Advancing Strategies for Methane Partial Oxidation to a Methyl Ester with Heterogeneous Catalysts

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Direct methane partial oxidation to liquid oxygenates (e.g. methanol) is a highly desired valorization pathway with limited actionable progress due to numerous challenges and despite decades of research [1-3]. For thermocatalytic systems, a steep selectivity-conversion trade-off remains independent of the catalyst that severely limits product yields. The first part of this contribution critically examines the current strategies to break through these limits and achieve high product yields, comprising work in catalyst design, additional co-reactants/protecting agents, and cycling schemes. From this, we highlight the most successful strategies and identify crucial gaps in bridging the vast scientific knowledge in methane activation and the technological necessities of viable methane valorization.

In the second part of the contribution, we describe recent advances from the group in the conversion of methane to an oxidation-resistant methyl ester, one of the most effective routes for high-yield methane conversion [2, 4]. We first introduce an improved system that targets key shortcomings in the conventional chemistry, namely the reliance on extremely aggressive acid solvents, economically impractical oxidants, and homogeneous catalysts [6]. Notably, we synthesize the first solid catalysts that can perform this chemistry using air as the oxidant. Under our improved reaction conditions, facilely synthesized Co/SiO_2 and Mn/TiO_2 display competitive performance on the basis ester production rates (~250 and ~610 μmol g_{cat}^{-1} h^{-1}, respectively) with negligible metal leaching in comparison to previously reported homogeneously catalyzed systems that employ stronger oxidants and higher methane partial pressures [5, 6]. Furthermore, we find that high metal dispersion is associated with high activity in this system, and the most efficient utilization of cobalt or manganese is realized at the lowest metal loadings. The conclusion of the contribution underscores impactful directions for further developing this high-yield strategy beyond conventional approaches.

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