Catalyst Selection for the Hydrosilylation Synthesis

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GE Advanced Materials - Silicones, in its quest to expand its global reach in research, has established a group of researchers with skills in chemistry, chemical engineering and polymer science at GE's John F. Welch Technology Centre (JFWTC), Bangalore, India. Various Centers of Excellence exist within these disciplines at JFWTC. Research teams within these Centers of Excellence work cooperatively with other GE technologists and technology teams in other parts of the globe to solve problems of interest to GE Advanced Materials. An example of such global collaboration is presented here with specific focus on Process Development of the hydrosilylation synthesis of beta-cyanoethyltriethoxysilane, \( \text{-CN(CH}_2\text{)}_2\text{Si(OC}_2\text{H}_5\text{)}_3 \), from acrylonitrile (H2C=CHCN) and triethoxysilane (HSi(OC2H5)3). The hydrosilylation produces both the alpha and beta isomers of cyanoethyl-triethoxysilane. The beta isomer is preferred for conversion to gamma-aminopropyltriethoxysilane, \( \text{-H}_2\text{N(CH}_2\text{)}_3\text{Si(OC}_2\text{H}_5\text{)}_3 \), an organofunctional silane used in coatings, adhesives and sealants and glass-reinforced resins. Hydrosilylation is accompanied by acrylonitrile reduction to propionitrile (CH3CH2CN) and disproportionation of triethoxysilane to ethyl silicate (Si(OC2H5)4). The hydrosilylation catalyst is required to optimize selectivity to beta-cyanoethyltriethoxysilane. The research team screened a wide range of transition metal catalysts. The results showed that preference for the beta isomer was greater with ruthenium catalysts. Rhodium catalysts favored the alpha isomer. Beta isomer selectivity was further enhanced \((\beta''/\beta'' > 100)\) when entrapped vapors were allowed to escape during the course of the reaction as well as with additive ketones such as mesityl oxide, methyl isobutyl ketone, t-butyl cyclohexanone and benzophenone. The data presented will highlight results for reactions in which these ketones were used in combination with triruthenium dodecacarbonyl (Ru3(CO)12).