

***In-Situ* ETEM Synthesis of Ni-Cu/TiO₂ Bimetallic Catalyst**

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Compared with Ni monometallic catalysts, Ni based bimetallic catalysts containing Cu exhibit better catalytic activity and selectivity [1]. However, the atomic mechanism of the role of the second metal element (Cu) on the catalyst properties and synthesis is not well understood. This is partly because the presence of two metallic salts prepared by the incipient wetness technique complicates the formation of homogeneous bimetallic particles, i.e., alloying and/or segregation of the bimetallic particles may exist in a supported bimetallic system. Therefore, we need to understand both the chemical states and the distribution of the two metals within the individual bimetallic nanoparticles in order to better address the enhancement of the catalyst properties by the second metal element.

Modern environmental transmission electron microscope (ETEM) provides us with a unique opportunity to understand the synthesis processes and structures of the catalytic nanoparticles under near-reactor conditions [2]. Here we use ETEM to investigate the atomic scale process occurring during the synthesis of 3wt.%Ni-1wt.%Cu/TiO₂ bimetallic catalyst from nitrate precursors (a suitable mixture of Ni and Cu nitrate solutions). The metal nanoparticles are formed *in situ* by reducing the precursor in 1.5 Torr of 20% H₂/ 80% N₂ at 300°C using a Tecnai F-20 ETEM. The morphology changes taking place on the oxide support during the reduction was followed using high-resolution imaging. *In-situ* electron energy loss spectroscopy (EELS) nanoprobe analysis of individual nanoparticles was performed to understand the local oxidation states and compositions of the final bimetallic catalysts.

Fig. 1(a) shows the formation of nanoparticles after 5 min reduction of bimetallic precursors. Notice in Fig. 1(b) that the larger particle A grows at the expense of the nearby smaller particles (indicated by the white arrows). Particles B and C (shown in Fig. 1(a)) merge together to form a bigger particle (indicated by an arrow in Fig. 1(b)) as time. These observations indicate that both ripening and coalescence occur during the growth of the nanoparticles in this bimetallic system. *In-situ* EELS line scan results across typical nanoparticles (shown in the Z-contrast images of Figs 1(c) and (d)) are given in Figs 1(e) and (f), respectively. Notice in Fig. 1(e) that both Ni and Cu EELS peaks are uniformly present across the whole particle, indicating a uniform alloying of the bimetallic components inside this nanoparticle. However, in the second particle the Ni signal in Fig. 1(f) is much stronger at the edge of the nanoparticle even though both Ni and Cu peaks are presented inside. This indicates that this bimetallic particle must have a surface segregation of Ni. The alloying and segregation behavior of the bimetallic Ni-Cu/TiO₂ nanoparticles is discussed based on the higher reducibility of Cu ions under reducing gases. The enhancement of the reducibility of Ni ions by the Cu species is also addressed.

References:

- [1] Li, Y., Chen J., Chang, L., and Qin, Y., *J. Catal.*, 1998, 178, 76.
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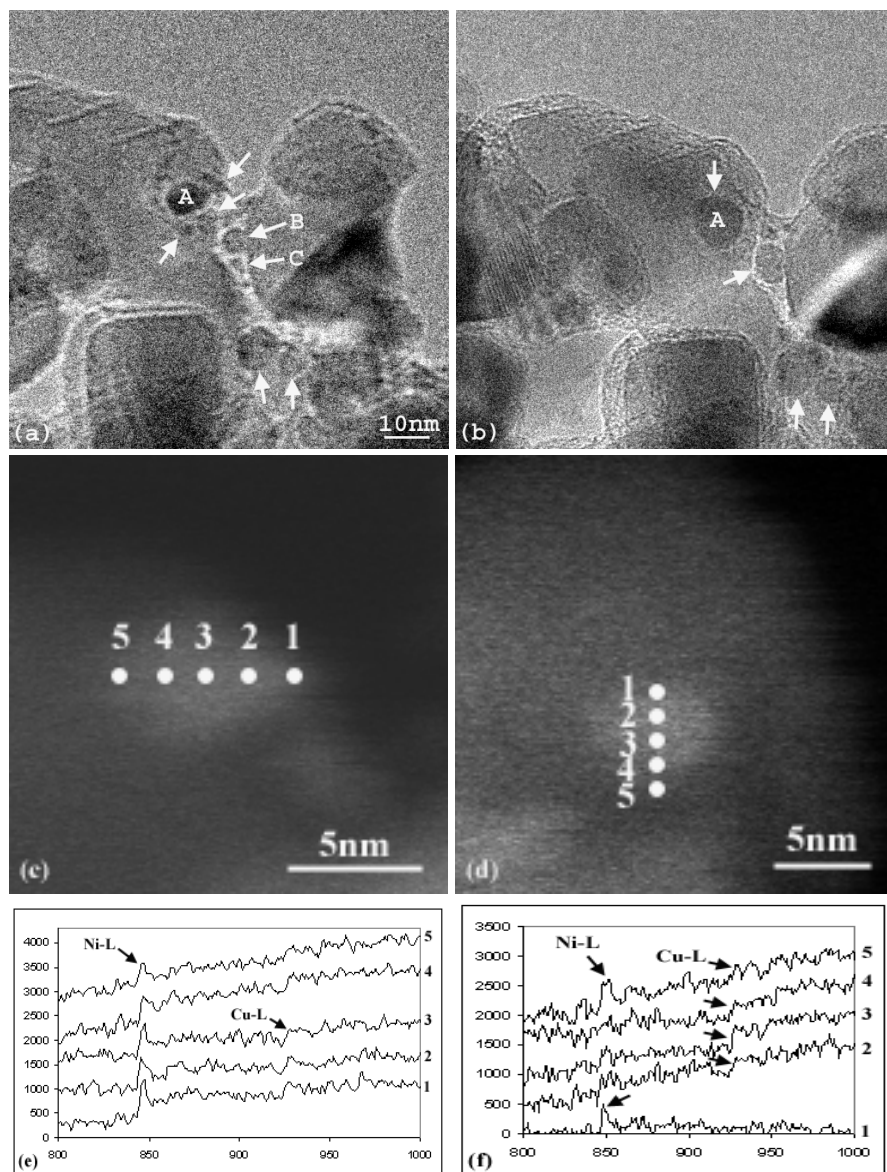


Figure 1. In-situ HREM images showing the evolution of Ni-Cu bimetallic particles on TiO₂ support reduced at 300°C for: (a) 5 min and (b) 60 min under 1.5 Torr of 20% H₂/ 80% N₂. The in-situ EELS line scan analysis of the composition distribution across the particles shown in the in-situ Z-contrast images of (c) and (d) are given in (e) and (f), respectively.