



Supported Liquid Phase Catalysts for Oxidative Dehydrogenation of Propane

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Introducing additives to supported vanadia catalysts has been intensively studied with the aim to improve the catalyst performance in oxidative dehydrogenation of propane (ODP)^{1,2}. Recently, it has been shown that melting phenomena influence the catalytic performance significantly when silica-supported vanadium oxide is modified by potassium³. Activity drops and selectivity increases markedly when the supported V-K oxide layer and/or segregated crystalline potassium vanadate phases are melting. The present study deals with the question whether liquefaction has a similar effect when other alkali oxides A_2O ($A = Cs, Rb$) are used as fluxing agents, *i.e.*, whether the phenomena described above arise from an impact of potassium or phase transition. For the purpose of reproduction and comparison, silica-supported vanadium oxide catalysts that contain K, Li, or Na oxide, respectively, were also prepared.



Aqueous suspensions of alkali carbonates and V_2O_5 with SiO_2 (Aerosil 300) were spray-dried and the resulting powders were treated in synthetic air at $620^\circ C$ for 16 hours. The catalysts were tested in the ODP reaction in a 1:1 feed of propane and oxygen (*i.e.*, $C_3H_8/O_2/N_2 = 7.5/7.5/85$ vol%) in an eight-fold parallel reactor. The catalyst that contains 37 mol% K exhibited

the formation of only one crystalline phase ($K_3V_5O_{14}$) in the solid state at room temperature. A sharp melting signal was observed by differential scanning calorimetry (DSC) at $410^\circ C$, which was attributed to melting of $K_3V_5O_{14}$ ³. CsV_2O_5 was the only detectable crystalline phase in all Cs-containing catalysts at low temperature. The phase transformation occurred in a broad temperature range between $430^\circ C$ and $446^\circ C$. Rb addition led to formation of the mixtures of $Rb_2V_4O_{11}$ and $Rb_3V_5O_{14}$ phases with melting points below $400^\circ C$.

The activity dropped when the melting point of the alkali vanadate phases was reached. Operando DSC revealed a clear correlation between melting and decrease in activity. In case of the K- and Rb-containing catalysts, selectivity rapidly increased after melting. The effects were less pronounced for the Cs-containing catalysts, perhaps due to the broad temperature range of melting. At higher temperatures, the selectivity of the all catalysts approached similar values.

Decrease in specific surface area or loss of oxygen can be excluded as reasons for the drop in activity. Structural reasons for the performance changes will be discussed based on spectroscopic investigations of the materials under operation and comparison with Li- and Na- catalysts, which shows no melting during catalysis.

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³H. Ahi, Thesis, DOI: [10.14279/depositonce-6711](https://doi.org/10.14279/depositonce-6711) (2017).