PROCESS INTENSIFICATION BY OXYGEN TRANSPORTING PEROVSKITE MEMBRANES FOR NOVEL APPLICATIONS: AROMATIZATION OF METHANE AND OSTWALD REACTION, COUPLING OF TWO REACTIONS

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The development of long-time stable perovskite materials allowed their use in novel applications like the transformation of methane into fuels and chemicals by aromatization reaction, the partial ammonia oxidation to NO (Ostwald reaction) in catalytic membrane reactors, and the oxi-dehydrogenation of alkans.

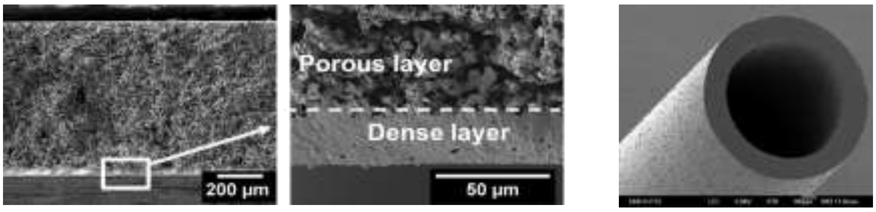
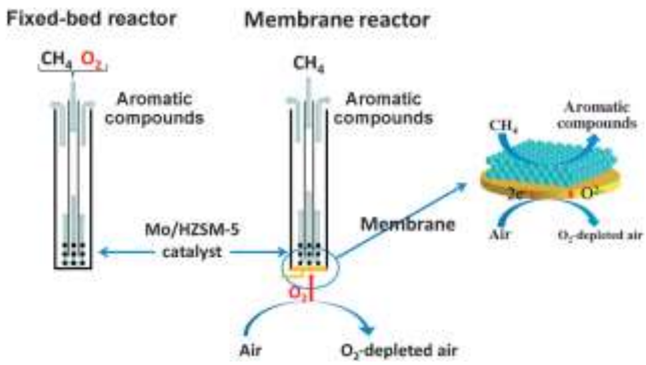


Figure 1: Planar disc membrane prepared in Forschungszentrum Juelich (Germany) by sequential tape casting of the composition $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and hollow fiber membrane of the composition $Ba(Co_{0.4}Fe_{0.4}Zr_{0.2})O_{3-\delta}$ prepared by Fraunhover Institute IGB Stuttgart.

Home-built membrane reactors with (i) planar oxygen-transporting perovskite disc membranes, and (ii) tubular hollow fiber perovskite membranes, have been used. In the case of methane aromatization, the membrane has only the job to separate oxygen from air to combust in situ the hydrogen liberated in the methane aromatization according to $6\ CH_4 \leftrightarrows C_6H_6 + 9\ H_2$. In the ammonia oxidation, the perovskite has two functions: It separates the oxygen from air and is itself the catalyst for the ammonia partial oxidation according to $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$. In our concept of coupling two reactions through an oxygen-transporting membrane, one reaction produces oxygen, the other consumes oxygen.

Catalyst deactivation by carbonaceous residues is the central problem of methane dehydro-cyclo-aromatization. If the reaction is conducted in a classical fixed bed reactor, the typical yield of about 8 % (benzene, toluene, naphthalene) at 750 °C drops to < 1 % after 10 h time on stream. However, if the abstracted hydrogen is selectively burnt to steam in a membrane reactor with oxygen separated from air through a perovskite membrane ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$) , the aromatics yield is after 10 h still > 3 %. In both fixed bed and membrane reactor, the usual Mo/H-ZSM-5 catalyst has been used [1].

Figure 2 Methane dehydro-cyclo-aromatization in a fixed bed and in a membrane reactor



As stated above, in the selective ammonia oxidation to NO, the perovskite membrane hat the functions to (i) supply oxygen by separation from air, and (ii) to act as catalyst by supplying this oxygen as highly selective lattice oxygen in a Mars and van Krevelen mechanism. Using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, at 850 °C a NO selectivity of 95% could be obtained. The industrial Ostwald process has the same selectivity, but uses expensive metallic Pd/Rh grids are used. The high selectivity in the membrane reactor is due to the continuous flux of selective lattice oxygen [2].

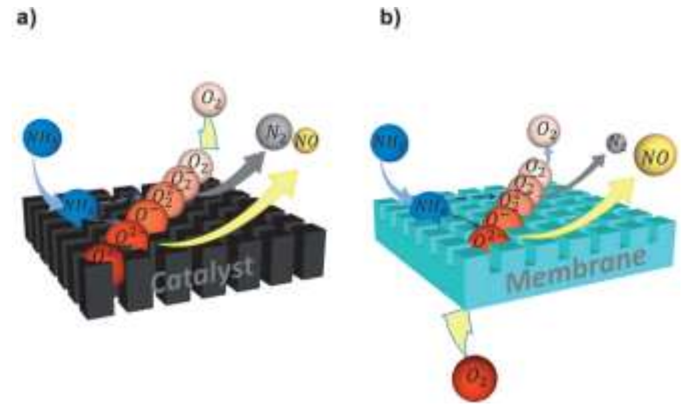


Figure 3. Ammonia oxidation over a) conventional packed bed perovskite catalyst, and b) a perovskite membrane.

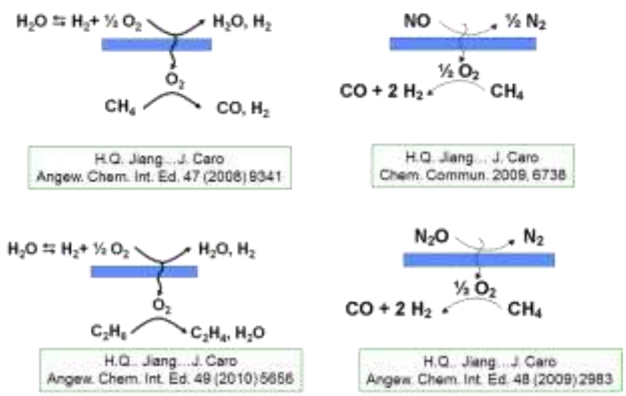


Figure 4. Coupling the oxygen-producing reactions thermal water splitting and NO_x decomposition with oxygen consuming reactions like methane partial oxidation or alkane-to-alkene partial oxidation.

In catalytic membrane reactors, catalyst and oxygen transporting membranes can be two different materials with two different functions like in the case of methane dehydro-cyclo-aromatization. In the ammonia partial oxidation, the perovskite has the dual function of oxygen separator and catalyst: it provides a continuous flux of highly selective lattice oxygen for the ammonia partial oxidation to NO.

References

[1] Z. Cao, H. Liang, H. Luo, S. Baumann, W.A. Meulenberg, J. Assmann, L. Mleczko, Y. Liu, J. Caro, Natural gas to fuels and chemicals: Improved methane aromatization in an oxygen permeable membrane reactor, *Angew. Chemie Int. Ed.* 52 (2013) 13794-13797

[2] Z. Cao, H. Jiang, H. Luo, S. Baumann, W.A. Meulenberg, H. Voss, J. Caro, ChemCatChem 6 (2014) 1190-1194.