

Electronic Supplementary Information

Nanocasting of CuAu alloy nanoparticles for methyl glycolate synthesis

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In this work, a facile approach for the synthesis of the CuAu alloy catalysts via ammonia evaporation deposition precipitation method (AE) is reported. Traditionally, the silica supported CuAu/SiO₂ bimetallic catalysts were prepared via two-step deposition precipitation method due to the opposite charge of AuCl₄⁻ and Cu²⁺: firstly depositing Au on the silica support, then depositing Cu on the Au/SiO₂ catalyst, after a certain reduction treatment, the deposited Cu could diffuse into the supported gold nanoparticles to form a partially ordered alloy structure (J. C. Bauer, et. al, *Phys. Chem. Chem. Phys.* 2011, **13**, 2571.). Two phase method (TP) was also conducted to prepare supported AuCu bimetallic catalyst. In the TP method, AuCl₄⁻ and Cu²⁺ species were firstly transferred from aqueous HAuCl₄ and Cu(NO₃)₂ solutions to toluene solution using a phase transfer reagent, dodecanethiol was then added to the solution and aqueous NaBH₄ was used to reduce the metal salts, after removing the solvent and protecting agent, the bimetallic nanoparticles were impregnated onto the support followed by calcination under inert atmosphere to obtain the final CuAu bimetallic catalysts (J. Llorca et. al, *J. Catal.* 2008, **258**, 187).

However, in our approach, the CuAu bimetallic catalyst was prepared via one-pot synthetic method and no organic solvent and protecting agent were used, also no other metals were introduced due to the H₂ reduction rather than the metal-containing reducer. After calcination, the catalyst was composed of Au/CuO/SiO₂, then AuCu/SiO₂ bimetallic catalyst could be obtained via H₂/Ar reduction. According to

the classic synthetic method, commercial silica supported CuAu alloy NPs catalyst (standard catalyst) were prepared via two step deposition precipitation method. The activity evaluation result showed that the TOF value over the standard catalyst (606 h^{-1}) was only 46% of that of CuAu/HMS under the same reaction conditions, which indicated the high efficiency of the alloy catalyst prepared via evaporation precipitation method. The ability to use HMS as a catalyst support is attractive because of its high surface-area, thermal stability, mechanical strength, and non-reducibility. More importantly, the interaction between Cu or Au and silica is weaker, which is convenient for investigating the performance of the bimetallic catalysts.

In the gas-phase ester hydrogenation reaction, Cu/HMS catalyst exhibited higher hydrogenation activity but lower selectivity to MG, while Au/HMS catalyst showed lower hydrogenation activity but higher selectivity to MG. In other words, both Cu and Au are active sites for this gas-phase hydrogenation reaction, the difference in catalytic hydrogenation activity might be originated from the particle size effect and other factors such as the surface properties of the two metals, which would deeply need to study in the following research. Generally speaking, for gold catalyst, the calculation of TOF value is based on the relationship between the degrees of dispersion (by XPS) and particle size (by TEM) (See reference G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, 41, 319). For Cu-based catalyst, the TOF value is calculated based on the surface exposed metallic surface area (by the N_2O titration) (See reference B. Denisea, R.P.A. Sneed, B. Beguina and O. Cherifi, *Appl. Catal.* 1987, 30, 353.). In our previous investigation, the exposed metallic surface area presents good linear relationship with the dispersion of copper species based on XPS (*see* A.Y. Yin, X.Y. Guo, W.L. Dai, K.N. Fan, *J. Phys. Chem. C*, 2010, 114, 8523; A.Y. Yin, X.Y. Guo, W.L. Dai, K.N. Fan, *Appl. Catal. A: Gen.* 2009, 349, 91.). Taking these facts into consideration and combining the formed CuAu alloy catalyst, the TOF value was calculated on the basis of the number of metal atoms on the surface calculated from particle size determined by TEM analysis.

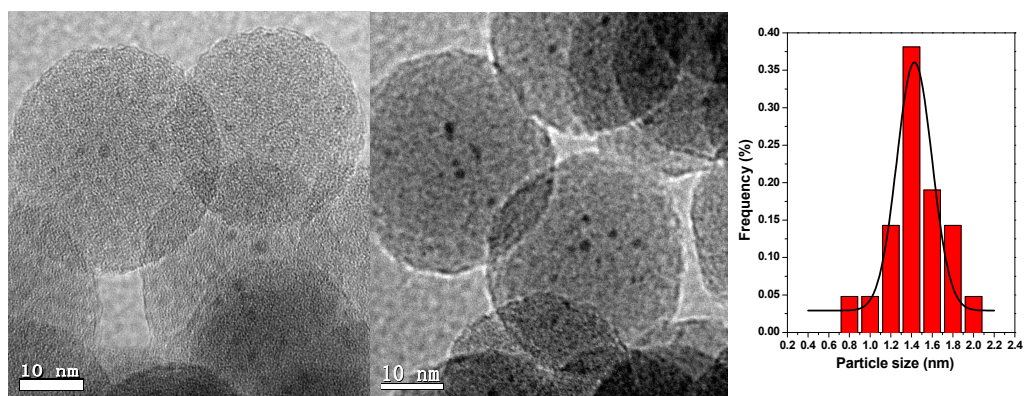


Figure S1. TEM image and Cu particle size distribution of Cu/HMS catalyst

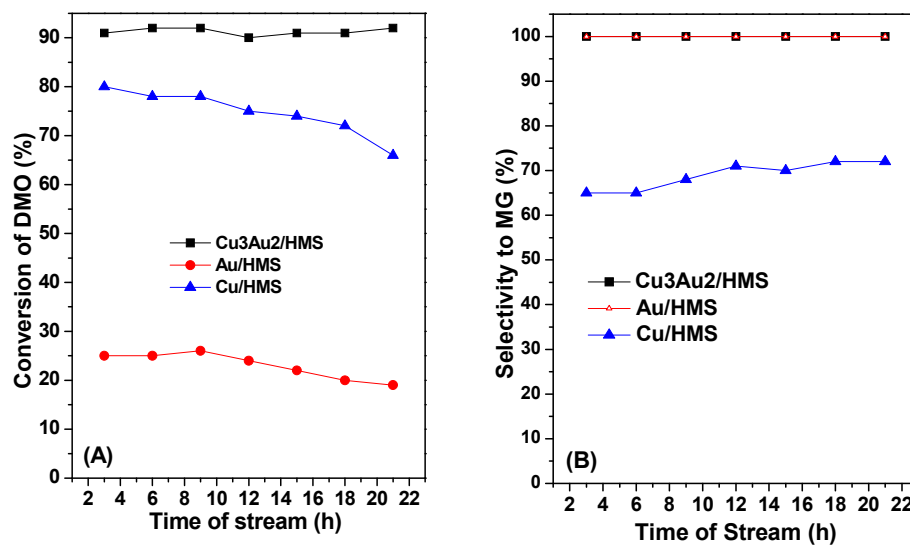


Figure S2. Catalytic performance of catalysts as a function of reaction time (A) conversion of DMO; (B) Selectivity to MG.