The Relevance of Phase Transitions in Na-Mn-W-Oxide Catalysts for the Oxidative Coupling of Methane
Maximilian James Werny, Hamideh Ahi

The Mn-Na$_2$WO$_4$/SiO$_2$ catalyst system for oxidative coupling of methane (OCM) has been extensively investigated over the last decades.\(^1\) The reaction temperatures applied in OCM are usually above 730°C. Under these reaction conditions, liquefaction of an active component that contains alkali and transition metal oxides should be taken into consideration. To investigate the influence of sodium on the physical and catalytic properties of supported Na-Mn-W-oxide model catalysts, we have studied the thermal behaviour of supported and unsupported mixtures of sodium oxide and manganese tungstate applying thermal analysis, X-ray diffraction, \textit{operando} Raman spectroscopy, and electron microscopy.

Mixtures of Na$_2$CO$_3$ and MnWO$_4$ have been prepared by grinding. The mixtures with or without steatite used as support (20 wt% loading) have been heated to 850°C for 1-16 h in flowing synthetic air (20 ml min$^{-1}$). Due to the use of MnWO$_4$ the Mn:W ratio was kept constant at 1:1, but the Na content was varied. The Na:Mn:W ratios ranges from 80:10:10 to 40:30:30.

Na$_2$WO$_4$ and MnWO$_4$ are the main supported phases formed. Phase composition varies depending on the composition of the mixtures. Thermal analysis reveals a complex melting behaviour showing two main endothermic events with on-sets at 570°C and 650°C, respectively. Based on the results of Raman spectroscopy these events are related to first order phase transition of Na$_2$WO$_4$ from the cubic structure to the orthorhombic structure, and to the melting point of Na$_2$WO$_4$, respectively. MnWO$_4$ melts at 1250°C.

The catalyst with the highest sodium content (80%) is characterized by the lowest activity and comparatively low selectivity. With increasing sodium content the activity increases. At comparable conversion the highest selectivity to C2 products (sum of ethane and ethene) has been achieved with the catalyst that contains the lowest amount of sodium.

Relations between the presence of a molten sodium tungstate and the onset of the activity in OCM have not been found. Under reaction conditions, significant changes in the Raman spectra of the catalysts occur that suggest substantial structural changes. The lattice vibrations of MnWO$_4$ disappear at 700°C. The observation is tentatively attributed to dissolution of MnWO$_4$ in molten Na$_2$WO$_4$, which seems to characterize the active state of the catalyst under reaction conditions of oxidative coupling of methane.

References