Oxychlorination of Ethane to Vinyl Chloride Over Copper ZSM-5

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Oxychlorination of ethylene to 1,2-dichloroethane (EDC) is a large-scale commercial reaction operated as one third of the 'balanced' vinyl chloride (VCM) process. In this operation, ethylene, HCl, and oxygen are passed over a fixed bed catalyst operating at ca. 200°C and converted to EDC at high conversion (>95%) and selectivity (>95%).[1]

The commercial catalysts utilized are comprised of copper chloride impregnated on an alumina carrier. Additives such as potassium chloride and lanthanum chloride are frequently added to improve catalyst selectivity and operability.[2,3] These catalysts are generally limited to operation below 250°C since loss of selectivity to carbon oxides (CO_x) and loss of activity due to copper halide migration are realized at higher temperatures.

Utilization of ethane as a replacement for ethylene in EDC production or alternatively in a one-step direct route to VCM is quite attractive due to lower feedstock prices and a simpler process configuration. Copper-containing ZSM-5 catalysts were found to be highly active and selective for the oxychlorination of ethane to VCM at 500°C.

These zeolite catalysts exhibit stable operation under steady-state reaction conditions as compared with copper on alumina or copper on silica systems which showed rapid deactivation primarily due to copper halide loss.

The Cu-containing ZSM-5 catalysts were studied utilizing a pulse reactor to ascertain some mechanistic understanding of the ethane to VCM reaction. Conversion and selectivity were found to be highly dependent upon the method of copper addition to the zeolite, the Si/Al ratio of the ZSM-5, and the identity and quantity of additional cationic species added to modify catalytic behavior. Activity and selectivity comparisons were made to copper on alumina and copper on silica systems utilizing the pulse reactor system and compared with data from steady-state experiments from a plug-flow reactor.

A sequence of catalyst states are proposed, Figure 1, to describe the dynamic redox and oxychlorination occurring with the copper centers in the ZSM-5 catalyst during the course of reaction. The catalyst moieties are named according to their observed colors under steady state conditions: green, gold, and white. Each of these individual catalyst states were preferentially formed, stabilized and then subsequently characterized by chemisorption and in situ catalytic reaction testing in the pulse reactor.

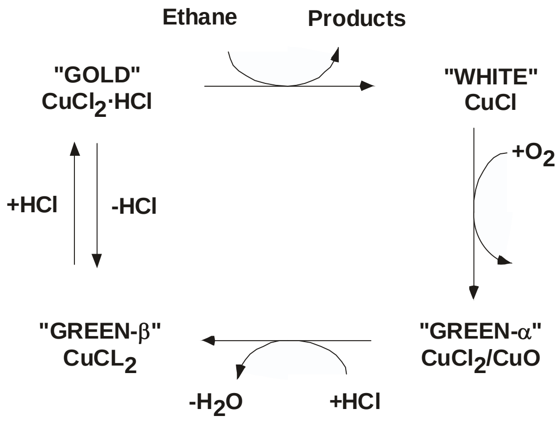

Figure 1. Catalytic reaction scheme proposed for copper ZSM-5 redox catalysts during ethane oxychlorination.

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[1] Weissermel, K. and Arpe, H.J. in "Industrial Organic Chemistry" p. 219. Wiley-VCH, Weinheim, 2003

[2] Rase, H.F. in "Handbook of Commercial Catalysts. Heterogeneous Catalysts" p. 295. CRC Press, Boca Raton, 2000

[3] Hodnett, B.K. in "Heterogeneous Catalytic Oxidation" p. 275. Wiley, New York, 2000