Catalytic Study of C_xH_y Species Modified Nanosized Copper Catalysts in Selective Propylene Oxidation by Dioxygen

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Abstract

Supported highly dispersed metal materials have been widely applied as catalysts in heterogeneous catalysis. In previous study, preparing highly dispersed copper nanoparticles (NPs) on mesoporous silica nanoparticles (Cu-MSNs) showed superior and stable catalytic activity for the selective propylene oxidation reaction. Considering the cost of the surfactant, we successfully developed a surfactant-free and controlled co-precipitation method for the nanoporous silica (NS) comprising loosely packing of 10-20 nm silica nanoparticles. This method used sodium silicate as a silica source and ethyl acetate as a pH modifier. By utilizing 3-aminopropyltrimethoxysilane (APTMS) as a metal chelating agent, $[Cu(APTMS)_4]^{2+}$ complex could be further introduced into the synthetic solution to prepare copper catalysts which modified by propylamine groups. The prepared CuNS sample was subsequently with heat treatment in the non-oxidizing atmosphere of nitrogen. During hydrogen reduction, the C_xH_y species were formed and adhered on the surface of metallic copper nanoparticles due to breaking the chemical bonds of APTMS, as evidenced by ^{29}Si CP-MAS NMR, H_2-TPR and *in-situ* Diffuse Reflectance Infrared Fourier Transformation Spectroscopy (DRIFTS). Based on *in-situ* X-ray absorption spectroscopy, the estimated average sizes of copper particles in the H_2-reduced catalysts were 1-2 nm. The H_2-reduced catalysts were further conducted in the selective oxidation of propylene to acrolein. The C_xH_y species were beneficial to the propylene conversion and maintained the acrolein selectivity as high as 70% at high temperature. At 260 ℃, the acrolein yield of C_xH_y species modified catalysts could be about three times higher than the catalyst without C_xH_y modification. The C_xH_y species could be removed by calcination in different conditions. The calcined catalysts were further reduced by hydrogen, resulting in different particle size of copper. However, due to the relatively low dispersity of copper, the activity of catalyst was poor comparing to the highly dispersed copper catalysts, indicating the dispersity of copper is crucial to the activity of catalysts.

Keywords – Selective propylene oxidation, surfactant-free, nanoporous silica, nanosized copper, C_xH_y species