Ammonia Oxidation

Perovskite Membranes in Ammonia Oxidation: Towards Process Intensification in Nitric Acid Manufacture**

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Ammonia is oxidized over PtRh alloy gauzes to form NO as the first step in the industrial production of nitric acid, a process that has remained practically unchanged for over 80 years. The reaction typically yields 94–96 % NO and 4–6 % by-products (N_2O and N_2) at 1073–1223 K.[1] Major drawbacks associated with the platinum-based catalysts are: 1) high production cost, 2) metal loss in the form of volatile oxides necessitate efficient metal recovery (Pd catchment) and refining systems, and 3) the production of N_2O, an environmentally harmful gas. Nitric acid manufacture is the largest single source of N_2O in the chemical industry (125×10^6 t CO_2-equiv per annum), and the development and implementation of abatement technology for this gas is required.[2] The above aspects have stimulated research towards replacing noble metals by oxide catalysts for NH_3 oxidation. Oxides may offer the advantage of lower investment, simpler manufacture, and reduced N_2O emission.[2,3] A vast number of patent applications have claimed promising performance of spinels or perovskites in the reaction, preferably containing Co, but also Fe, Mn, Bi, or Cr.[3] Laboratory, pilot, and industrial tests have typically been carried out in fixed-bed reactors with oxides in the form of

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particles, pellets, or monoliths. Several key aspects have prevented the industrial implementation of oxide catalysts: 1) relatively low NO selectivity (< 90 %), 2) rapid deactivation under relevant reaction conditions, and 3) the lower optimal operating temperature compared to noble metal catalysts causes difficulties with the steam balance in a revamped plant.[2]

Herein we present the first lanthanum ferrite-based perovskite membranes for ammonia oxidation, with which NO selectivities up to 98 % and no N_2O formation were attained. Our strategy was to combine in a single membrane reactor the separately reported properties of the above perovskites as oxygen conductors[4] and catalysts for NH_3 oxidation.[5] Accordingly, the applied configuration, depicted in Figure 1, integrates the separation of O_2 from air at the feed side by transport through oxygen vacancies in the mixed conducting membrane, and the reaction of oxygen with ammonia on the membrane surface at the permeate side. The surfaces of the membrane at the feed and permeate sides function as reduction ($O_2 \rightarrow 2\,O^{2-}$) and oxidation ($NH_3 \rightarrow NO$) catalysts, respectively. This gives rise to a radically intensified process for nitric acid manufacture, as large amounts of inert N_2 (2/3 of the total flow in today's plants) are excluded.

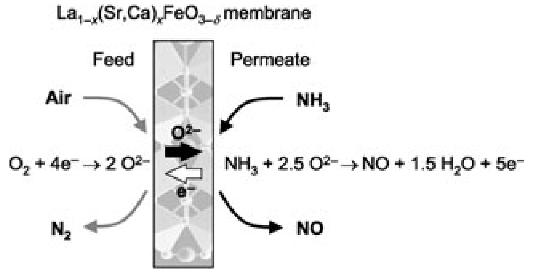

Figure 1. NH_3 oxidation to NO with mixed conducting membranes.

Important features of perovskite membranes in ammonia oxidation include oxygen flux $J(O_2)$, selectivity to NO $S(NO)$, and chemical stability in reducing and oxidizing atmosphere at high temperature. These interrelated parameters can be tailored by tuning the degree of calcium and strontium substitution in lanthanum ferrite-based perovskites $La_{1-x}(Sr, Ca)_xFeO_{3-\delta}$. A higher degree of substitution x increases the number of oxygen vacancies δ and thus the oxygen flux, but at the expense of lower chemical stability.[4,6,7] Furthermore, La substitution by alkaline earth cations in the perovskite structure is also known to influence the catalytic properties of these mixed oxides.[3] This can be caused by variation in the charge and/or coordination of 3d cations, changes in surface chemical composition, and development of microheterogeneities at the catalyst surface.

The preparation and characterization of the perovskite powders and the applied procedure for testing the membranes in the form of dense disks are described in the Experimental Section. For a $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ membrane disk as an illustrative example, Figure 2 shows the typical dependence of NO selectivity and O_2 flux on the inlet NH_3 flow at different temperatures. In the temperature range investigated, NO selectivities in the range of 90–100 % can be obtained by adjusting the inlet NH_3 flow. No N_2O was formed (< 10 ppm) in these experiments, and N_2 was the only N-containing by-product. Ammonia conversion (80–95 %) increases with increasing temperature and decreases at high ammonia flow rates. The oxygen flux is expected to increase with temperature at a fixed oxygen potential gradient. Under our experimental conditions, however, the oxygen flux is almost exclusively controlled by the ammonia flow rate and thus independent of temperature. The NO selectivity, however, is dependent on temperature, and moreover exhibits a maximum with the inlet ammonia flow. As expected, the NO selectivity decreases in favor of N_2 under conditions of excess ammonia as a result of favorable recombination of adsorbed NH_x fragments.[3,8] The additional observation of decreasing selectivity at low ammonia flow rates, which gives rise to the maximum, is attributed to partial oxidation on the hot reactor walls of NH_3 bypassing the membrane with excess oxygen recombining and escaping the membrane surface. The faster reaction at high temperature explains the decrease in the maximum NO selectivity when going from 1000 K (98 %) to 1333 K (92 %). Implicitly, with these membrane materials, higher NO selectivities than those displayed in Figure 2 would have been obtained if wall effects could be excluded. The shift of the NO selectivity maximum to lower ammonia molar flow with decreasing temperature reflects the reduced oxygen flux (at constant oxygen potential) at lower temperatures.

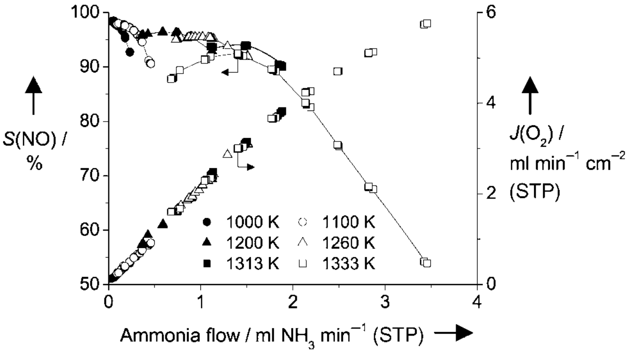

Figure 2. NO selectivity and O_2 flux versus inlet ammonia flow at different temperatures for a $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ membrane.

Figure 3 shows the maximum NO selectivity and corresponding oxygen flux as functions of the degree of substitution of Ca and Sr in the lanthanum ferrite perovskites at 1200 K. As expected, the oxygen flux is proportional to the degree of substitution. The maximum NO selectivity (95–96 %) does not depend on the type and degree of substitution within this range, and this indicates similar catalytic performance of these membrane compositions. Wu et al.[5] studied NH_3 oxidation at 1073 K in a fixed-bed reactor with catalyst particles and reported optimal NO selectivities ($\approx$ 95 %) for $x = 0.2$–0.7 in $La_{1-x}Sr_xFeO_3$. For the membrane reactor described herein, the optimum degree of substitution is determined by a combination of maximum flux with absolute chemical stability under process conditions. This optimum degree of substitution of Sr and Ca probably lies in the range of $x = 0.1$–0.2.

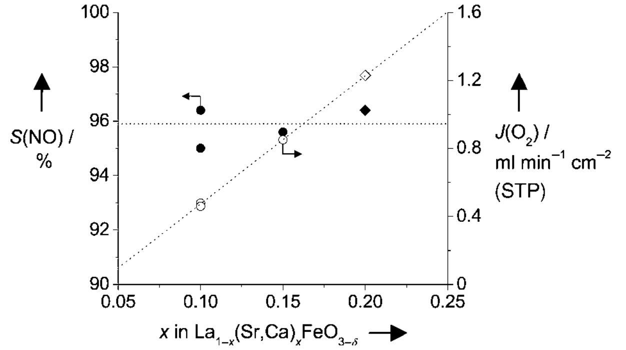

Figure 3. Maximum NO selectivity (solid symbols) and corresponding oxygen flux (open symbols) at 1200 K versus the degree of substitution in Ca- (circles) and Sr-substituted (diamonds) lanthanum ferrite perovskites.

The above results demonstrate the potential of Ca- and Sr-substituted lanthanum ferrite membranes for the high-temperature oxidation of ammonia; the NO selectivities of up to 98% are comparable to those of state-of-the-art PtRh alloys.[1,2] In addition, formation of undesirable N_2O is totally suppressed. The implementation of an ammonia oxidation process based on oxygen-conducting membranes would constitute a major step change in nitric acid production (a top-ten product in the bulk chemicals industry) and have a strong impact on the fertilizer industry. Apart from the superior NO selectivity, in situ separation of O_2 from air by membranes enables extremely compact and intensified production units, as N_2 represents about 70% of the total flow in a current plant. The reduction in total flow would allow a drastic size decrease in key plant units, including the absorption tower and the tail-gas train, as well as intensification in piping. Moreover, energy savings for compression of the NO_x gas before the absorption step, which requires high pressure, further contributes to an improved nitric acid production process. In summary, a more efficient and sustainable process can be attained, which is especially attractive for nitric acid production that is decentralized from large existing plants.

Our current research for further implementation of membrane technology in ammonia oxidation focuses on scaling up membrane disks to monolithic membranes, with which surface areas in the range of 2000–3000 m^2 per cubic meter of reactor can be obtained, depending on cell size and wall thickness.[9] The reactor design involves the distribution of ammonia and air in a monolithic structure with square channels in a chess-board pattern (one channel for ammonia and the four surrounding channels for air). The significantly increased surface area to reactor volume ratio of monoliths will enable application of substantially higher ammonia concentrations on the permeate side compared to the disk configuration used in the present study.

Experimental Section

Lanthanum ferrite-based perovskites $La_{1-x}A_xFeO_{3-\delta}$ (A = Ca, Sr; x = 0.1–0.2) were prepared by a conventional wet complexation route with citric acid. Standardized solutions (1 M) of the metal nitrates were mixed with citric acid in a molar ratio of acid to total cations of 3. The resulting solution was slowly heated to 433 K (40 $K h^{-1}$) to ensure complete complexation and left overnight at this temperature to dry. After further heating to 773 K for 5 h in flowing air to remove organic matter and final calcination at 1173 K for 10 h, all powders were single-phase perovskites as evidenced by XRD. The particle size, obtained by laser scattering, was in the range of 0.1–0.5 μm. Dense membrane disks (>95% of theoretical density) were made by uniaxial pressing and sintering at 1573 K. After final grinding and polishing, membrane disks with a diameter of 10 mm (≈80 mm^2) and a thickness of ≈0.9 mm were obtained. The disks were mounted in a quartz microreactor, sketched in Figure 4, which was heated to 1333 K for sealing with gold rings. The oxidation of ammonia was investigated at 1000–1333 K by feeding an equimolar O_2/Ar mixture to the feed side, and NH_3/He mixtures to the permeate side. The inlet ammonia flow was varied in the range of 0.05–4.5 ml min^{-1} (STP), with a total flow of 130 ml min^{-1} (STP). Product gases were analyzed on-line with a mass spectrometer and a gas chromatograph. Freedom from leakages was verified by the absence of Ar on the permeate side. The NO selectivity was obtained from the concentrations at the reactor outlet according to $S(NO) = c(NO)/[c(NO) + 2c(N_2O) + 2c(N_2)]$. The oxygen flux $J(O_2)$ was determined from the measured concentrations of all O-containing species. Stable membrane performance over the typical testing period (10 days) was verified by periodically repeating measurements under selected temperature/flow conditions.

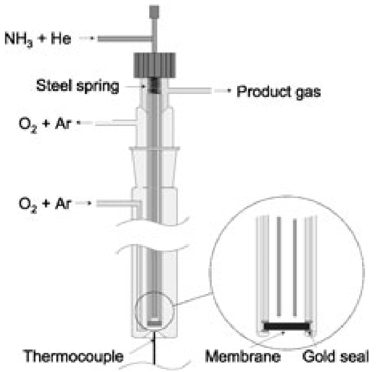

Figure 4. Quartz reactor used in the membrane tests.

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