New Ceramic Membrane Enables First Direct Conversion of Natural Gas to Liquids without CO_2 Emissions

A team of scientists from CoorsTek Membrane Sciences, the University of Oslo/NO, and the Instituto de Tecnología Química/ES has developed a new process to use natural gas as raw material for aromatic chemicals. The process uses a novel ceramic membrane to make the direct, non-oxidative conversion of gas to liquids possible for the first time – reducing cost, eliminating multiple process steps, and avoiding any carbon dioxide (CO_2) emissions.

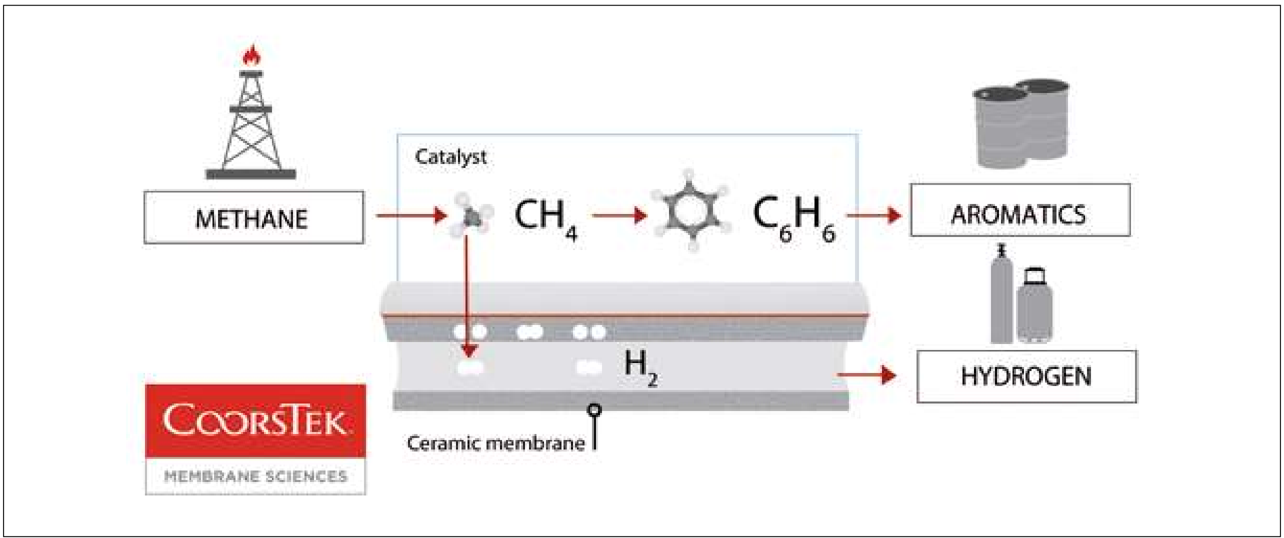

Fig. 1
CoorsTek active ceramic membrane technology converts membrane to aromatic chemicals in a single-step process

The challenges of natural gas conversion

Natural gas constitutes a large fraction of the world's hydrocarbon resource, but much of this resource is stranded without economically viable paths to market. Even when available for industrial conversions, the high stability of the methane molecule leads to energy losses associated with multi-stage processing in large chemical plants, which use oxygen or steam to activate the methane in what is known as synthesis gas (syngas) processing.

Temperature and pressure have historically been the main parameters chemists and engineers can work with to control reactions. Catalysts can improve speed and selectivity, without promoting reactions beyond their chemical equilibrium limit. Integrating a ceramic ion-conducting membrane into the reactor enables an increase in the productivity of industrially appealing processes which are otherwise impractical due to strong thermodynamic constraints. Along with scientists from the University of Oslo and the Institute of Chemical Technology (Valencia/ES), engineered ceramics

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maker CoorsTek (Golden, www.coorstek.com) has developed a specialized reactor that integrates an ion-conducting membrane to shift the thermodynamic equilibrium of the reaction and drive the process toward increased product formation without generating carbon dioxide.

Nonoxidative methane (CH_4) dehydroaromatization (MDA) is a promising catalytic route that directly converts natural gas into valued petrochemicals such as benzene. The MDA reaction is conventionally run at ~700 °C in the presence of bifunctional catalysts comprising carbided molybdenum nanoclusters dispersed in acidic shape-selective zeolites such as ZSM-5 and MCM-22. The process suffers from two major hurdles that challenge its further development and industrial implementation: (1) the per-pass conversion is limited by thermodynamics, and (2) the catalyst activity rapidly drops with time on stream because of the accumulation of polyaromatic-type coke on the external zeolite surface that impedes the access to internal active sites.

Attempts to overcome thermodynamic limitations by selective removal of the coproduct H_2 from the reactor using other ceramic membranes, for instance, $La_{5,5}W_{0,6}Mo_{0,4}O_{11,25-\delta}$($LWM_{0,4}$), were limited by enhanced coke formation that accelerated catalyst decay. Strategies based on fine-tuning the zeolite acidity and porosity and cofeeding small amounts of CO_2, CO, H_2, and H_2O with CH_4 were applied to stabilize the catalyst by restraining the production of coke, but with limited success.

Ceramic membrane technology enables a better conversion process

The technology involving this novel ceramic membrane reactor offers a pathway around these obstacles. The conversion process uses it to make the direct, non-oxidative conversion of gas to liquids possible for the first time – reducing cost, eliminating multiple process steps, and avoiding any carbon dioxide (CO_2) emissions. The resulting aromatic precursors are source chemicals for insulation materials, plastics, textiles, and jet fuel, among other valuable products.

"Consider the scale of the oil, gas, and petrochemicals industry today", says Dr Jose Serra, Professor with Instituto de Tecnología Química (ITQ) in Valencia, a leading research lab for hydrocarbon catalysis. "With new ceramic membrane reactors to make fuels and chemicals from natural gas instead of crude oil, the whole hydrocarbon value chain can become significantly less expensive, cleaner, and leaner. By using a ceramic membrane that simultaneously removes hydrogen and injects oxygen, we have been able to make liquid hydrocarbons directly from methane in a one-step process.

As a bonus, the process also generates a high-purity hydrogen stream as a byproduct. At a macro level it is really very simple – inexpensive, abundant gas in and valuable liquid out through a clean, inexpensive process. At a nanochemistry level, however, where molecules interact with catalyst and membrane at a temperature around 700 °C, there were many factors to engineer and control in order to render just the specific valuable molecules needed to make the new process work."

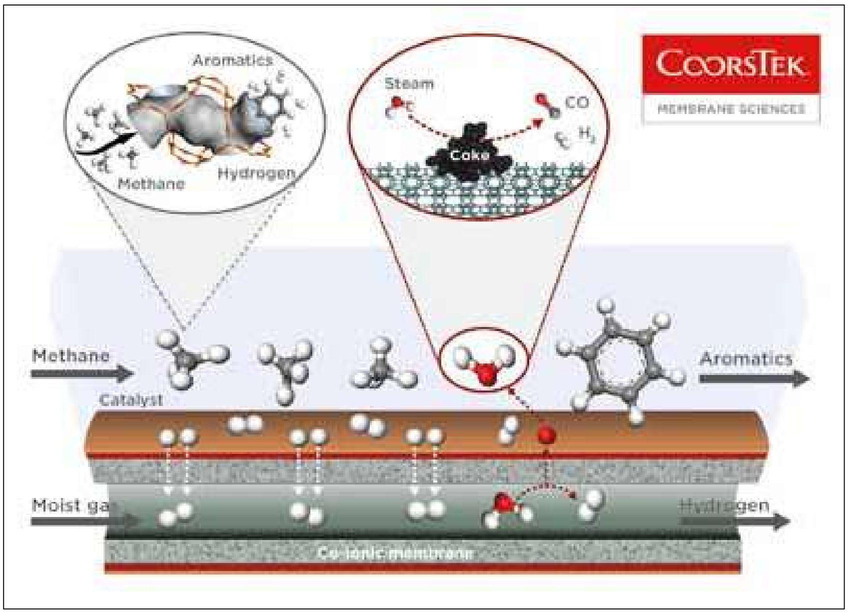

Fig. 2
CoorsTek co-ionic ceramic membrane drives simultaneous control of H_2 extraction and O_2 injection, leading to enhanced aromatics yield and catalyst stability

This innovative catalytic membrane reactor (CMR) for intensification of the MDA process that resulted in high and prolonged aromatic yields. In addition, a high-purity H_2 stream is produced during CMR operation. The CMR is driven by a tailored co-ionic membrane that enables fast and accurate simultaneous control of H_2 extraction and injection of oxygen species along the catalyst bed. The concerted action of both functions leads to marked gains in aromatics yield and catalyst stability and, consequently, in the viability of MDA technology.

The membrane is a proton-conducting ceramic material with electrodes similar to a solid-oxide fuel cell. It provides a means of removing hydrogen from the reaction and thus shifting the thermodynamic equilibrium toward formation of aromatic rings as reaction products.

The CoorsTek reactor is also designed to allow oxygen to be injected across the membrane surface to remove carbon deposits, thus preventing coke buildup from killing catalyst activity.

Heated natural gas flows into the ceramic reactor, where it encounters shape-selective zeolite catalysts. As methane molecules are activated at catalyst active sites and products begin to form, hydrogen is transported across the solid ceramic membrane as protons to recombine as hydrogen on the other side. Copper electrodes on the reaction side of the membrane and nickel electrodes on the hydrogen-permeate side aid the hydrogen transport process.

With high-volume manufacturing, we can make membrane reactors from active ceramics that are cost competitive with conventional catalytic reactors for gas processing. While the reactor costs will be similar, the results enabled by this new process have the potential to significantly improve both the financial and environmental costs of chemical production.