



SLURRY-PHASE DIRECT SYNTHESIS OF ALLYLCHLOROSILANES

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Allylchlorosilanes are useful intermediates for the synthesis of organic specialties and other allyl organofunctional silanes such as allyldiethoxysilane and allyltriethoxysilane. Sarkar¹ has reviewed various methods for their synthesis. However, Direct Synthesis from silicon and allyl chloride is not among them. Hurd² obtained a mixture of allyldichlorosilane (ADCS, $C_3H_5SiHCl_2$) diallyldichlorosilane (DADCS, $(C_3H_5)_2SiCl_2$) and allyltrichlorosilane (ATCS, $C_3H_5SiCl_3$) when allyl chloride and copper-silicon alloys were reacted in a fixed bed at 230 -300°C. He reported the facile polymerization of the products at temperatures > 150°C. This resulted in the accumulation of high-boiling residues and occlusion of the silicon particles. Ultimately, silicon conversion was low and the reaction was unstable. This has been corroborated by other authors³⁻⁹ who used fixed³, stirred⁴ or rotating bed⁵ reactors. Yeon, et al.⁴ found that mixtures of HCl and allyl chloride favored allyldichlorosilane formation. They also reported that zinc inhibited the reaction and that cadmium was an effective promoter. US 3,440,267 disclosed a copper-catalyzed slurry-phase Direct Synthesis of allylchlorosilanes at 150 – 300°C in mineral oil. Polymer formation and its control were not reported. We¹⁰ have reported polymerization of allylchlorosilanes during the slurry-phase reaction of allyl chloride with cyclone solids containing 1.2 – 1.5 wt% Al, and 0.5 – 0.8 wt% Zn as the silicon source. Now, we¹¹ disclose that polymerization is Lewis Acid catalyzed and can be inhibited with Lewis bases such as hexamethyldisiloxane, tetramethylurea and sulfur-containing additives comprising mercaptans (thiols), thioethers, thiourea, phenothiazine and thioesters to enable stable Direct Synthesis of allylchlorosilanes. This improved Direct Synthesis of allylchlorosilanes also enables recovery of value from methylchlorosilane solid silicon waste streams (grinding fines, spent mass, cyclone and filter fines) and contributes to sustainable organosilane manufacture.

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