

Time-resolved XAS studies on ethylene oxidation over Cu-Pd-exchanged Y zeolite catalysts

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The Wacker process is one of the most efficient organic synthetic methods for manufacturing aldehydes and ketones. This liquid-phase homogeneous process however, suffers from the difficulty in the separation of the products from the catalyst solution; high corrosivity associated with HCl excess; and the formation of undesired chlorinated byproducts [1]. Thus, many studies involving the heterogenization of a chloride-free solid-vapor Wacker catalyst system were done to overcome these problems. However, most of these catalyst systems either lacked sufficient activity or stability due to inefficient reoxidation of palladium; and the reaction mechanism of heterogeneous Wacker oxidation has not been fully established. Clarifying the reaction mechanism of ethylene oxidation was the aim of this time-resolved XAS study.

Heterogeneous Wacker catalysts were prepared by ion exchange of palladium and copper ions on zeolite Y because this catalyst is closely similar to the homogeneous system and it is one of the most active and stable catalysts for heterogeneous Wacker oxidation [2]. Time-resolved XAS measurements [3], with a resolution of 0.5 seconds, were performed at the Cu and Pd K-edges in transmission mode at the SuperXAS beamline of the Swiss light source (SLS, Villigen, Switzerland). Experiments were performed in a quartz capillary reactor cell connected to a mass spectrometer under catalytic conditions where reactants were added or cut-off abruptly from the feed to monitor time-resolved structural and oxidation state changes in the catalyst.

Lower Pd loading reduced the particle sintering and a higher Cu/Pd ratio (≥ 2) resulted in a more active and selective catalyst for Wacker oxidation. The time-resolved variations of the fraction of Pd and Cu species in Pd(1%)Cu(5%)-Y, derived from the linear combination fits of their respective XANES spectra, show the immediate reduction of a portion of Pd(II) species to Pd(0) and the transfer of electrons to Cu(II) species to form Cu(I) upon exposure of the catalyst to the reactant feed (C_2H_4 , H_2O , O_2). After reaching its maximum, the fraction of Cu(I) species approached near-zero values suggesting its involvement as a reaction intermediate, forming hydrated cupric ions. The sudden removal of O_2 in the feed resulted in the formation of Cu(I) at the expense of hydrated cupric species and a slight reduction of Pd(II) to Pd(0) but there was no evidence of Cu(0) and Pd(I) formation. This suggests a one-electron transfer from two Cu(II) ions to reoxidize Pd(0) to Pd(II), corroborated by an optimum Cu/Pd ≥ 2 in an active Wacker catalyst.

These sub-second operando XAS measurements provide the first direct evidence of electron transfer between zero-valent palladium and bivalent copper under catalytic conditions during heterogeneous Wacker oxidation. On the other hand, the sudden removal and readdition of O_2 revealed more pronounced changes in the fraction of copper species than those of palladium underscoring the role of O_2 in reoxidizing reduced copper species similar to the homogeneous reaction. These results lead to a deeper understanding of the reaction mechanism involved in the Wacker process, which in turn is needed to design and engineer better heterogeneous catalysts.

References:

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