(Ni,Cu) catalysts for ethanol dehydrogenation: performances vs. synthesis

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Significance and Relevance

Renewable hydrogen as an energy vector will play a crucial role in the next future. In this work, hydrogen was produced as a by-product of the dehydrogenation reaction of bioethanol to acetaldehyde, an important chemical compound. The stability and activity of the Cu-based catalyst, the most investigated for this reaction, was significantly improved by a small amount of Ni addition at low temperatures, giving better results than the commercial catalyst.
This research provides fundamental understanding in the frame of renewable hydrogen production in the context of energy transition.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion, H_2 storage and transportation, green H_2 production, hydrogen vectors

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Considering the global environmental crisis, it is of paramount importance to identify and develop new, innovative, and environmentally friendly sources of energy[1]. Among the various potential energy carriers, hydrogen is a promising option. According to long-term forecasts (until 2050), H_2 will be a key player in the global economy, accounting for up to 20% of energy use[2]. The global demand for hydrogen is approximately 70 Mt_{H_2}/year, with current production exceeding 95% derived from fossil fuels[3]. Among the potential research path, the dehydrogenation of bioethanol to acetaldehyde is a promising avenue. In fact, bioethanol, produced by the fermentation of biomass, is expected to become a primary intermediate in the emerging industrial organic chemistry based on green chemicals. Among the studied active phases, Cu- has gained increasing interest due to its low cost and greater environmental compatibility than copper chromite catalysts, which are the conventional catalyst for this reaction. The main weakness is the rapid catalyst deactivation due to carbon deposition and metal sintering[4,5]. In the open literature, it has been demonstrated that the addition of Ni to nanoscale copper alloys enhances the stability and performance of the catalyst[6]. The objective of this study is to investigate the bioethanol dehydrogenation on (Cu,Ni) catalysts as a function of preparation and to study the interaction of reactants and adsorbed species-intermediates on the catalyst surface in operando condition by FT-IR.

Materials and Methods

The (Ni,Cu)/Al_2O_3 catalysts were prepared by hydrothermal treatment (HT) and optimized solid combustion synthesis (SCS), maintaining a total metal loading of 7.5 wt.%. The prepared catalysts were characterized by XRD, FE-SEM, FT-IR, UV-vis-NIR, and BET. The catalytic performances were carried out and compared to commercial Cu-based catalyst in a laboratory scale plant in a quartz fixed bed tubular reactor with 7.9 (v/v)% ethanol in the temperature range 423-773 K. The reactant products were analyzed by GC and GC-MS to evaluate bioethanol conversion and acetaldehyde yield and selectivity. Operando DRIFTS experiments are ongoing and are carried out by FT-IR spectrophotometer and Praying Mantis accessory and cell (Harrick).

Results and Discussion

Figure 1 shows the catalytic performances in the bio-ethanol dehydrogenation reaction (7.9% v/v) obtained with monometallic (Cu) and bimetallic (Cu,Ni) catalysts. The Cu-based catalyst, Cu (SCS), exhibited superior catalytic performance in terms of acetaldehyde production compared to the commercial catalyst at temperatures below 573 K. This behavior can be attributed to the homogeneous dispersion of Cu on the Al_2O_3 support. Furthermore, the bimetallic catalysts exhibited enhanced catalytic performance compared to the monometallic catalyst, indicating a synergistic effect between Ni and Cu, especially for the catalyst prepared by HT. At low temperatures, the (Cu,Ni) (HT) catalyst demonstrated remarkable activity (90% ethanol conversion and 71% acetaldehyde selectivity at 523 K), with an H_2 production of 0.40 mg/min.

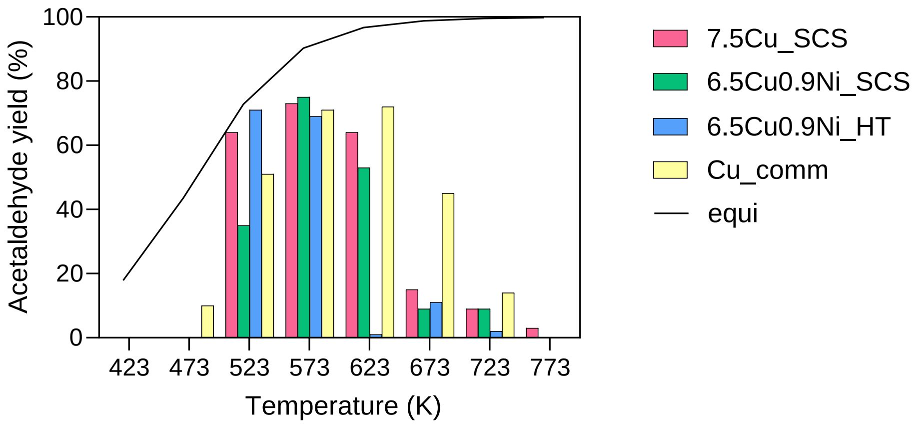

Figure 1. Catalytic performances obtained with the monometallic and bimetallic catalysts.

The catalysts pre-reduction resulted in enhanced catalytic performance at lower temperatures with both prepared bimetallic catalysts.

In conclusion, the addition of Ni to the Cu-based catalyst resulted in improved catalytic performance in terms of bio-ethanol conversion and acetaldehyde selectivity, in particular at low temperatures.

References

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Acknowledgements

G.G. and E.S. acknowledge the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3—Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union—NextGenerationEU project title "Network 4 Energy Sustainable Transition—NEST" (project code PE0000021).