Heterogeneous Catalysis

International Edition: DOI: 10.1002/anie.201609991
German Edition: DOI: 10.1002/ange.201609991

Hydrogen-Permeable Tubular Membrane Reactor: Promoting Conversion and Product Selectivity for Non-Oxidative Activation of Methane over an Fe©SiO_2 Catalyst

Mann Sakbodin, Yiqing Wu, Su Cheun Oh, Eric D. Wachsman, and Dongxia Liu**

Abstract: *Non-oxidative methane conversion over Fe©SiO_2 catalyst was studied for the first time in a hydrogen (H_2) permeable tubular membrane reactor. The membrane reactor is composed of a mixed ionic–electronic $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ thin film ($\approx 20\ \mu m$) supported on the outer surface of a one-end capped porous $SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ tube. Significant improvement in CH_4 conversion was achieved upon H_2 removal from the membrane reactor compared to that in a fixed-bed reactor. The Fe©SiO_2 catalyst in the H_2 permeable membrane reactor demonstrated a stable $\approx 30\,\%$ C_{2+} single-pass yield, with up to 30% CH_4 conversion and 99% selectivity to C_2 (ethylene and acetylene) and aromatic (benzene and naphthalene) products, at the tested conditions. The selectivity towards C_2 or aromatics was manipulated purposely by adding H_2 into or removing H_2 from the membrane reactor feed and permeate gas streams.*

Methane (CH_4), an abundant natural resource, is the main constituent of natural gas and oil-associated gases. Studies on CH_4 conversion have explored indirect conversion of CH_4 to synthesis gas ($CO + H_2$) followed by Fischer–Tropsch synthesis of higher hydrocarbons,[1] oxidative coupling of CH_4 to C_{2+} hydrocarbons,[2] and non-oxidative CH_4 conversion (NMC) to H_2, light hydrocarbons and aromatics.[3] In comparison with the first two approaches, NMC is more simple and selective given its unique capability in forming C_{2+} hydrocarbons and H_2 while circumventing the intermediate energy intensive steps.[1a,3a,4] However, kinetic and thermodynamic constraints in NMC lead to low CH_4 conversion at practical reaction conditions.[5]

Considerable efforts have been placed on the development of membrane reactors comprised of active catalysts and H_2 permeable membranes for NMC reactions.[6] The molybdenum/zeolite (Mo/ZSM-5) has been the most extensively studied catalyst.[7] H_2 or O_2 permeable membranes, such as metal alloys[8] and ionic/electronic conducting ceramics,[6d–f,9] capable of H_2 withdrawal from or O_2 addition into the reactor were exploited to alleviate the barriers for equilibrium conversion. Although a substantial enhancement of the CH_4 conversion has been predicted when a H_2 permeable membrane was used in conjunction with a NMC catalyst, the parallel experimental studies on NMC process in membrane reactors were not favorable due to the lack of membranes with sufficient H_2 permeation flux and the accelerated catalyst deactivation under H_2 removal conditions.[6b,d,10]

Herein we report a tubular membrane reactor (Figure 1) that is comprised of a mixed ionic–electronic conducting $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane and the iron©silica (Fe©SiO_2) catalyst to improving CH_4 conversion while maintaining catalyst durability and selectivity to C_2 and aromatic products under H_2 removal conditions. The $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane was designed with thickness around 20 μm with an active surface area of 12 cm^2 supported on 1 mm thick $SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ tube with a diameter of 6 mm (Figure 1 A,B). This type of tubular membrane reactors have been studied for H_2 production from water-gas shift and CO_2 reforming of CH_4 reactions in previous reports.[11] Fe©SiO_2 catalyst has lattice-confined single iron sites embedded in the silica matrix, which has been demonstrated to have superior NMC performance by Bao and co-authors.[12] The integration of the Fe©SiO_2 (containing 0.5 wt% Fe) catalyst in the $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane reactor for NMC showed an enhancement in CH_4 conversion compared to that in a fixed-bed reactor. The NMC reaction showed up to 30% CH_4 conversion, 99% selectivity to C_2 and aromatics, and a long catalyst lifetime at the tested conditions. The product selectivity towards light hydrocarbon (acetylene and ethylene) or heavy aromatics (benzene and naphthalene) was manipulated by adding H_2 into or removing H_2 from the $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane reactor. The tubular membrane reactor design increases the H_2 permeable surface area and avoids need for sealing of membrane in the high temperature heating zone, leading to more stable and higher H_2 permeation compared to the disk-shaped membrane design in most previous studies.[6] Figure 1 C demonstrates the set-up of the H_2 permeable membrane reactor for the NMC reactions. To our knowledge, this is the first time active, stable and tunable product selectivity has been realized for NMC over Fe©SiO_2 catalyst in a H_2 permeable membrane reactor.

The H_2 permeation through the $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane in the membrane reactor was measured prior to the catalysis tests. Figure 2 A shows that the permeated H_2 flux was increased with the H_2 concentration on the feed side. In addition, the H_2 permeation flux increased as the temperature increased due to the increase in ambipolar conductivity of the $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane. A further analysis shows that the H_2 permeation flux was proportional to the

---

[*] M. Sakbodin, Y. Wu, S. C. Oh, E. D. Wachsman, D. Liu
Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742 (USA)
E-mail: ewach@umd.edu
liud@umd.edu
E. D. Wachsman, D. Liu
University of Maryland Energy Research Center, University of Maryland, College Park, MD 20742 (USA)

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201609991.

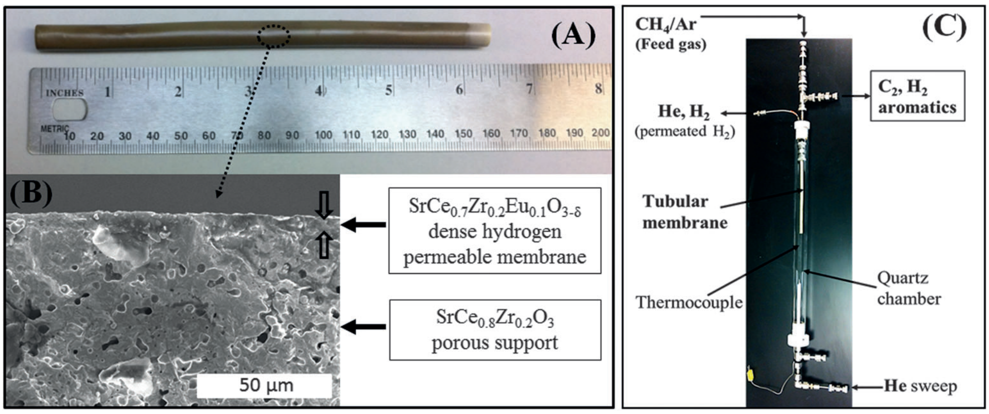


Figure 1. H_2 permeable tubular membrane reactor and experimental setup for NMC reaction. A) As-prepared $SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ membrane tube, B) SEM image showing the cross-sectional image of membrane tube reactor comprised of $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ thin film on the porous $SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ tubular support, and C) assembly of H_2 permeable membrane reactor for CH_4 conversion in NMC over Fe©SiO_2 catalyst.

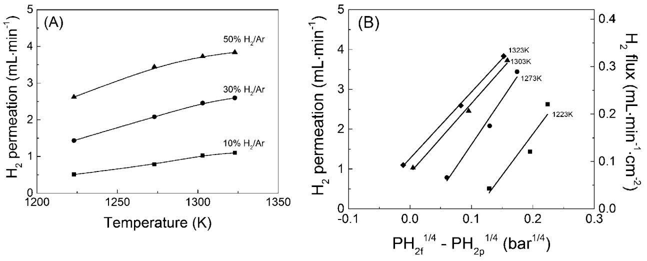


Figure 2. H_2 permeation flux through $SrCe_{0.8}Zr_{0.2}O_{3-\delta}$ membrane in the packed-bed membrane reactor as a function of A) temperature and B) H_2 partial pressure, respectively.

transmembrane H_2 partial pressure gradient with a 1/4 dependence (Figure 2B). The Wagner equation[13] explains the H_2 permeation behaviors through the $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane in the tubular reactor (Section S2, Supporting Information).

The CH_4 conversion and product selectivity as a function of reaction temperature in both fixed-bed and H_2 permeable membrane reactors are shown in Figure 3. An increase in CH_4 conversion with increasing temperature was observed in both types of reactors due to the endothermic nature of the NMC reaction. The simultaneous removal of H_2 from the membrane reactor shifted the reaction to the product side, and thus increased the CH_4 conversion. Higher H_2 permeation flux at higher temperature and higher H_2 partial pressure differences are expected, according to Wagner equation[13] and Figure 2, to lead to an increase in CH_4 conversion. The percent increase in CH_4 conversion from fixed-bed to membrane reactors, comparing Figure 3A and B, however, showed a decreasing trend. The discrepancy in CH_4 conversion between this analysis and experimentally measurement might be caused by deposition of carbon species on the membrane surface in the catalyst activation stage that reduced the H_2 flux or by complex chemistry in membrane reactor which involved multiple types of hydrocarbon species influencing H_2 permeation dynamics. The production and permeation rates of H_2 at each reaction temperature have been quantified (Table S1, Supporting Information). The enhancement in CH_4 conversion caused by H_2 removal has been evaluated by considering a right-hand side shift of the reaction equation ($CH_4 = 3/52\,C_6H_6 + 5/104\,C_{10}H_8 + 7/104\,C_2H_4 + 2/104\,C_2H_2 + 19/13\,H_2$) according to the Le Châtelier's principle. The calculated CH_4 conversion is nearly the same as those measured (Table S1), which indicated the effectiveness of the H_2 permeable membrane reactor in shifting the CH_4 conversion in the NMC chemistry.

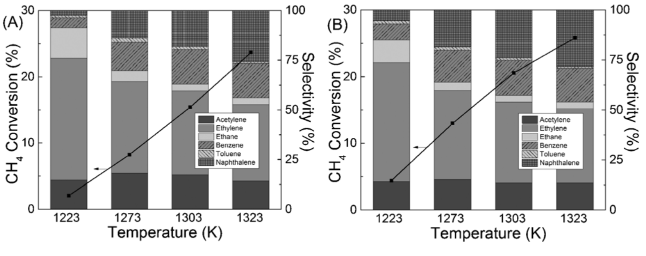


Figure 3. CH_4 conversion and product selectivity over Fe©SiO_2 catalyst A) in a fixed-bed and B) packed-bed membrane reactor at different temperatures (space velocity = 3200 mL g^{-1} h^{-1}).

Figure 3 also shows the effects of H_2 removal on the product selectivity of the NMC reaction. In the fixed-bed reactor, the reaction was very selective toward C_2 (ethylene, acetylene and ethane, ca. 90%), and only small amount of aromatics (< 10%) were formed at 1223 K. As the temperature increased, the selectivity shifted from smaller C_2 products to aromatics (benzene, toluene and naphthalene). Comparing the product selectivities between the fixed-bed and the H_2 permeable membrane reactors, the membrane reactor was slightly less selective for C_2 and more selective for aromatic products. The yields for both C_2 and aromatics of the membrane reactor are higher at all temperatures tested compared to the fixed-bed reactor.

The manipulation of the sweep side environment which is expected to influence the catalysis chemistry inside the membrane reactor was carried out by flowing sweep He gas at different flow rates (20, 50 and 100 mL min^{-1}) and switching He to H_2 sweep gas, respectively. Figure 4A shows that CH_4 conversion increased with an increase of He flow to 50 mL min^{-1} and doubled at 100 mL min^{-1} He flow compared to that in fixed-bed reactor. The high sweep He flow carried away more H_2 through the membrane reactor. The CH_4 conversion was calculated based on the permeated H_2 (Table S2, Supporting Information), and matched well with the measured conversion in the membrane reactor. For comparison, H_2 was purposely added back to the membrane reactor by flowing H_2 as sweep gas. The CH_4 conversion was

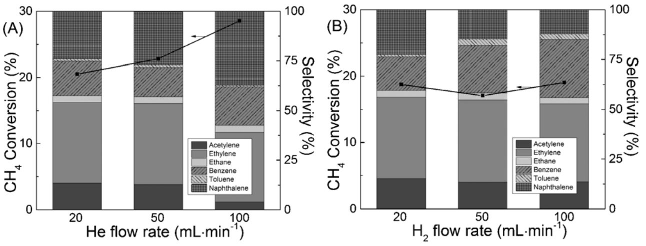


Figure 4. CH_4 conversion and product selectivity over Fe©SiO_2 catalyst in a packed-bed membrane reactor at different A) He or B) H_2 sweep gas flow rates (temperature = 1303 K, space velocity = 3200 mL g^{-1} h^{-1}).

slightly reduced (Figure 4 A and B) because the reaction was shifted to the reactant side according to Le Châtelier's principle.

The product selectivity towards C_2 or aromatics was tuned by varying the type of sweep gases and their flow rates. The selectivity to naphthalene increased with increasing He flow rate (Figure 4 A) while the C_2 and benzene products increased with increasing H_2 flow rates (Figure 4 B). Bao and coauthors[12] hypothesized that the lattice confined single Fe site initiates CH_4 dehydrogenation to generate methyl ($^{\bullet}CH_3$) and hydrogen ($^{\bullet}H$) radicals, which subsequently release from the surface and undergo a series of gas-phase reactions to form dehydrogenated and cyclized products. The manipulation of sweep gas type influences the concentrations and types of hydrogen species in the reactor which impacts the product selectivity. A control experiment was done by co-feeding H_2 in the CH_4 feed in the fixed-bed reactor to examine the influence of H_2 addition through the membrane reactor. To significantly mitigate naphthalene formation, a concentration of ca. 15 % H_2 in the CH_4 feed was needed, which led to a severe reduction in CH_4 conversion (Figure S3, Supporting Information). The slight sacrifice of CH_4 conversion but tuning product to C_2 and benzene compared to naphthalene is unique for the NMC reaction in the H_2 permeable $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane reactor. On the other hand, an increase in CH_4 conversion and aromatic product formation were achieved with the H_2 permeable membrane reactor with He sweep gas flow. Both ends of products are attractive chemicals used in industry. The employment of the H_2 permeable membrane reactor in the present study could shift the building block supplies from the CH_4 catalysis chemistry.

The stability of the Fe©SiO_2 catalyst in NMC reaction in the H_2 permeable membrane reactor was tested by running the reaction at 1303 K for 60 hours. No obvious deactivation was observed during this test (Figure 5). The CH_4 conversion remained at ≈20 % throughout this run at this tested reaction condition. Selectivities to C_2 (65 %), benzene (18 %) and naphthalene (15 %) were constant, and the total selectivity to these products remained > 99 %. In contrast, H_2 removal resulted in accelerated coking on the Mo/ZSM-5 catalyst in other membrane reactors.[6e,8a] This has been a major obstacle to realize a practical NMC reaction in H_2 permeable membrane reactors. In addition to the stability of the Fe©SiO_2 catalyst, this long-term test also demonstrated the stability of the $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ tubular ceramic membrane reactor under reducing hydrocarbon atmosphere. The combination of high CH_4 conversion, high and tunable selectivity, and durability in the H_2 permeable membrane reactor is notable.

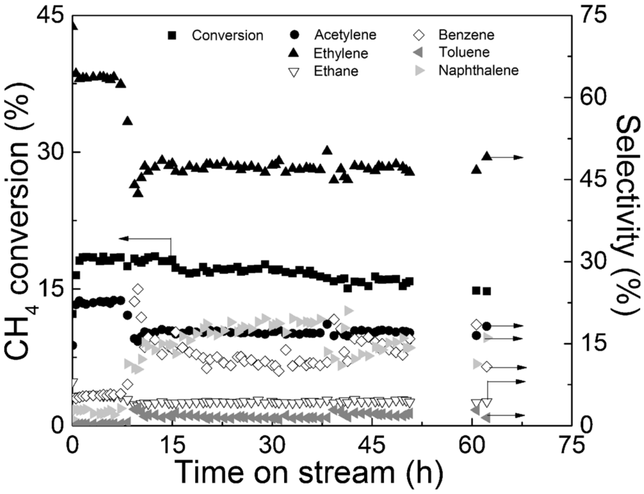


Figure 5. Long-term stability test of the packed-bed H_2 permeable tubular membrane reactor with the Fe©SiO_2 catalyst at 1303 K and 3200 mL g^{-1} h^{-1} space velocity.

In summary, the integration of a mixed ionic–electronic H_2 permeable $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ membrane and Fe©SiO_2 catalyst into a catalytic tubular membrane reactor was demonstrated for the first time for NMC reaction. The removal of H_2 from NMC reactions led to a significant increase in CH_4 conversion. The product selectivity to C_2 and aromatics as well as catalyst durability were not influenced significantly by the H_2 removal, which is distinctly different from all the previous studies[6e,8a] on H_2 permeable membrane reactor for NMC reactions. The present work is the first successful demonstration of the H_2 permeable ceramic membrane reactor on shifting reaction equilibrium to benefit CH_4 conversion while not impacting product selectivity and catalyst durability in NMC reactions. The capability of tuning products towards C_2 (ethylene and acetylene) or aromatic (benzene and naphthalene) products with high single-pass yields open up new possibilities for NMC processes. The integration of Fe©SiO_2 catalyst in the high temperature H_2 permeable $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ tubular membrane reactor enables new routes for transformation of CH_4 into high value-added chemicals and fuels.

Experimental Section

The H_2 permeable membrane reactor was prepared by tape casting of the $SrCe_{0.8}Zr_{0.2}O_3$ slurry and rolling end-capped tubular-type supports, and then followed by colloidal coating of a thin dense $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$ layer on the supports. Details on the synthesis of the membrane materials and the fabrication of the membrane reactor are described in previous reports[11a,d,13] and in the Supporting Information. Fe_2SiO_4 was firstly prepared via the sol–gel method published by DeAngelis et al.[14] Fe©SiO_2 was synthesized by fusing Fe_2SiO_4 and SiO_2 at 1973 K for 6 hours in air. The tests for leakage, H_2

permeation and NMC reactions in the tubular membrane reactors were described in details in the Supporting Information.

Acknowledgements

We acknowledge support from the National Science Foundation (NSF-CBET 1264599 and 1351384), Maryland NanoCenter and its NispLab. The NispLab is supported in part by the NSF as a MRSEC Shared Experimental Facility. M.S. and Y.W. thank the Harry K. Wells and Hulka Energy Research Fellowships, respectively, from University of Maryland Energy Research Center (UMERC) for the support of their research.

Keywords: Fe©SiO_2 · membrane reactor · natural gas · non-oxidative methane conversion · $SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-\delta}$

---

[1] a) R. Horn, R. Schlogl, *Catal. Lett.* **2015**, *145*, 23–39; b) D. Pakhare, J. Spivey, *Chem. Soc. Rev.* **2014**, *43*, 7813–7837; c) D. A. Hickman, L. D. Schmidt, *Science* **1993**, *259*, 343–346; d) A. T. Ashcroft, A. K. Cheetham, J. S. Foord, M. L. H. Green, C. P. Grey, A. J. Murrell, P. D. F. Vernon, *Nature* **1990**, *344*, 319–321; e) M. Gupta, M. L. Smith, J. J. Spivey, *ACS Catal.* **2011**, *1*, 641–656.

[2] a) G. E. Keller, M. M. Bhasin, *J. Catal.* **1982**, *73*, 9–19; b) J. S. Lee, S. T. Oyama, *Catal. Rev.* **1988**, *30*, 249–280; c) A. L. Tonkovich, R. W. Carr, R. Aris, *Science* **1993**, *262*, 221–223.

[3] a) J. J. Spivey, G. Hutchings, *Chem. Soc. Rev.* **2014**, *43*, 792–803; b) M. C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R. M. Navarro, J. L. G. Fierro, *Catal. Today* **2011**, *171*, 15–23; c) Z. R. Ismagilov, E. V. Matus, L. T. Tsikoza, *Energy Environ. Sci.* **2008**, *1*, 526–541; d) L. S. Wang, L. X. Tao, M. S. Xie, G. F. Xu, J. S. Huang, Y. D. Xu, *Catal. Lett.* **1993**, *21*, 35–41.

[4] D. J. Wang, J. H. Lunsford, M. P. Rosynek, *Top. Catal.* **1996**, *3*, 289–297.

[5] a) C. Guéret, M. Daroux, F. Billaud, *Chem. Eng. Sci.* **1997**, *52*, 815–827; b) L. Li, R. W. Borry, E. Iglesia, *Chem. Eng. Sci.* **2001**, *56*, 1869–1881.

[6] a) J. Caro, *Chem. Ing. Tech.* **2014**, *86*, 1901–1905; b) Z. W. Cao, H. Q. Jiang, H. X. Luo, S. Baumann, W. A. Meulenberg, J. Assmann, L. Mleczko, Y. Liu, J. Caro, *Angew. Chem. Int. Ed.* **2013**, *52*, 13794–13797; *Angew. Chem.* **2013**, *125*, 14039–14042; c) M. C. Iliuta, B. P. A. Grandjean, F. Larachi, *Ind. Eng. Chem. Res.* **2003**, *42*, 323–330; d) L. Li, R. W. Borry, E. Iglesia, *Chem. Eng. Sci.* **2002**, *57*, 4595–4604; e) O. Rival, B. P. A. Grandjean, C. Guy, A. Sayari, F. Larachi, *Ind. Eng. Chem. Res.* **2001**, *40*, 2212–2219; f) S. M. Liu, X. Y. Tan, K. Li, R. Hughes, *Catal. Rev.* **2001**, *43*, 147–198; g) S. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P. Vestre, W. Coors, A. Martínez, T. Norby, J. Serra, *Science* **2016**, *353*, 563–566; h) J. Xue, Y. Chen, Y. Wei, A. Feldhoff, H. Wang, J. Caro, *ACS Catal.* **2016**, *6*, 2448–2451.

[7] a) B. M. Weckhuysen, D. J. Wang, M. P. Rosynek, J. H. Lunsford, *J. Catal.* **1998**, *175*, 347–351; b) D. J. Wang, J. H. Lunsford, M. P. Rosynek, *J. Catal.* **1997**, *169*, 347–358; c) R. W. Borry, Y. H. Kim, A. Huffsmith, J. A. Reimer, E. Iglesia, *J. Phys. Chem. B* **1999**, *103*, 5787–5796; d) W. Ding, S. Li, G. D. Meitzner, E. Iglesia, *J. Phys. Chem. B* **2001**, *105*, 506–513.

[8] a) M. C. Iliuta, F. Larachi, B. P. A. Grandjean, I. Iliuta, A. Sayari, *Ind. Eng. Chem. Res.* **2002**, *41*, 2371–2378; b) S. Natesakhawat, N. C. Means, B. H. Howard, M. Smith, V. Abdelsayed, J. P. Baltrus, Y. Cheng, J. W. Lekse, D. Link, B. D. Morreale, *Catal. Sci. Technol.* **2015**, *5*, 5023–5036.

[9] a) S. H. Hamakawa, H. T. Iwahara, *J. Electrochem. Soc.* **1994**, *141*, 1720–1725; b) J. Kniep, Y. S. Lin, *Ind. Eng. Chem. Res.* **2010**, *49*, 2768–2774; c) S. Cheng, V. K. Gupta, Y. S. Lin, *Solid State Ionics* **2005**, *176*, 2653–2662; d) X. Qi, Y. S. Lin, *Solid State Ionics* **2000**, *130*, 149–156.

[10] a) Y. Song, Y. B. Xu, Y. Suzuki, H. Nakagome, Z. G. Zhang, *Appl. Catal. A* **2014**, *482*, 387–396; b) Y. Q. Wu, L. Emdadi, S. C. Oh, M. Sakbodin, D. X. Liu, *J. Catal.* **2015**, *323*, 100–111; c) Y. Q. Wu, L. Emdadi, Z. P. Wang, W. Fan, D. X. Liu, *Appl. Catal. A* **2014**, *470*, 344–354.

[11] a) H. Yoon, S. J. Song, T. Oh, J. L. Li, K. L. Duncan, E. D. Wachsman, *J. Am. Ceram. Soc.* **2009**, *92*, 1849–1852; b) T. Oh, H. Yoon, J. L. Li, E. D. Wachsman, *J. Membr. Sci.* **2009**, *345*, 1–4; c) J. L. Li, H. Yoon, T. K. Oh, E. D. Wachsman, *Int. J. Hydrogen Energy* **2012**, *37*, 16006–16012; d) J. L. Li, H. Yoon, E. D. Wachsman, *Int. J. Hydrogen Energy* **2012**, *37*, 19125–19132.

[12] X. G. Guo, G. Z. Fang, G. Li, H. Ma, H. J. Fan, L. Yu, C. Ma, X. Wu, D. H. Deng, M. M. Wei, D. L. Tan, R. Si, S. Zhang, J. Q. Li, L. T. Sun, Z. C. Tang, X. L. Pan, X. H. Bao, *Science* **2014**, *344*, 616–619.

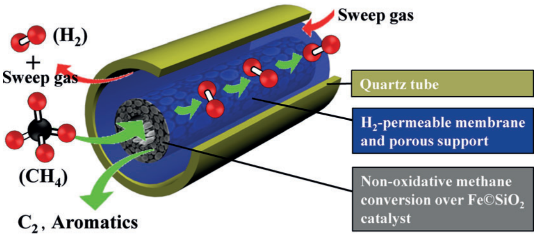
[13] J. Li, H. Yoon, E. Wachsman, *J. Membr. Sci.* **2011**, *381*, 126–131.

[14] M. T. DeAngelis, A. J. Rondinone, M. D. Pawel, T. C. Labotka, L. M. Anovitz, *Am. Mineral.* **2012**, *97*, 653–656.

Manuscript received: October 12, 2016
Final Article published: ■■ ■■, ■■■■

Communications

Heterogeneous Catalysis



Adding value to natural gas: A hydrogen-permeable tubular ceramic membrane reactor was developed enabling Fe©SiO$_2$-catalyzed CH$_4$ upgrading to higher hydrocarbons. The Fe©SiO$_2$ catalyst demonstrated a stable 30% C$_{2+}$ single-pass yield, with up to 30% CH$_4$ conversion and 99% selectivity to C$_2$ and aromatic products.