Integration of nine steps for producing ammonia and liquid-fuel synthesis gases in one membrane reactor

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With the support by the National Natural Science Foundation of China and the Chinese Academy of Sciences, the research team led by Prof. Yang Weishen (杨维慎) and Prof. Zhu Xuefeng (朱雪峰) at the State Key Laboratory of Catalysis, Dalian Institute of Physical Chemistry, Chinese Academy of Sciences, proposed a new catalytic membrane reactor for one-step producing the ammonia synthesis gas (ASG, $H_2/N_2=3$) and liquid fuel synthesis gas (LFSG, $H_2/CO=2$), which was published in *Angew Chem Int Ed* (2016, 55: 8566 —8570).

In recent years, coupling catalytic reactions in membrane reactors have been regarded as an efficient way to achieve process intensification. Mixed ionic-electronic conducting (MIEC) membranes are effective for the coupling catalytic reactions. Before realizing the concept of simultaneously producing two types of synthesis gases in one membrane reactor, they have solved the problems related to the long-term stability of the MIEC membranes by coating porous catalyst layers on both surfaces of membranes to inhibit the negative effects of the enrichment of S and Si impurities, and by introducing nano particles into the grain boundaries to inhibit the unfavorable phase transformation. These findings were published in *Angew Chem Int Ed* (2013, 52: 3232—3236) and *Nano Letter* (2015,15: 7678—7683), respectively.

Ammonia synthesis and liquid fuel synthesis via the Fischer-Tropsch process are two important processes in chemical industries. The preparations of the two types of synthesis gases are very critical for ammonia and liquid fuel synthesis. However, in industrial processes, six main steps are required to convert cleaned natural gas to ASG and three main steps to liquid fuel synthesis gas LFSG. The complicated technologies for ASG and LFSG production consume huge energy and releasea huge amount of CO_2. To solve these problems, the concept of simultaneously producing ASG and LFSG in one MIEC membrane reactor was creatively proposed and successfully demonstrated by experiments with excellent performance. Air and water with an appropriate ratio are fed to one side (side I) of the membrane, while methane is fed to the other side (side II). At high temperatures, driving by high oxygen partial pressure gradient across the membrane, oxygen from air and water permeates through the MIEC membrane to side II, where they react with methane to form LFSG, meanwhile electrons migrate from side II to side I to keep the electric neutrality of the whole process. The resultant gases on side I with a suitable H_2/N_2 ratio are ready for ammonia synthesis after drying. Compared with industrial processes, the membrane reactor has many advantages: high process intensification (shortening the six-step process for ASG production and three-step process for LFSG production to a one-step process), ~ 63% energy saving, high safety, environmental friendly and clean ASG product.

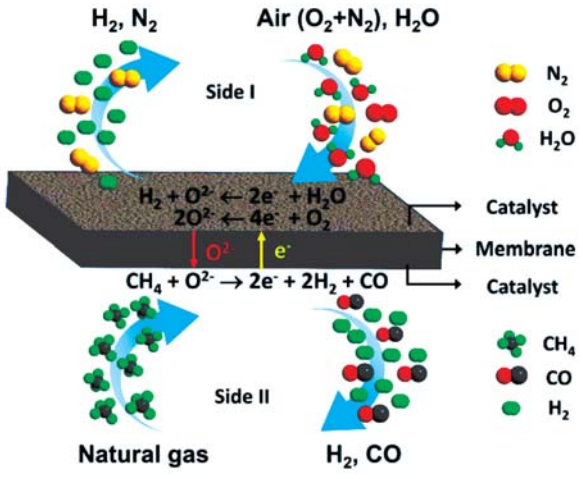

Figure Concept of the MIEC membrane reactor for simultaneously producing ASG and LFSG.