

Selective Oxidation of Methane to Methanol at Low Temperatures with Molecular Inspired Solid Catalysts

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Introduction

Methane is an abundant material found world-wide, particularly in form of natural gas. The ability to directly convert methane to methanol in economically satisfactory yields is an important goal of the oil and gas industry. Current technologies or catalytic systems for a direct utilization suffer from low selectivities owing to overoxidation to carbon dioxide. These systems typically involve high temperatures and high energy intermediates like radicals leading to unselective methane conversion. A highly promising alternative is the low-temperature oxidation of methane to methanol via C-H activation mediated by late transition metal complexes. The catalytic system developed by the group of R. Periana involving a molecular Pt(bpym)Cl₂ complex and fuming sulfuric acid is considered to be the most active one. Under reaction conditions methane is converted to methylbisulfate wherein hydrogen sulfate is acting as a protecting group against further oxidation. This intermediate can be hydrolyzed in a subsequent step resulting in a high overall selectivity to methanol. An industrial application was ruled out due to drawbacks like e.g. product and catalyst separation [1].

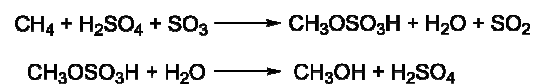


Figure 1. Methane conversion to methylbisulfate and subsequent hydrolysis to methanol.

We overcame the latter problem developing solid catalysts for the low-temperature oxidation of methane [2][3]. Covalent Triazine Frameworks (CTF), which resemble the bipyrimidyl ligand, were used as a kind of solid ligand to mimic the Periana catalyst. These polymers can be modified coordinatively with a platinum(II) species and can stand the harsh oxidizing reaction conditions due to their unique structure. Our current investigations are focused on catalyst optimization and development of alternative solid ligands. In particular, we have identified novel nitrogen doped carbons obtained from hydrothermal carbonization of various biomass sources [4][5] as high potential materials reaching TONs above 1000 and higher.

Experimental

Catalytic tests were carried out in an autoclave (Hastelloy C) that was filled with oleum (20 wt.% SO₃) and the catalyst, before it was closed and pressurized with 45 bar CH₄. The reactor was heated up to 215°C for 2.5 h. Gas phase components were analyzed by FT-IR while the liquid phase was hydrolyzed to give free methanol that was analyzed via HPLC. CTF materials and mesoporous nitrogen-doped carbons from glucose/albumin (HC-Alb) or from chitin biomass (HC-Lob) were prepared as described elsewhere [2][4][5]. Platinum coordination was carried out in water for 24 h at room temperature.

Results/Discussion

Platinum modified CTF materials achieved stable catalytic performance over several runs in direct methane oxidation. Turnover numbers of about 300, which are comparable to the Periana catalyst, were obtained with selectivities to methanol of ≥ 75%. Moreover, nitrogen doped carbons from biomass sources could be modified via coordination of a Pt(II) species analogous to the CTF materials. Carbon framework composition and the kind of nitrogen sites could be controlled by thermal treatment under inert atmosphere. Only carbons that possess fully aromatic nitrogen were stable in the strongly acidic solvent without decomposition. Interestingly, Pt-modified HC-Alb materials achieved high single run activity but subsequent recycle steps showed significantly lower catalytic activity due to Pt leaching. We assume that this deactivation effect is caused by an unstable Pt coordination within the carbon framework analogous to previously tested polybenzimidazole material [3]. In contrast, Pt-HC-Lob, which was calcined at 900°C, showed remarkable stability over three runs with TONs of about 1000. This activity is superior to the molecular Periana system although long term durability still has to be investigated. The enhanced activity can be explained by either more favourable electronic structure at the metal centre due to the solid ligand backbone or by structural properties of the nitrogen doped carbons. Interestingly, preliminary results show that porosity has a strong impact on catalytic performance. It was possible to boost the activity of existing Pt-CTF materials by selective variation of pore structure. Catalytic performances of these new materials provide new insights into possible pathways for catalyst design for direct methane oxidation.

References

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