Gas to Liquids: Natural Gas Conversion to Aromatic Fuels and Chemicals in a Hydrogen-Permeable Ceramic Hollow Fiber Membrane Reactor

Jian Xue,† Yan Chen,‡ Yanying Wei,*,† Armin Feldhoff,† Haihui Wang,*,‡,§ and Juergen Caro*,†

†Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstrasse 3A, D-30167 Hannover, Germany
‡School of Chemistry & Chemical Engineering, South China University of Technology, No. 381 Wushan Road, Guangzhou 510640, China
§School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

ABSTRACT: The performance of a dense ceramic hydrogen-permeable membrane reactor for the nonoxidative methane dehydroaromatization (MDA), according to the equilibrium reaction $6\text{CH}_4 \rightleftharpoons \text{C}_6\text{H}_6 + 9\text{H}_2$ with a 6 wt % Mo/HZSM-5 bifunctional catalyst was investigated. A U-shaped ceramic hollow fiber membrane of the composition $\text{La}_{5.5}\text{W}_{0.6}\text{Mo}_{0.4}\text{O}_{11.25-\delta}$ (LWM0.4) has been used for the in situ removal of $\text{H}_2$ to overcome thermodynamic constraints. The yield of aromatics (benzene, toluene, naphthalene) in the MDA could be increased in the beginning of the aromatization reaction by $\sim 50\% - 70\%$, in comparison with the fixed-bed reactor, because $40\% - 60\%$ of the $\text{H}_2$ abstracted have been extracted at $700^\circ\text{C}$ with a weight hourly space velocity (WHSV) of $840\ \text{cm}^3\ \text{g}_{\text{cat}}^{-1}\ \text{h}^{-1}$. These advantages of the membrane reactor operation decrease with time on stream, since the removal of $\text{H}_2$ boosts not only $\text{CH}_4$ conversion and yield of aromatics, but also catalyst deactivation by deposition of carbonaceous deposits. However, the catalyst system could be regenerated by burning the coke away with air.

KEYWORDS: natural gas conversion, nonoxidative methane dehydroaromatization, hydrogen-permeable ceramic membrane, hollow fiber membrane, gas-to-liquids technologies, catalyst regeneration

With the increasing demands for liquid fuels, gas-to-liquids (GTL) technologies are attracting considerable academ-
equilibrium limitation.\textsuperscript{13} Usually, palladium and its alloys are applied as membranes for the \textit{in situ} extraction of H\textsubscript{2} during the MDA reaction.\textsuperscript{14} However, these Pd alloy membranes were not suitable for MDA, because the endothermic MDA requires high temperatures of at least 700 °C; however, at this temperature—especially in the presence of hydrocarbons—the Pd alloy membranes undergo degradation.\textsuperscript{15} Therefore, ceramic membranes, which can operate at high temperatures and in the presence of hydrocarbons, are needed to support the MDA.\textsuperscript{16} In a simulation paper, Iglesia developed a concept for the design and optimization of catalysts and membranes for the nonoxidative conversion of CH\textsubscript{4}.\textsuperscript{16a} It was predicted that a bifunctional catalyst such as Mo/H-ZSM-5, in combination with a continuous removal of H\textsubscript{2}, should lead to an increased CH\textsubscript{4} conversion at practical residence times of \approx 100 s. In a subsequent pioneering paper, this group used a ceramic membrane (SrCe\textsubscript{0.95}Yb\textsubscript{0.05}O\textsubscript{3−δ}), but the improvements in the MDA process were very modest (6% improvement of methane conversion, almost no increase in yield of aromatics at 950 K), because of the low H\textsubscript{2} permeability of the membrane (only 6.4% H\textsubscript{2} removal efficiency).\textsuperscript{16b}

Dense ceramic membranes exhibiting mixed proton and electron conductivity, at high temperatures, can selectively permeate H\textsubscript{2} rather than other gases from H\textsubscript{2}-containing mixtures under the driving force of a H\textsubscript{2} partial pressure gradient across the membrane. U-shaped hollow fiber membranes with a high area-to-volume ratio can avoid the membrane breakage, because of thermal expansion or shrinkage, and they can be easily assembled to a reactor module.\textsuperscript{17} Therefore, in the nonoxidative MDA, we applied a U-shaped high-flux H\textsubscript{2}-permeable ceramic hollow fiber membrane with a composition of La\textsubscript{5.5}W\textsubscript{0.6}Mo\textsubscript{0.4}O\textsubscript{11.25−δ} (LWM0.4).\textsuperscript{18} In this paper, we study the increase in the CH\textsubscript{4} conversion and the aromatics yield in the classical nonoxidative MDA \textit{in situ}, by removing the H\textsubscript{2} from the MDA reactor at the reaction temperature of 700 °C through a U-shaped H\textsubscript{2}-selective LWM0.4 hollow fiber.

As illustrated in Figure 1, in the LWM0.4 hollow fiber reactor, helium-diluted CH\textsubscript{4} (36 vol % CH\textsubscript{4}) with a weight hourly space velocity (WHSV) of 840 cm\textsuperscript{3} g\textsuperscript{−1} h\textsuperscript{−1} is used as feed on the shell side of the hollow fiber membrane to produce aromatics and H\textsubscript{2} through MDA on the bifunctional Mo/HZSM-5 catalyst, which is coated around the fiber. The H\textsubscript{2} that is produced is removed to the core side of the fiber with a low H\textsubscript{2} partial pressure, where H\textsubscript{2} is swept away \textit{in situ}, using CO\textsubscript{2} or argon. To assess the impact of the H\textsubscript{2} removal, for comparison, fixed-bed reactor experiments were conducted without H\textsubscript{2} removal (no sweep gas).

The performances of the MDA reaction in the fixed-bed reactor and the membrane reactor are shown in Figure 2. According to a slightly higher CH\textsubscript{4} conversion over the thermodynamic value of 12% at 700 °C and an increased selectivity for aromatics in the membrane reactor, in comparison with the fixed-bed reactor, the starting yield of aromatics in the membrane reactor (Figure 2b) is \approx 47% higher than that in the fixed-bed reactor (Figure 2a). However, these differences become smaller with increasing time-on-stream. Similar results have been observed when using argon as a sweep gas, as shown in Figure S2 in the Supporting Information.

Because of the continuous removal of H\textsubscript{2}, coking is enhanced in the membrane reactor, which also has been observed for the MDA in Pd alloy membrane reactors.\textsuperscript{14b,d,e} Figure 3 shows the comparison of the yield of aromatics in the fixed-bed reactor and the membrane reactor (Figure 3a). As the accumulated amount of aromatics show, the higher performance of the membrane reactor over the fixed-bed reactor is maintained for a long period (Figure 3b). Figure 3c shows the product distribution as a function of time. For both reactor types, coke is the main product of the MDA reaction. However, \approx 10% more aromatics are formed in the membrane...
reactor, in comparison with the fixed bed (Figure 3c). The yield of aromatics of the membrane reactor is higher than that of the fixed-bed reactor in the first 300 min, because of the extracted H₂. However, because of the enhanced coking due to the H₂ removal, after 10 h time-on-stream, the relationship is opposite: now the membrane reactor produces 10% less aromatics but 10% more coke than the fixed-bed reactor. Similar findings have been reported by refs 14b, d, and e. The same results are found with argon as the sweep gas, as shown in Figure S3 in the Supporting Information. However, it follows from Figures 3a and 3b that the instantaneous aromatics formation and the accumulated yield of aromatics, for the membrane reactor, are always higher than for the fixed-bed reactor, within the first 1000 min.

Figure 4 shows that 40%–60% of the H₂ generated has been extracted by the LWM0.4 membrane, while only 6% of the produced H₂ was removed by the SrCe0.95Yb0.05O3−δ membrane.16b The H₂ extraction decreases with time-on-stream, because of the deposition of carbonaceous residues on the membrane and the decreased H₂ partial pressure in the feed side, as a result of the reduced CH₄ conversion. The H₂ fluxes through the LWM0.4 hollow fiber membrane, as a function of time, can be found in Figure S4 in the Supporting Information. The H₂ flux is slightly lower for CO₂ as the sweep gas than for argon as the sweep gas. This is a common finding for ceramic membranes, because of the stronger adsorptive interaction of CO₂ with the perovskite surface, which suppresses the surface exchange reaction more than argon.18b,19 Compared with the Pd alloy membrane reactor, whose permeability declined to 20% of the initial permeation flux after 60 min and went down after 900 min of operation,10,15 our ceramic LWM0.4 membrane reactor still exhibits a considerable H₂ permeation flux.

The oxidative regeneration of the coked membrane reactor requires both stable membranes and catalysts. Usually, Pd alloy membranes can be only regenerated under reductive conditions in diluted H₂; the coke cannot be totally removed, and the MDA performance did not completely recover.10,14c Since our ceramic membrane and our catalyst are stable under oxidative conditions, our membrane–catalyst system could be completely regenerated in air. After coke combustion, the MDA reaction was conducted again, as shown in Figure 5, and the regenerated membrane reactor possesses a comparable MDA performance similar to that observed in the first run.

Figure 3. (a) Yield of aromatics (benzene, toluene, naphthalene), (b) cumulative yield of aromatics, and (c) main product distribution, as a function of time for the fixed-bed reactor without sweep and the catalytic membrane reactor swept with CO₂.

Figure 4. Hydrogen removal efficiency (expressed as a percentage) of the abstracted hydrogen through the LWM0.4 membrane in the case of the MDA catalytic membrane reactor.

Figure 5. Nonoxidative MDA reaction performance of the regenerated LWM0.4 hollow fiber membrane reactors swept with CO₂. Regeneration conditions: T = 700 °C; feed side, ΦCH₄ = 30 cm³ min⁻¹; sweep side, no gas flow; t = 5 h.
so that the LWM0.4 membrane–Mo/HZSM-5 catalyst system is stable under MDA reaction conditions and can be regenerated.

**CONCLUSION**

In summary, this work demonstrates the successful application of a U-shaped hydrogen-permeable hollow fiber ceramic membrane of the composition La$_{5.5}$W$_{0.6}$Mo$_{0.4}$O$_{11.25-\delta}$ (LWM0.4) to support methane dehydrocyclization to aromatic compounds. The LaWM0.4 ceramic membrane is different toward hydrogen-selective palladium membranes, because it is stable over a long period under the reaction conditions of the MDA at 700 °C. If the hydrogen is removed through the LWM0.4 hollow fiber membrane, the yield of aromatics (benzene, toluene, naphthalene) can be increased by 47% (using CO$_2$ as the sweep gas) to 70% (using argon as the sweep gas). Approximately 50% of the abstracted hydrogen has been removed through the hydrogen-permeable ceramic membrane. Because of this hydrogen extraction, the deposition of MDA at 700 °C is stable over a long period under the reaction conditions of the MDA at 700 °C.

**REFERENCES**


