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 \cite{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 \cite{2}. Time-resolved XAS measurements \cite{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\textsubscript{2}H\textsubscript{4}, H\textsubscript{2}O, O\textsubscript{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\textsubscript{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 readition of O\textsubscript{2} revealed more pronounced changes in the fraction of copper species than those of palladium underscoring the role of O\textsubscript{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:
\cite{1} Smidt, J. et al. \textit{Angewandte Chemie (International Ed. in English)}, 1, 80–88 (1962)
\cite{2} Espeel, P. et al. \textit{Chemical Communications}, 10, 669-671 (1991)