Design of Cr- and Fe-containing MOF catalysts for mild oxidation of methane

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The challenge of direct methanol production from methane has been engaging researchers worldwide for decades, but still no feasible solution exists. The reason of this is well-known: C–H bond in methane is considerably more stable than that in methanol, and it makes extremely difficult achieving high yields of methanol without its further oxidation to formic acid and carbon dioxide. An attractive pathway to solve this problem consists in design of the catalyst’s active sites as isolated metal-oxygen clusters of specific electronic and geometric structure. The inspiration for this strategy comes from Fe- and Cu-oxoclusters in methane monooxygenases (MMOs), natural enzymes capable of converting methane to methanol in mild aqueous conditions [1, 2]. Artificial catalysts based on Fe- and Cu-modified zeolites further proved the correctness of this approach [3, 4], although they could not meet the activity and selectivity of their natural counterparts.

Following this principle, we have recently suggested a fundamentally new catalyst for methane to methanol conversion, based on metal-organic frameworks (MOFs). We showed that partial exchange of Al$^{3+}$ cations by Fe$^{3+}$ in the MIL-53(Al) framework results in formation of an active system, able to activate methane and convert it to methanol using hydrogen peroxide as oxidant [5]. In the current work we broaden this approach by introducing Cr$^{3+}$ in the structure of MIL-53(Al). We found out that MIL-53(Al, Cr) catalyst is active in methane-to-methanol conversion and demonstrates higher methanol selectivity than MIL-53(Al, Fe) catalysts. Comparison of catalytic properties and in-depth characterization of MIL-53(Al, Cr), MIL-53(Al, Fe) and trimetallic MIL-53(Al, Cr, Fe) MOFs shows how the ratio between different types of Cr and Fe active sites influences the product distribution. This gives insights for the rational design of MOF-based catalysts for mild methane oxidation.


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