An Efficient Oxygen Activation Route for Improved Ammonia Oxidation through an Oxygen-Permeable Catalytic Membrane
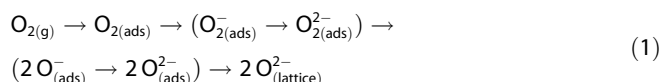
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Upon using a reactant/oxygen mixture as co-feed in partial oxidation, adsorbed surface molecular oxygen species can cause low selectivity. We propose a concept different from the conventional co-feed partial oxidation process in packed-bed reactors. In this new configuration, the activation of oxygen is separated from the catalytic oxidation by using an oxygen-permeable membrane to suppress the formation of nonselective surface molecular oxygen species. A continuous flux of lattice oxygen through the membrane allows highly selective partial oxidation. In the oxidation of ammonia to NO, the NO selectivity was improved from 77 to 95 % if a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ oxygen-permeable catalytically active membrane was used at 850 °C instead of a co-feed fixed bed reactor.

Extensive research efforts have been devoted to improve the Ostwald process ($4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O$), as this step covers approximately 90 % of the cost of nitric acid production.[1] For many years, nitric acid producers relied on platinum group metal alloy gauzes as catalysts that show very good activity and 94–96 % NO selectivity with the formation of N_2 and N_2O as byproducts. However, the utilization of Pt–Rh gauzes is expensive and is linked to N_2O emission and platinum loss in the form of volatile oxides. These facts stimulated research towards the development of new catalysts and new processes

for the oxidation of ammonia. A series of less expensive oxides, especially cobalt oxide (Co_3O_4) and perovskite structure oxides, such as Ca- or Sr-substituted $LaMnO_3$, $LaCoO_3$, and $LaFeO_3$, have been reported to show promising catalytic performance towards ammonia oxidation.[2] Considering that N_2 from air represents approximately 70 % of the total flow in the current plants, Pérez-Ramírez et al. proposed a novel process for the oxidation of ammonia by using a lanthanum ferrite based oxygen-permeable membrane reactor, in which the oxygen for the ammonia oxidation was separated from air and in situ supplied through the membrane; moreover, N_2 in the air flow was completely kept on the other side of the membrane. By using a $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ membrane as the reactor for the oxidation of ammonia, high NO selectivities (95–98 %) were obtained only upon feeding very limited amounts of ammonia ($< 0.5 \, cm^3 min^{-1}$ NH_3 in a total flow of 130 mL min^{-1} at 1100 K).[3] To obtain a larger oxygen permeation flux, Sun et al. recently employed a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane with high oxygen permeability for the oxidation of ammonia.[4] However, the NO selectivities were relatively low ($< 70 \%$). It is, therefore, desirable to study the catalytic process on the membrane surface to improve the membrane-based oxidation of ammonia further.

During ammonia oxidation on metal oxide catalysts, following the concept of Mars and van Krevelen, the participation of lattice oxygen[5] was found to play a very important role in the formation of NO.[6] The formation of lattice oxygen by reoxidation of the oxygen-depleted metal oxides by gaseous oxygen has been suggested as follows [Eq. (1)]:[7]

$$O_{2(g)} \rightarrow O_{2(ads)} \rightarrow (O^-_{2(ads)} \rightarrow O^{2-}_{2(ads)}) \rightarrow$$
$$(2 O^-_{(ads)} \rightarrow 2 O^{2-}_{(ads)}) \rightarrow 2 O^{2-}_{(lattice)} \quad (1)$$

First, oxygen molecules adsorb on the oxide surface, and the adsorbed O_2 becomes reduced and is incorporated into the metal oxide as lattice oxygen O^{2-}, as shown in Figure 1 a. Many efforts have been taken to identify the role of various oxygen species. It is accepted that ammonia can be directly oxidized by lattice oxygen to NO,[8] and a low selectivity for NO is related to high concentrations of adsorbed molecular oxygen species that react with adsorbed ammonia to form nitrogen.[9] Very recently, Biausque et al. reported that one key route to form N_2 in the oxidation of ammonia over perovskite $LaCoO_3$ consisted in the reaction of adsorbed ammonia with adsorbed oxygen species such as peroxide (O^{2-}_2) and superoxide (O^-_2)

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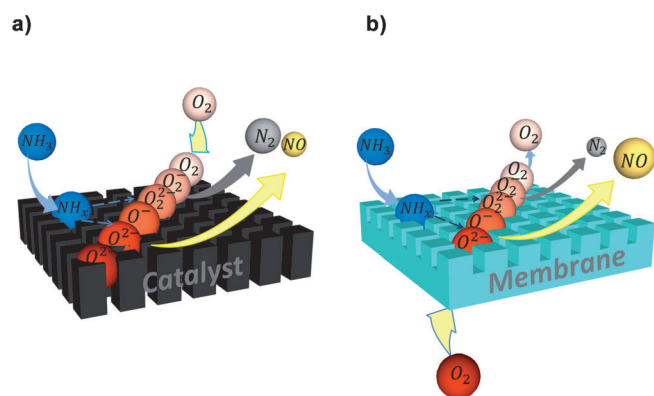Supporting information for this article is available on the WWW under
http://dx.doi.org/10.1002/cctc.201400048.

a)

b)

Figure 1. Ammonia oxidation over a) a conventional packed-bed perovskite catalyst and b) a perovskite membrane. In a), oxygen as a co-feed becomes incorporated into the oxide catalyst and adsorbed molecular oxygen species are present at the early stage of incorporation. In b), for which a membrane is in operation, lattice oxygen species and atomic oxygen species are present at the early stage of oxygen release.

Figure 2. SEM micrographs of a cross-section of a fresh LSCF membrane.

species.[10] These experimental findings led us to the assumption that a high selectivity for NO could be achieved if the only oxygen species involved in the ammonia oxidation was lattice oxygen or atomic surface oxygen species.[11] However, this concept is difficult to implement, as the formation of weakly bound molecular oxygen species is the first and unavoidable step in the activation of oxygen in conventional catalytic packed-bed reactors with an oxygen/ammonia mixture as co-feed.[12]

To minimize the formation of surface molecular oxygen species, herein we developed a concept to separate the activation of oxygen from the catalytic process through an oxygen-permeable membrane.[13] As illustrated in Figure 1 b, O_2 is reduced to lattice oxygen O^{2-} on the air side of the membrane, which is locally separated from the catalytic oxidation of ammonia where oxygen is consumed. As lattice oxygen, the oxygen ions diffuse through the membrane to the permeate side at which a lower oxygen partial pressure exists. However, given that the first oxygen species present on the ammonia side before oxygen release is lattice oxygen, a proper consumption of the lattice or atomic oxygen species by the oxidation of ammonia may effectively suppress the formation of nonselective surface molecular oxygen species. Consequently, a high selectivity for NO can be expected.

This work demonstrates that the use of an oxygen-permeable membrane with sufficient surface area can supply catalytically selective lattice oxygen or atomic surface oxygen species and suppress the formation of nonselective molecular oxygen species. A newly developed asymmetric ultrathin perovskite LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) membrane was used.[14] As shown in Figure 2, a thin (25 μm), dense LSCF layer is supported by a mechanically stable porous LSCF layer that is approximately 800 μm thick. The LSCF material was selected as the oxygen-permeable membrane, as it combines high permeability with an intrinsic catalytic activity towards the oxidation of ammonia.[2, 15] This, as a rule, is a prerequisite for use in membrane reactors.
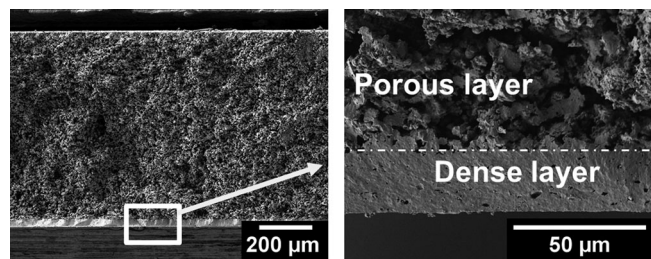
To verify our concept, the oxidation of ammonia in the membrane reactor with oxygen supplied as lattice/atomic oxygen was compared with the direct feeding of gaseous oxygen (co-feed mode) by using the same LSCF membrane as the catalyst at 850 °C (Figure S1, Supporting Information). In the co-feed mode, if the oxygen and ammonia are jointly fed to the porous support side of the LSCF membrane, the LSCF membrane acts only as a contact catalyst providing a large surface. However, in the membrane mode, oxygen for the oxidation of ammonia is separated from air by the LSCF membrane layer. We show the results of this comparison in Figure 3. The
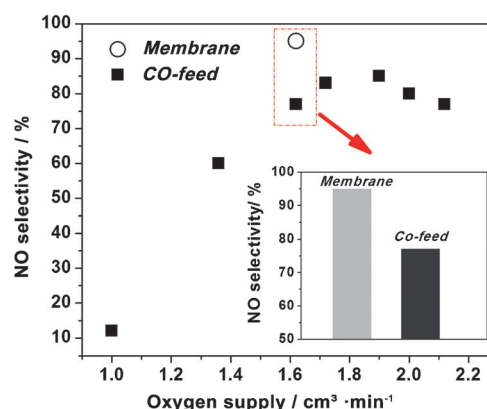

Figure 3. NO selectivity in the oxidation of ammonia for the two different operation modes at 850 °C in a LSCF membrane reactor. The porous support layer of the asymmetric LSCF membrane was facing the NH_3/O_2 mixture in the co-feed mode or facing pure NH_3 in the membrane mode (membrane mode, air side: $F_{air} = 100$ cm³ min⁻¹; ammonia side: $F_{all} = 100$ cm³ min⁻¹, $F_{NH_3} = 1.6$ cm³ min⁻¹ $F_{Ne} = 1$ cm³ min⁻¹, $F_{He} =$ balance; co-feed mode: $F_{Ne} = 1$ cm³ min⁻¹, $F_{NH_3} = 1.6$ cm³ min⁻¹, $F_{O_2} + F_{He} = 97.4$ cm³ min⁻¹). The inset shows the NO selectivity for the two different modes if supplying 1.6 cm³ min⁻¹ oxygen.

highest NO selectivity obtained in the membrane mode after reasonable optimization of the reaction parameters was 95 %, whereas the maximum NO selectivity in the co-feed mode was only 77 %. Notably, the amount of permeated oxygen in the membrane reactor mode and the co-feed fixed-bed reactor mode was the same. Given that the operating temperature for both reactors was also the same, the strength of the bonding of oxygen to the surface was also comparable. The only difference between the co-feed mode and the membrane mode was the way in which oxygen was supplied: In the co-feed

fixed-bed reactor, adsorption and reduction of gaseous oxygen and the oxidation of ammonia take place in the same compartment. As we can expect from the reduction of oxygen shown in Figure 1a, in the fixed-bed co-feed reactor, adsorbed molecular oxygen species can react with ammonia to form undesired nitrogen. In contrast, in the membrane mode the activation of oxygen is separated from the catalytic reaction, and therefore, the formation of nonselective surface molecular oxygen species can be suppressed. The NO selectivity as a function of the fed oxygen was also tested in a small range for the co-feed mode, as shown in Figure 3, but the NO selectivity obtained in the membrane reactor was always higher than that in the co-feed mode.

In an additional experiment, instead of the porous support layer, the dense layer of the LSCF membrane was exposed to the ammonia side. Figure 4 shows the NO selectivity and the
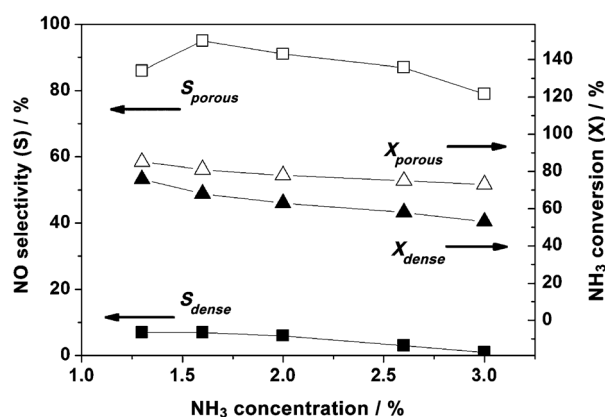

Figure 4. NO selectivity and ammonia conversion in the oxidation of ammonia as a function of the concentration of ammonia in the feed in the two different operation modes of the LSCF membrane reactor at 850 °C with the porous support layer to ammonia and the dense layer to the ammonia side (air side: $F_{air} = 100$ cm^3 min^{-1}; ammonia side: $F_{all} = 100$ cm^3 min^{-1} $F_{NH_3} = 1.3$–3.0 cm^3 min^{-1}, $F_{Ne} = 1$ cm^3 min^{-1}, $F_{He} =$ balance).

conversion for the ammonia oxidation reaction plotted versus the concentration of ammonia in the feed gas for these two operation modes: Either the dense LSCF or the porous LSCF support layer was facing ammonia. If the ammonia oxidation took place on the surface of the dense LSCF layer, a low NO selectivity (<10%) was found, whereas the selectivity was approximately 90% if ammonia oxidation took place on the porous LSCF support. Although the ammonia conversions were comparable for these two operation modes (Figure 4), the NO yield was much lower on the dense LSCF layer than on the porous LSCF layer that was used as a large contact surface for the oxidation of ammonia. Given that the surface morphology—porous versus dense—was the major difference, the surface area appears to be the determining factor for the performance of the membrane reactor. Relative to a dense surface, as shown in Figure 5a, the porous layer provides a much higher surface area. The permeated oxygen ion (atomic) can be sparsely distributed through the porous network, and this leads to sufficient suppression of the formation of nonselective
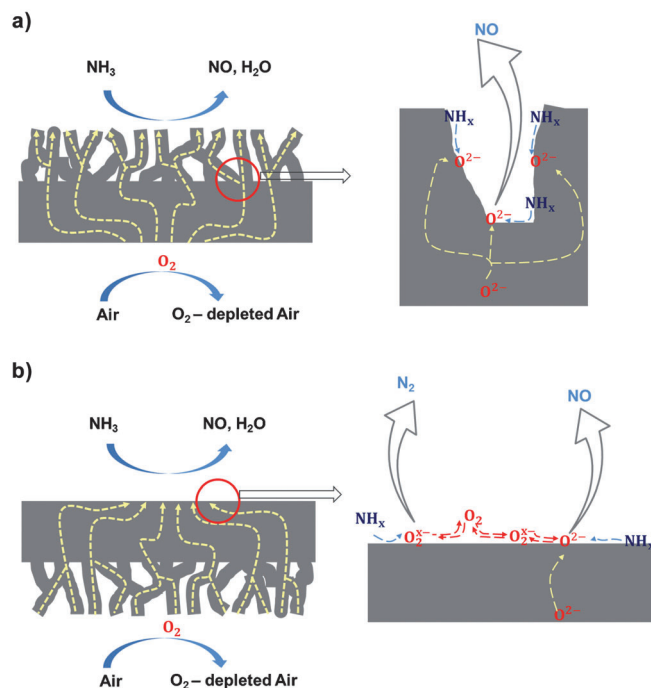

Figure 5. Asymmetric oxygen-permeable membrane with a) a porous surface and b) a smooth surface facing the ammonia side of the membrane reactor.

surface oxygen species (molecular).[16] Therefore, there are more lattice oxygen and atomic surface oxygen species that can be consumed in selective oxidations before molecular oxygen species are formed. In contrast, if the dense membrane layer faces the ammonia oxidation side, the relatively high concentration of permeated oxygen ions can combine to form weakly bound oxygen species that then desorb as molecular oxygen from the dense LSCF side, as shown in Figure 5b; this enhances the formation of the undesired nitrogen byproduct as discussed above. With the help of the residual partial pressure of oxygen at the outlet of the ammonia side (Figure 6), it might be helpful to further reveal the dominating step in both modes. If the dense side faces ammonia, the oxygen partial
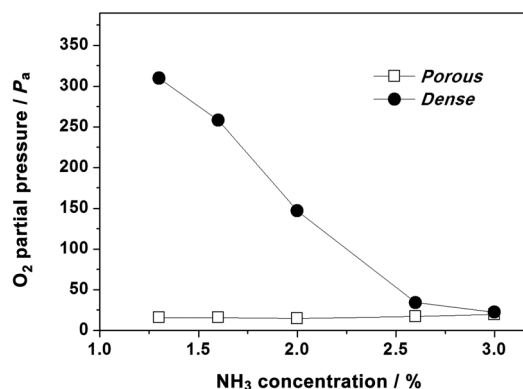

Figure 6. The residual oxygen partial pressure on the ammonia oxidation side as a function of the concentration of ammonia in two different operation modes, that is, porous and dense side, of the asymmetric membrane at the reaction side. 1 bar = 100 kPa.

pressure is clearly higher; this is indicative of a higher concentration of weakly bound surface molecular oxygen species. In this case, the recombination of the lattice oxygen probably occurs prior to the reaction between the lattice oxygen and ammonia, and thus, ammonia is mainly oxidized to nitrogen. This finding further explains the low selectivity for NO if the dense side faces ammonia.

Under the assumption that the good performance of the membrane reactor in the ammonia oxidation reaction benefits from the specific oxygen supply and the surface morphology of the membrane, that is, the manner in which the oxygen is supplied, the two oxygen-permeable pervoskite materials, LSCF and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), were compared by using comparable asymmetric membranes (Figure 7). Given that the BSCF membrane showed a higher oxygen transport
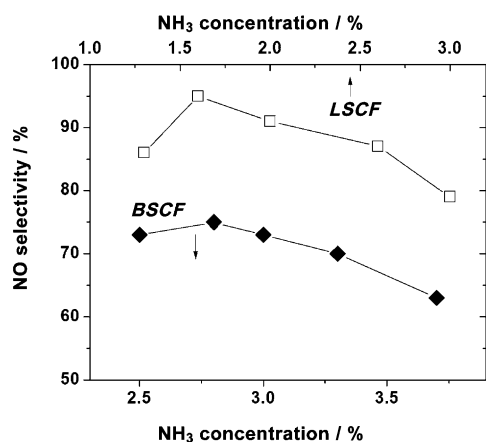

Figure 7. NO selectivity in the oxidation of ammonia as a function of the concentration of ammonia in the feed gas in membrane reactors with asymmetric BSCF and LSCF membranes (porous support side of the asymmetric membranes to the ammonia side, $T = 850\,°C$; air side: $F_{air} = 100\ cm^3\,min^{-1}$; ammonia side: $F_{all} = 100\ cm^3\,min^{-1}$, $F_{Ne} = 1\ cm^3\,min^{-1}$, $F_{He} = $ balance).

rate, a higher ammonia conversion could be realized, but LSCF showed a significantly higher selectivity for NO. Although a selectivity for NO of approximately 90% was achieved in the LSCF reactor, the best selectivity obtained in the BSCF reactor was approximately 75%. This finding is easily understood, as BSCF exhibits a faster surface exchange rate owing to the fact that it has a higher oxygen vacancy mobility than LSCF.[17] Therefore, a higher concentration of nonselective molecular oxygen species is expected on the membrane surface of BSCF than on that of LSCF, because the recombination of lattice oxygen is easier on BSCF, which results in a higher amount of active peroxide and superoxide ions. This leads to a decrease in the selectivity for NO at the expense of an increase in the formation of nitrogen. Evidently, the dominating oxygen species delivered by the membrane play a big role in the final product distribution.

In conclusion, we presented a novel route to activate oxygen for a better catalytic performance in the selective oxidation of ammonia to NO by using an oxygen-permeable perovskite membrane, in which the formation of catalytically non-selective molecular oxygen species was suppressed. The large surface provided by the porous perovskite layer diluted the permeated oxygen ions (lattice oxygen) and suppressed the formation of weakly bound molecular surface oxygen species, which thus led to a high selectivity for NO. In the oxidation of ammonia, 95% NO selectivity and 81% ammonia conversion were achieved in a catalytic membrane reactor with an asymmetric perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ oxygen-permeable catalytically active membrane at 850 °C. The oxygen used in the selective oxidation of ammonia was taken from the perovskite membrane, and the membrane was reoxidized on the air side. In the classical Mars and van Krevelen mechanism, this reoxidation takes place by gaseous oxygen present in the co-feed. This work may open the door for various selective oxidation processes and a detailed analysis of their mechanisms.

[1] V. A. Sadykov, L. A. Isupova, I. A. Zolotarskii, L. N. Bobrova, A. S. Noskov, V. N. Parmon, E. A. Brushtein, T. V. Telyatnikova, V. I. Chernyshev, V. V. Lunin, *Appl. Catal. A* **2000**, *204*, 59–87.

[2] Y. Wu, T. Yu, B.-S. Dou, C.-X. Wang, X.-F. Xie, Z.-l. Yu, S.-R. Fan, Z.-R. Fan, L.-C. Wang, *J. Catal.* **1989**, *120*, 88–107.

[3] a) J. P. Pérez-Ramírez, B. Vigeland, *Angew. Chem.* **2005**, *117*, 1136–1139; *Angew. Chem. Int. Ed.* **2005**, *44*, 1112–1115; b) J. Pérez-Ramírez, B. Vigeland, *Catal. Today* **2005**, *105*, 436–442.

[4] S. Sun, M. Rebeilleau-Dassonneville, X. Zhu, W. Chu, W. Yang, *Catal. Today* **2010**, *149*, 167–171.

[5] a) H. Over, Y. D. Kim, A. P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, G. Ertl, *Science* **2000**, *287*, 1474–1476; b) A. Bueno-López, K. Krishna, M. Makkee, J. A. Moulijn, *J. Catal.* **2005**, *230*, 237–248; c) J. L. Gunjakar, T. W. Kim, H. N. Kim, I. Y. Kim, S. J. Hwang, *J. Am. Chem. Soc.* **2011**, *133*, 14998–15007.

[6] R. Dittmeyer, J. Caro in *Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, S. 2221.

[7] A. Bielański, J. Haber, *Catal. Rev. Sci. Eng.* **1979**, *19*, 1–41.

[8] Y. Kosaki, A. Miyamoto, Y. Murakami, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 617–618.

[9] a) B. Bahrami, V. G. Komvokis, M. S. Ziebarth, O. S. Alexeev, M. D. Amiridis, *Appl. Catal. B* **2013**, *130–131*, 25–35; b) E. V. Kondratenko, J. Pérez-Ramírez, *Appl. Catal. A* **2005**, *289*, 97–103.

[10] G. Biausque, Y. Schuurman, *J. Catal.* **2010**, *276*, 306–313.

[11] Y. Xu, A. V. Ruban, M. Mavrikakis, *J. Am. Chem. Soc.* **2004**, *126*, 4717–4725.

[12] a) R. Merkle, J. Maier, *Angew. Chem.* **2008**, *120*, 3936–3958; *Angew. Chem. Int. Ed.* **2008**, *47*, 3874–3894; b) J. Pérez-Ramírez, E. V. Kondratenko, *J. Catal.* **2007**, *250*, 240–246; c) J. Pérez-Ramírez, F. Kapteijn, K. Schöffel, J. A. Moulijn, *Appl. Catal. B* **2003**, *44*, 117–151; d) E. V. Kondratenko, H. Wang, V. A. Kondratenko, J. Caro, *J. Mol. Catal. A* **2009**, *297*, 142–149.

[13] a) C. S. Chen, S. J. Feng, S. Ran, D. C. Zhu, W. Liu, H. J. M. Bouwmeester, *Angew. Chem.* **2003**, *115*, 5354–5356; *Angew. Chem. Int. Ed.* **2003**, *42*, 5196–5198; b) J. Sunarso, S. Baumann, J. M. Serra, W. A. Meulenberg, S. Liu, Y. S. Lin, J. C. Diniz da Costa, *J. Membr. Sci.* **2008**, *320*, 13–41; c) Z. P.

Shao, H. Dong, G. X. Xiong, Y. Gong, W. S. Yang, *J. Membr. Sci.* **2001**, *183*, 181–192; d) H. Q. Jiang, H. H. Wang, S. Werth, T. Schiestel, J. Caro, *Angew. Chem.* **2008**, *120*, 9481–9484; *Angew. Chem. Int. Ed.* **2008**, *47*, 9341–9344; e) H. Jiang, Z. Cao, S. Schirrmeister, T. Schiestel, *J. Caro, Angew. Chem.* **2010**, *122*, 5790–5794; *Angew. Chem. Int. Ed.* **2010**, *49*, 5656–5660; f) Y. Liu, X. Zhu, M. Li, H. Liu, Y. Cong, W. Yang, *Angew. Chem.* **2013**, *125*, 3314–3318; *Angew. Chem. Int. Ed.* **2013**, *52*, 3232–3236; g) H. H. Wang, Y. Cong, W. S. Yang, *Chem. Commun.* **2002**, 1468–1469.

[14] J. M. Serra, J. Garcia-Fayos, S. Baumann, F. Schulze-Küppers, W. A. Meulenberg, *J. Membr. Sci.* **2013**, *447*, 297–305.

[15] S. Baumann, J. M. Serra, M. P. Lobera, S. Escolástico, F. Schulze-Küppers, W. A. Meulenberg, *J. Membr. Sci.* **2011**, *377*, 198–205.

[16] C. Batiot, B. K. Hodnett, *Appl. Catal. A* **1996**, *137*, 179–191.

[17] a) R. M. L. Wang, Y. A. Mastrikov, E. A. Kotomin, J. Maier, *J. Mater. Res.* **2012**, *27*, 2000–2008; b) L. Wang, R. Merkle, J. Maier, *ECS Trans.* **2009**, *25*, 2497–2505; c) F. S. Baumann, J. Fleig, H. U. Habermeier, J. Maier, *Solid State Ionics* **2006**, *177*, 3187–3191; d) H. J. M. Bouwmeester, H. Kruidhof, A. J. Burggraaf, *Solid State Ionics* **1994**, *72*, 185–194.