

Nanostructured surfaces

Nanostructure of the catalyst surface $\text{CuCl}_{(1,2)}$ on $\gamma\text{-Al}_2\text{O}_3$

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Structure of CuCl_2 active catalyst centres used for ethylene oxidative chlorination (EOC) on the $\gamma\text{-Al}_2\text{O}_3$ carrier was described.

Namely two types of catalysts were considered – deposited catalyst X1 of the firm «Harshow», with copper chlorides supported onto an alumina surface, and permeated MEDC-B catalyst located in the internal pores of the support of the firm «Sud-Chemie Catalysts». CuCl_2 interactions with $\gamma\text{-Al}_2\text{O}_3$ surface groups ($\equiv\text{Al-OH}$) lead to complex compounds formation with $[\text{CuCl}_4]^{2-}$ and $[\text{CuCl}_2]^{-1}$. A new mechanism of metal-complex catalysis of the ethylene oxidative chlorination reaction into 1,2-dichloroethane with $\text{Al}_2\text{O}_3[\text{CuCl}_4]^{2-}$ and $\text{Al}_2\text{O}_3[\text{CuCl}_2]^{-1}$ surface metal complexes reacting with ethylene, hydrogen chloride, and oxygen was proposed.

Differential thermal analysis modeling catalysts' industrial tests. MEDC-B catalyst has higher dehydration and dehydrochlorination rate, and higher 210-220 °C EOC temperature range compared with X1 catalyst (200-210 °C). MEDC-B catalyst is more stable, but less active in the lower 190-210 °C EOC temperature range, thus its optimal EOC temperature range is 210-220 °C. Lower total weight loss of 17 % during MEDC-B catalyst heating compared with 20 % for X1 is caused by the smaller amounts of the adsorbed and structured water, and by smaller dehydrochlorination losses.

Average process rates comparison for the three samples is quite interesting. MEDC-B catalyst dehydration rate increases as a result of $[\text{CuCl}_4]^{2-}$ and $\gamma\text{-Al}_2\text{O}_3$ interactions. Modified $[\text{CuCl}_4]^{2-}$ catalyst acts as chlorine transmitter during its reduction and dehydrochlorination in the 200-250 °C range which is within the 215-225 °C range of ethylene oxidative chlorination catalyst working temperature. X1 catalyst dehydration and dehydrochlorination temperature range is 180-250 °C ($\Delta T=70$ °C) while for MEDC-B it is 200-250 °C ($\Delta T=50$ °C).

Working temperature range reduction by 20 °C for MEDC-B compared with X1 catalyst is beneficial for ethylene oxidative chlorination reaction into 1,2-EDC and significantly increases process selectivity. Deposited X1 catalyst has a larger 190-210 °C working range which causes side reactions of ethylene combustion and oxidative chlorination into trichloroethylene. While X1 catalyst selectivity does not exceed 95-97 %, MEDC-B selectivity is 97-99 %. Based on industrial tests ethylene combustion to CO and CO_2 diminishes to 1.5-2 % for MEDC-B. The amount of the permeated MEDC-B catalyst active phase is evenly distributed throughout $\gamma\text{-Al}_2\text{O}_3$ structure which diminishes carrier influence on ethylene combustion observed in industrial EOC technological processes.

Thus the definition nanostructure catalyst surface oxidative chlorination of ethylene determine the conversion of raw materials, as well as yield and selectivity of the process and lead to fewer byproducts, organochlorine waste that will improve the environmental and economic component of the industrial process in the production of 1,2-dichloroethane and vinyl chloride in global scale.

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