The Promotional Effect of Zinc for Copper-Zinc Catalysts in Selective Propylene Oxidation by Dioxygen

Hsi-An Chen[1], Chun-Jiun Cheng[1], Nien-Chu Lai[1], Ying-Chen Huang[1], Chia-Min Yang[1,2,*]

[1] Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan
[2] Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan
**cmyang@mx.nthu.edu (Professor Dr. Chia-Min Yang)*
k0130191122@gmail.com (Hsi-An Chen)
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Supported catalysts containing highly dispersed metals often exhibit high activity in heterogeneous catalysis. It remains challenging to achieve high metal dispersion on mesoporous or high-surface-area supports. It is even more challenging to develop cost-effective synthetic strategies to make such materials. Previously, we reported a "pH-jump" synthesis of mesoporous silica nanostructures (MSNs) using sodium silicate as a silica source and ethyl acetate as a pH modifier [1]. The method has been successfully applied to the direct synthesis of metal-containing MSNs. For the copper-containing MSNs thus prepared [2], the incorporated copper species transformed to nanosized metallic particles after hydrogen treatment and the reduced catalysts exhibited superior catalytic activity and stability for the selective oxidation of propylene by dioxygen [2], a reaction we have extensively studied for years [3,4]. In this contribution, a further extension of the synthetic strategy to cost-effective, surfactant-free one-pot preparation of nanoporous silica materials containing single (e.g. copper) or multiple (e.g. copper/zinc) metals is introduced. In the absence of surfactants, the syntheses generally resulted in high-surface-area materials comprising aggregates of loosely packed 10~20-nm silica nanoparticles. For the copper-containing materials with a Cu/Si of 0.03, versatile content of zinc could be co-incorporated. The prepared Cu-Zn/SiO_2 catalysts were further conducted in the selective oxidation of propylene to acrolein. A volcano plot in activity with respect to the zinc content was observed, with an optimized Zn/Cu ratio (X) equaling to 0.10, the yield of acrolein was about three times higher than that of catalyst with X equaling to 0. The synergistic effect between zinc and copper was further investigated by H_2 TPR, *in-situ* XAS and *in-situ* Diffuse Reflectance Infrared Fourier Transformation Spectroscopy (DRIFTS). In the presence of electron donor, ZnO, the catalyst showed red shift for *in-situ* DRIFTS of CO adsorption [6], which CO can only irreversibly bind to the Cu(I) sites. Degrees of red shift were consistent with the trend of activity of catalysts, suggesting that Cu(I) species may be the active sites [2, 5] for the selective oxidation of propylene to produce acrolein. The results show promise of the cost-effective surfactant-free synthesis in making efficient metal-containing nanoporous catalysts.

Keyword: selective propylene oxidation, nanoporous silica, nanosized copper/zinc, surfactant-free, one-pot synthesis

References

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