

Catalyst Development for Synthesis of Dimethyldichlorosilane from SiCl₄ in a 2-Step process

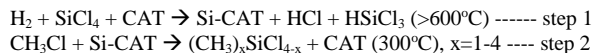
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A low cost, low energy and scalable Si-chemistry that runs parallel to the current direct process to produce Dimethyldichlorosilane (Me₂SiCl₂), which is hydrolyzed to produce polydimethylsiloxane (PDMS) was developed by Dow Performance Silicones (hDCC). The direct process¹ (Rochow-Muller) relies on the energy intensive carbothermic reduction of SiO₂ and elemental silicon feedstock accounts for ~60% of PDMS production cost. A new route was created to make low energy route to make methylchlorosilanes without going through metallurgical grade Si. A path was identified that involves 3 reactions, the first one being the carbochlorination of mineral SiO₂ sources at <1000°C to produce SiCl₄, which is then reacted with CH₃Cl to produce Me₂SiCl₂ in a 2-step process using a catalyst²⁻³. This new process capability showed a range of potential impacts from high conversion of Me₂SiCl₂ as well as monomer flexibility, improved selectivity of Me₂SiCl₂ and more efficient raw material utilization. This presentation primarily focuses on the development of a new generation copper aluminate type spinel catalysts for the production of dimethyldichlorosilane (Me₂SiCl₂) from SiCl₄ in a 2-step process⁴.

The following reactions are carried out on a catalyst (CAT).



The catalyst selection for the 2-step process was challenging as the process involves severe reaction conditions which include reacting with H₂ and SiCl₄ feed gases at above 650°C in a fluid bed reactor. Copper based catalysts were evaluated in the 2-step process due to potential similarities of step-2 reaction with the direct process. High surface area, large pore volume and homogeneous dispersion are all important characteristics of the catalyst for high activity and cycle stability.

Though, γ-Al₂O₃ is the most widely used as a support material for several hydrotreating commercial processes, a considerable drawback with γ-Al₂O₃ is that it is not resistant to SiCl₄ during the course of reaction and will be transformed to aluminum chloride. Alumina has several advantages as a support material and if all these advantages associated with this support are incorporated in a catalyst system, it will be an ideal catalyst for the 2-step process. If γ-alumina support is transformed in to alpha-alumina (or a more stable phase) and

associate with copper, the resulting catalyst may inherit the favorable physical properties and retaining hydrogenation activity of SiCl₄ in step-1 and will be less reactive towards SiCl₄.

Both γ-alumina and copper aluminate possess the same structure (cubic-close packed), which results automatically in a dispersed CuO on alumina single phase, which was confirmed by XRD analysis. In the reduction of spinel compound, CuAl₂O₄ and part of CuO closely associated with CuAl₂O₄ were reduced much slower than bulk CuO or supported CuO catalysts. However, once reduced, a phase change is forced and most of the alumina is converted to alpha phase containing atomically dispersed copper nanoparticles.

In this study, various compositions of copper aluminate type spinel materials were synthesized by wet impregnation and physical mixing methods and investigated in the 2-step process. The catalytic performance of these copper aluminates was superior to those of conventional copper catalysts. More uniform distribution of CuAl₂O₄ and complete formation of CuAl₂O₄ phase in the catalyst/ supports due to high calcination temperatures thus higher Cu mobility/diffusion are believed to help strengthen the particle integrity and could minimize AlCl₃ formation in the process.

Copper aluminates were found to exhibit superior activity over other conventional catalysts and hold better particle integrity in lab scale fixed bed and fluid bed reactors. The catalysts were characterized by XRD, SEM/EDS, N₂O pulse chemisorptions and particle size distribution analysis and correlated with activity results in the 2-step process to make Me₂SiCl₂ from SiCl₄. High rate of methylchlorosilane production on spinel catalysts in step-2 was attributed to the smaller particle sizes and “meta-stable” copper silicide (Cu₃Si) that is formed during the step-1 reaction. In-situ XRD analysis confirmed the high reactivity of copper in spinel compared to other conventional catalysts. SEM analysis has shown the Cu association with alumina in fresh catalysts and the dissociation of Cu from support was less in the spent catalysts compared to conventional silica supported copper catalysts.

Mass and energy balances of a full scale process show 30% less energy consumption in comparison to the current direct process.

REFERENCES

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