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Looking for stability: from aerosol Cu/SiO_2 catalysts to bimetallic $NiCu/SiO_2$ for the bioethanol dehydrogenation

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Among the employed metals for dehydrogenation reactions, Cu has been largely studied in several industrial processes[1]. Particularly for the ethanol to acetaldehyde reaction, with the rise of biomass technology and bioethanol availability[2], many efforts have been carried out by researchers to develop new active copper-based catalysts[3]. Nevertheless, their rapid deactivation is still an unresolved challenge. For Cu supported catalysts, mainly metal sintering and coking are found to be detrimental for the catalyst lifetime[4]. Cu sintering causes a drop in active surface area and the exposure of the catalytically non-innocent support, with a consequent drop in acetaldehyde selectivity as well as the formation of side products that trigger fouling. Among the supports, silica is promising. In fact, Cu/SiO_2 catalysts are reported as highly selective to acetaldehyde because of the relative inertness of silica. Despite of this, SiO_2 is known to establish only weak interactions with supported metal nanoparticles, and the latter are therefore particularly prone to sintering. The design of deactivation-resistant catalysts that will demonstrate both high activity levels and long-term stability is still demanded in this domain. Thus, leveraging on an effective one-pot synthesis technique (Aerosol Assisted Sol Gel method (AASG)[5]), we firstly developed highly active and selective aerosol Cu/SiO_2 catalysts with a stronger intimacy between the active phase and the support[6]. With the teachings gained from a deep characterisation of fresh and exhausted catalysts, we identified the key parameters that govern both the high activity and the causes of deactivation. Then, we decided to further tailor the catalysts activity and stability by synthesizing bimetallic catalysts. Since Ni is reported[7] as a suitable candidate to improve thermal stability and catalytic activity of Cu, the effect of its addition has been investigated. A series of bimetallic $Ni\text{-}Cu/SiO_2$ catalyst was prepared. The synthesized materials have been tested in the ethanol dehydrogenation reaction and extensively studied looking also at the deactivation effects, by a complete characterization survey based on N_2 physisorption, XRD, FT-IR, DR-UV-VIS, XPS, TEM, TGA-MS. Remarkably, the bimetallic catalysts showed surface areas higher than 400 m^2/g and an homogeneous dispersion of the two elements, both in the bulk and at the surface. Furthermore, the best formulation, maintained stable and higher than 65% ethanol conversion at 523 K for 8 hours.

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