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N_2O Decomposition

Direct Decomposition of Nitrous Oxide to Nitrogen by In Situ Oxygen Removal with a Perovskite Membrane**

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Nitrous oxide (N_2O) has recently received much attention as it greatly contributes to the greenhouse effect[1] and causes severe destruction of the ozone layer in the stratosphere.[2] N_2O is produced by both natural and anthropogenic sources;[3–5] N_2O emissions that can be reduced in the short term are associated with chemical and energy industries.[6,7] The major N_2O emission of chemical production comes from adipic acid and nitric acid plants. In the past decades, significant efforts have been devoted to the development of technologies for N_2O reduction. Possible methods include: 1) non-selective catalytic reduction (NSCR), 2) selective catalytic reduction (SCR), and 3) catalytic decomposition of N_2O to O_2 and N_2. NSCR has been developed for NO_x removal and has shown potential for reducing N_2O. However, NSCR is not the optimum choice because of high secondary emissions of CO_x and high cost of the reductant.[8,9] SCR of N_2O with hydrocarbons has been extensively investigated over iron-based zeolites.[10–13] The major drawback of this process are also the high costs associated with the consumption of reductants.[7]

Direct catalytic decomposition of N_2O without addition of reducing agents is an attractive and economical option to reduce N_2O emission. Catalysts, including supported noble metals, metal oxides, and perovskites, are active in direct catalytic N_2O decomposition.[14–16] The commercial iron–zeolite catalysts perform quite well in the presence of other gases, such as O_2, NO_x, or H_2O, even in the presence of CO_2 and SO_2.[17] However, metal oxide catalysts suffer from oxygen inhibition, and a low reaction rate of the N_2O decomposition is observed.

To avoid inhibition by adsorbed oxygen, the O_2 formed can be directly removed from the reaction zone by an oxygen-selective membrane. A novel perovskite membrane,[18–27] which also acts as the catalyst, has the composition $BaCo_xFe_yZr_{1-x-y}O_{3-\delta}$ (BCFZ) with hollow-fiber geometry.[18–21]

The basic concept is shown in the Figure 1: N_2O catalytically decomposes on the perovskite membrane surface to N_2 and surface oxygen (O*) according to Equation (1).

$$N_2O \rightarrow N_2 + O^* \quad (1)$$

Afterwards, O* is removed as oxygen ions (O^{2-}) through the membrane, and local charge neutrality is maintained by counterdiffusion of electrons (e^-). To ensure a sufficient driving force for the oxygen transport through the membrane, and thus rapid removal of oxygen, methane is fed to the permeate side of the membrane to consume the permeated oxygen by the partial oxidation of methane (POM) to synthesis gas according to $CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^-$. As a result, surface oxygen (O*) can be quickly removed by the membrane once it is generated from N_2O decomposition. Therefore, the average amount of adsorbed oxygen (O*) is decreased on the catalyst surface, and a higher reaction rate of the N_2O decomposition is obtained.

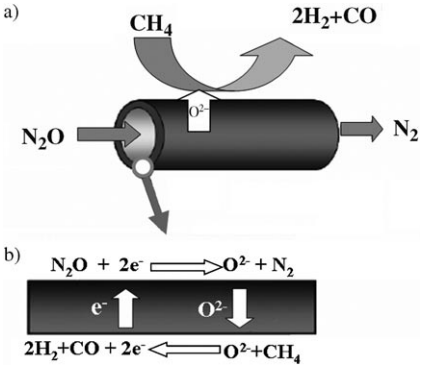

Figure 1. a) Mechanism of the direct decomposition of N_2O to N_2 with in situ removal of the rate-inhibiting surface oxygen by a perovskite hollow fiber membrane. b) Details of the membrane reaction.

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To demonstrate this concept, we carried out experiments with and without oxygen removal using a BCFZ perovskite hollow fiber membrane. In the first set of experiments, N_2O was fed to the core side and no sweep gas was applied at the shell side, so that none of the oxygen surface species produced by the decomposition of N_2O were removed by permeation through the membrane (Supporting Information, Figure S1). The BCFZ membrane thus functions as a catalyst only.

The results of these investigations are shown in Figure 2a. The N_2O decomposition increases with increasing temperature; however, the conversion is relatively low (< 30% even

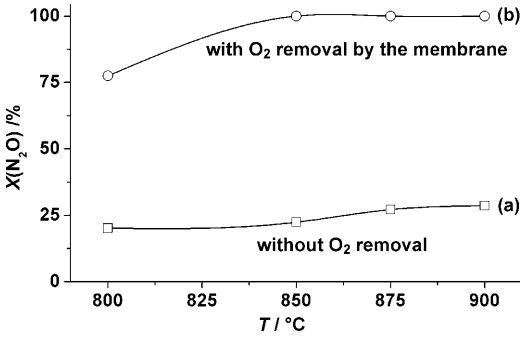

Figure 2. Conversion of N_2O at different temperatures with or without oxygen removal by the membrane. Core side: 30 $cm^3 min^{-1}$ ($F_{N_2O} = 6$ $cm^3 min^{-1}$, $F_{He} = 24$ $cm^3 min^{-1}$). Shell side: a) no oxygen-consuming sweep gas applied, b) with methane as oxygen-consuming sweep gas, 40 $cm^3 min^{-1}$ ($F_{CH_4} = 8$ $cm^3 min^{-1}$, $F_{Ne} = 12$ $cm^3 min^{-1}$, $F_{H_2O} = 20$ $cm^3 min^{-1}$). Membrane area: 0.86 cm^2. Amount of nickel-based catalyst on shell side: 1.2 g.

at 900 °C). The catalytic decomposition of N_2O on the perovskite membrane surface proceeds mainly in two steps: 1) decomposition of N_2O into N_2 and adsorbed surface oxygen (O*) according to Equation (1), and 2) desorption of surface oxygen as O_2 to the gas phase according to Equation (2).

$$O^* \rightleftharpoons {}^1/_2\, O_2 + * \qquad (2)$$

Equation (2), that is, the oxygen–oxygen recombination, is known to be the rate-limiting step in N_2O decomposition.[28,29] As the surface oxygen O* generated by the N_2O decomposition occupies the surface active sites for the decomposition of N_2O, only a low N_2O conversion is obtained.

In the second set of experiments, methane was fed to the shell side (Supporting Information, Figure S1). In contrast to the poor conversion of the first set, in the second set, the N_2O decomposition is significantly improved (Figure 2b). At a temperature of 850 °C, N_2O is already completely decomposed. The reason for this enhanced conversion is an increased removal of the adsorbed surface oxygen. In contrast to the first experiment, the adsorbed surface oxygen, along with desorption to the gas phase, can be also removed directly by the perovskite material functioning as a membrane. The active centers are thus less occupied by adsorbed oxygen on the catalyst surface and therefore the reaction rate is increased.

In the direct catalytic decomposition of N_2O, most of the metal oxide catalysts cannot tolerate the coexistence of oxygen in the feed because the oxygen inhibits the N_2O decomposition. However, oxygen as co-feed has no negative effect on the N_2O decomposition in the membrane reactor. Table 1 shows the N_2O conversion and oxygen concentration

Table 1: Oxygen concentration in the off-gas as a function of the oxygen concentration in the mixed N_2O/O_2 feed gas at 100% N_2O conversion.[a]

$C(O_2)$ in the fed N_2O of the core side [vol.%]	$C(O_2)$ in the exit of the core side [vol.%]
0	0.011
5	0.014
7.5	0.019
15	0.022

[a] At 875 °C. Core side: 30 $cm^3 min^{-1}$ ($F_{N_2O} = 6$ $cm^3 min^{-1}$, $F_{O_2} = 1.5$–4.5 $cm^3 min^{-1}$, F_{He} = balance). Shell side: 40 $cm^3 min^{-1}$ ($F_{CH_4} = 18$ $cm^3 min^{-1}$, $F_{H_2O} = 22$ $cm^3 min^{-1}$). Membrane area: 0.86 cm^2. Amount of nickel-based catalyst on shell side: 1.2 g.

at the reactor outlet as a function of oxygen concentration in a mixed N_2O/O_2 feed. A complete conversion of N_2O is always achieved, which does not change with increasing oxygen concentration in the range studied in the feed, as both the co-fed and the produced oxygen are removed continuously by the membrane.

Figure 3 shows the influence of the N_2O concentration on the N_2O decomposition. Both low (5%) and high (50%) N_2O concentrations can be effectively treated (conversion of $N_2O > 99.9\%$) using the BCFZ membrane reactor.

The membrane approach presented herein involves the in situ removal of pure oxygen, which could then be utilized. An attractive option for the use of this oxygen is in the production of N_2-free synthesis gas. In Figure 4, N_2O in the core side was completely converted. Simultaneously, synthesis gas is obtained by partial oxidation of methane. Using suitable reaction conditions, a methane conversion of over 90% and a CO selectivity of 90% was achieved for at least 60 h of operation. The technology is more feasible when the concen-

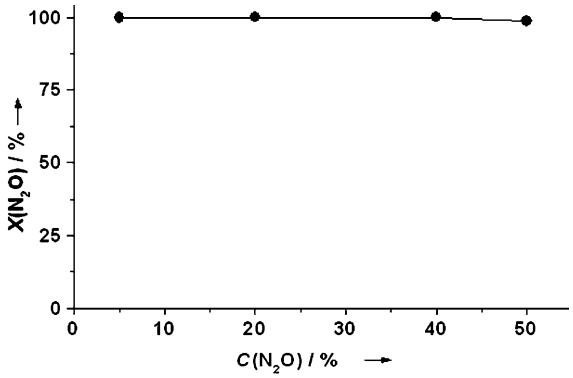

Figure 3. Influence of the N_2O concentration in the fed gas on the N_2O conversion at 875 °C.Core side: 30 $cm^3 min^{-1}$ ($F_{N_2O} = 1.5$–15 $cm^3 min^{-1}$, F_{He} = balance). Shell side: 40 $cm^3 min^{-1}$ ($F_{CH_4} = 8$ $cm^3 min^{-1}$, $F_{Ne} = 12$ $cm^3 min^{-1}$, $F_{H_2O} = 20$ $cm^3 min^{-1}$). Membrane area: 0.86 cm^2. Amount of nickel-based catalyst on shell side: 1.2 g.

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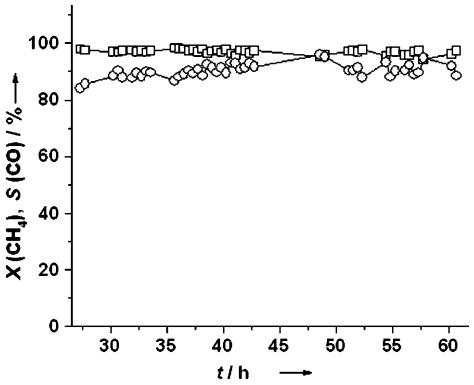

Figure 4. Methane conversion $X(CH_4)$ (□) and CO selectivity $S(CO)$ (○) as a function of time on-stream at 875 °C with 100% N_2O conversion. Core side: 30 $cm^3 min^{-1}$ (F_{N_2O} = 6 $cm^3 min^{-1}$, F_{O_2} = 1.5 $cm^3 min^{-1}$, F_{He} = 22.5 $cm^3 min^{-1}$). Shell side: 40 $cm^3 min^{-1}$ (F_{CH_4} = 23 $cm^3 min^{-1}$, F_{H_2O} = 17 $cm^3 min^{-1}$). Membrane area: 0.86 cm^2. Amount of nickel-based catalyst on shell side: 1.2 g.

trations of nitrous oxide in the off-gas are sufficient high, such as in adipic acid plants.

In conclusion, a perovskite membrane reactor is proposed for the N_2O abatement from exhaust gases. The ceramic membrane fulfills a double role: it catalyzes the decomposition of N_2O on the membrane surface, and it increases the reaction rate by overcoming the rate-limiting removal of surface oxygen, thus increasing the number of active surface sites required for the N_2O decomposition. A reducing agent has to be used; this agent, for example methane, can however be used for the production of N_2-free synthesis gas by partial oxidation using the removed oxygen from N_2O decomposition as an oxidant.

The work presented herein is the new concept to enhance the reaction rate of heterogeneous catalytic processes, in which the recombination and/or desorption of one of the reaction products is the rate-limiting step. Using a semipermeable membrane, which facilitates in situ removal of an inhibiting species on a catalyst or catalyst support, helps to effectively reduce the surface concentration of the inhibiting species and therefore increases the reaction rate.

Experimental Section

The dense BCFZ perovskite hollow-fiber membranes were manufactured by phase inversion spinning followed by sintering.[18–21] Figure S1 (Supporting Information) shows diagrams of the membrane reactor used in this study. Two ends of the hollow fiber were coated by commercially available gold paste. After sintering at 950 °C, a dense gold film, which is not permeable to oxygen, was obtained. Such gold-coated hollow fibers can be sealed by silicon rubber rings and the uncoated part of the fiber (3.0 cm) that is permeable to oxygen can be kept in the middle of the oven, ensuring isothermal conditions. A mixture of N_2O and helium was fed to the core side and a mixture of CH_4 and helium was fed to the shell side. A nickel-based steam reforming catalyst (Süd-Chemie AG) was packed around and behind the hollow fiber membrane. To avoid coke formation on the catalyst, H_2O was also fed to the shell side. The H_2O flow rate was controlled by a liquid mass flow controller (Bronkhorst) and completely evaporated at 180 °C before it was fed to the reactor. All gas lines to the reactor and the gas chromatograph were heated to 180 °C to avoid condensation. The concentrations of the gases at the exit of the reactor were determined by on-line gas chromatography (Agilent 6890 with a carboxen 1000 column, which was periodically switched from the core-side to the shell-side of the membrane to measure the gas compositions on both sides of the membrane). The CH_4 conversion $X(CH_4)$, the CO selectivity $S(CO)$ and the N_2O conversion were calculated as shown in Equations (3)–(5).

$$X(CH_4) = \left(1 - \frac{F(CH_4,\text{out})}{F(CH_4,\text{in})}\right) \times 100\,\% \quad (3)$$

$$S(CO) = \frac{F(CO,\text{out})}{F(CH_4,\text{in}) - F(CH_4,\text{out})} \times 100\,\% \quad (4)$$

$$X(N_2O) = \left(1 - \frac{F(N_2O,\text{out})}{F(N_2O,\text{in})}\right) \times 100\,\% \quad (5)$$

In these equations, $F(i)$ is the flow rate of species i on the shell or core side of the hollow fiber membrane.

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