SELECTIVE DEHYDROGENATION OF ETHANOL ON NICU NANOPARTICLES AND NANOPOROUS NICU

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Abstract

We report that Ni-containing Cu nanoparticles (NiCu NPs) and nanoporous Cu (np-NiCu) materials are very active for the selective dehydrogenation of ethanol to acetaldehyde and hydrogen, with a nearly 100% selectivity and a good stability. Although monometallic Cu catalysts are also active, a quick deactivation of Cu catalyst was observed. Adding a small amount of Ni in the Cu metal surface significantly decreases the apparent activation energy of the Cu catalysts, and also greatly improves their stability. Hence highly dispersed Ni or even Ni single atoms on the Cu surface do not only stabilize the morphology of Cu catalysts but also directly participate in the ethanol dehydrogenation reaction.

Keywords

Ethanol dehydrogenation, Acetaldehyde, Nanoporous, Stability, Selectivity.

Introduction

The selective dehydrogenation of ethanol to acetaldehyde and hydrogen is an important industrial reaction for the synthesis of acetaldehyde. (DeWilde et al., 2014) It is also an essential first step in ethanol steam reforming and ethanol partial oxidation reactions. It has been reported that supported monometallic Cu NPs are active for this reaction; however, a quick deactivation of the catalyst was observed even in the first hours of the reaction. (Santacesaria et al., 2012) The deactivation is likely due to the sintering of Cu NPs at the high reaction temperature. (Tu and Chen, 2001).

In current work we are investigating the addition of small amounts of Ni in the Cu surface as potential exit route for the desorption of H₂, to boost the activity of copper, similar to what we have recently reported for PtCu single atom alloys used as selective methanol dehydrogenation catalysts (Shan et al. submitted). Of course, the stabilization of Cu against sintering is of primary interest. Although supported Ni NPs are also active for the dehydrogenation of ethanol, CO and CO₂ are the major products. Silica supported NiCu NPs were prepared through a colloidal synthesis procedure. Alternatively, np-NiCu was prepared through a dealloying of Zn-Cu alloys followed by a liquid salt impregnation/freeze drying Ni addition process. Our characterization data show that Ni is highly dispersed or even atomically dispersed on the Cu surface. The highly dispersed Ni or isolated Ni atoms play a key role in the dehydrogenation of ethanol to acetaldehyde and hydrogen; they not only stabilizing the morphology of Cu catalysts against coarsening, but also directly participate in the reaction, at a
minimum as the exit route for the association of H atoms and desorption of molecular H₂.

**Results and discussion**

Our XRD, STEM, and EXAFS characterizations show that Ni is highly dispersed or even atomically dispersed on the Cu surface. Adding a small amount of Ni does not change the lattice structure of the Cu host, while our catalysis data show this small amount of Ni does drastically improve the catalytic performance of the NiCu alloys.

Figure 1 shows an Arrhenius-type plot of the reaction rate on monometallic Cu NPs, NiCu NPs, and np-NiCu catalysts. The apparent activation energy determined from the Arrhenius plot of monometallic Cu NPs is 70±5 kJ/mol; while for Ni₀.₀₀₁Cu NPs, Ni₀.₀₁Cu NPs and np-Ni₀.₀₀₃Cu it is 49±5 kJ/mol, 47±5 kJ/mol and 53±5 kJ/mol respectively. Note that the apparent activation energy of np-Cu is also 70±5 kJ/mol, indicating similar catalytic activity of np-Cu with supported Cu NPs. Apparently, adding a small amount of Ni to the Cu surface significantly decreases the apparent activation energy of the catalysts, or in other words promotes the reactivity. The mechanism for this is currently under investigation.

**Figure 1.** Arrhenius-type plot of the selective ethanol dehydrogenation reaction rate on monometallic Cu NPs, NiCu NPs, and np-NiCu catalysts.

Figure 2 shows the stability of monometallic Cu NPs, NiCu NPs, and np-NiCu in the ethanol dehydrogenation reaction at 250 °C. Monometallic Cu NPs show a clear drop of the activity after just one hour reaction; while NiCu NPs and np-NiCu show no measurable deactivation after the reaction for 8 h. SEM analysis of the used np-NiCu catalysts shows no ligament coarsening, unlike np-Cu which shows more than 54% deactivation in 19 h, with concomitant considerable coarsening.

**Figure 2.** Stability tests of Cu NPs, NiCu NPs, and np-NiCu in the selective ethanol dehydrogenation reaction at 250 °C.

**Conclusions**

Adding small amount of Ni to the Cu surface significantly increases the reactivity of the catalysts in the selective ethanol dehydrogenation reaction, and also greatly improves the stability of the catalysts. Our data show that the presence of highly dispersed Ni or isolated Ni atoms in the Cu surface not only stabilize the morphology of Cu catalysts but have a direct effect on the reaction mechanism.

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**References**


