favored the diffusion of reagents and promoted a rise in the selective conversion of ethanol to ethyl acetate.

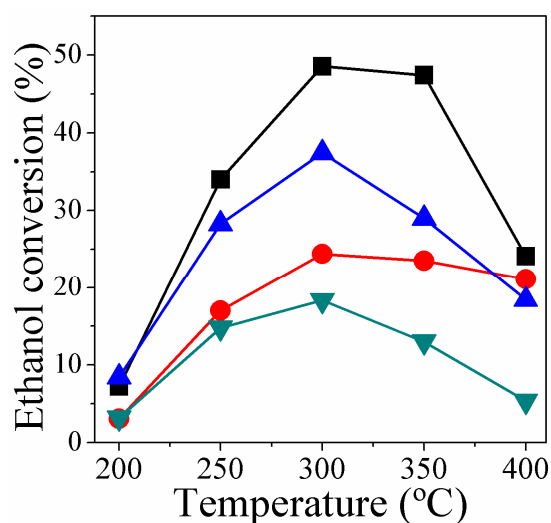


Figure 1: Ethanol conversion in the dehydrogenation reaction for 10 wt. % copper impregnated on ZrO₂ supports. Cu/Zr-1 (■); Cu/Zr-2 (●); Cu/Zr-3 (▲) and Cu/Zr-4 (▼).