

Sustainable Nitrogen-Based Fertilizer Production from Sun, Air, and Water



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Abstract In the DüSol research project, the technology of sustainable fertilizer production is developed and demonstrated on the basis of solar thermal redox cycle processes. The focus is on the unexplored step of solar thermal air separation for the production of nitrogen. For this reaction, corresponding materials are identified by thermodynamic calculations and qualified and optimized on a laboratory scale. In combination with material development, a prototype reactor is designed based on computer-aided calculation tools. In a test campaign in the new high-performance simulator for concentrated solar radiation SynLight at the Technology Center in Jülich, this reactor is being tested and the solar thermal nitrogen production demonstrated. These experimental works go hand in hand with the overall process simulation and optimization, which lead to a comprehensive economic analysis.

Keywords Fertilizer production · Thermochemistry · Air separation · Solar reactor · Concentrated sunlight

Introduction

There is an ever-growing demand for ammonia production that already reached globally 200 million tons per year by 2018 and is forecasted to increase to over 350 million tons per year by 2050 [1]. The application segment is dominated by the fertilizer industry, since the most important fertilizer and the world's most widely produced chemical is urea. Ammonia is synthesized via the Haber–Bosch process, for which the required hydrogen and nitrogen are currently provided by using fossil fuels. The process consumes about 2% of the world's commercial energy, which corresponds

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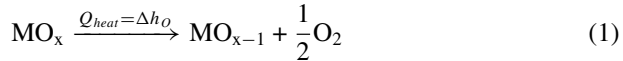
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G. Gaustad et al. (eds.), *REWAS 2019*, The Minerals, Metals & Materials Series,
https://doi.org/10.1007/978-3-030-10386-6_5

to approx. 2 trillion kWh. This work proposes a novel approach to produce ammonia from the raw materials water and air only by utilizing solar energy directly—without the detour of electricity, which is inevitably associated with energy conversion losses.

The proposed ammonia production route consists of two coupled solar-heated thermochemical cycle processes, which aim to specifically remove oxygen from gases. This applies both to gases that have atomically bound oxygen (water vapor), as well as for oxygen-containing gas mixtures (air). The applied redox material is oxidized in a two-stage process with the corresponding gas, and then thermally reduced. The energy required for this is provided by concentrated solar radiation that has the potential to play a major role in the future global energy mix.

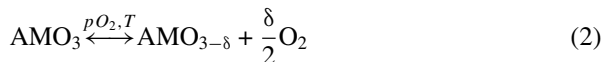
In the first cycle, H_2O is used for oxidation and hydrogen is produced. This process has already been successfully tested by DLR on a pilot scale [2]. The second innovative cycle uses air as the oxidant. The air is deprived of oxygen and thereby pure nitrogen is produced. Both gases together, N_2 and H_2 , are subsequently converted to ammonia in the well-established Haber–Bosch process.

The focus of the current work is the unexplored solar thermal air separation for the production of nitrogen for the Haber–Bosch process, which requires N_2 with oxygen contamination below 10 ppm. During thermochemical reduction–oxidation (redox) cycles, the redox material (typically metal oxide) is thermally reduced at high temperature



while heat is converted to chemical energy in an amount equal to the enthalpy of the reduction reaction, and with the release of gaseous oxygen. During the reduction step, this stored energy can then be converted back to heat by the reverse reaction to drive the air separation step for N_2 production. The absorbed O_2 during the oxidation step could later be released and utilized for fertilizer production, e.g., in the Ostwald process for ammonium nitrate synthesis.

Perovskites are promising redox materials that are described with the general formula $AMO_{3-\delta}$, where the A site typically features an alkali, alkaline earth or rare earth metal cation, whereas the M site is occupied in most cases by transition metal cations. The occurrence of an oxygen non-stoichiometry δ ($\delta = 0-0.5$) in $AMO_{3-\delta}$ perovskites, as well as the close structural relationship between perovskites and their defect-ordered reduced form $A_2M_2O_5$ (brownmillerite) allow for fast redox kinetics. Furthermore, the partial reduction that is described by Eq. 2 ensures the stability of these materials since during the redox cycle, oxygen moves through the lattice without a decomposition of the crystal structure.



Another advantage of perovskites is their tuneable composition, since the A and M sites can be occupied by a number of ions. The possible formation of a given composition is limited by the Goldschmidt tolerance factor [3]:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_M + r_O)} \quad (3)$$

In most cases, the perovskite forms the desired ideal cubic lattice until $1 < t < 1.02$. The tolerance factor can be controlled by selecting the required alkali metal on the A site, while the B site can be occupied by a number of transition metals with the possibility of adding other metals in small quantities. With this method, the reduction enthalpy can be tuned in the range of $\Delta H^0 = 100\text{--}500 \text{ kJ/mol}^{-1}$.

The selection of the metal ions was based on the rule that the oxygen affinity of the material should be low enough to allow thermal reduction in air at moderate temperatures, but high enough to enable full reoxidation of the reduced form to its initial state in air. A measure of the reducibility of oxide is its reduction enthalpy (ΔH_{red}), a lower ΔH_{red} results in a lower reduction onset temperature.

In this work, the feasibility of using perovskites as redox materials for solar thermochemical air separation is demonstrated. The choice of the applied redox material $\text{SrFeO}_{3-\delta}$ is based on our previous results [4]. Furthermore, the raw materials used to make $\text{SrFeO}_{3-\delta}$, strontium carbonate and iron oxide are very inexpensive, due to abundant natural resources at world market prices below \$1 per kg, allowing for economical use as a redox material. The concept is first validated in laboratory-scale experiments performed in an IR furnace, followed by scaling up the process to a 20 kW solar reactor.

Experimental

Synthesis of $\text{SrFeO}_{3-\delta}$ Particles

$\text{SrFeO}_{3-\delta}$ was synthesized by a solid state reaction between the raw materials, strontium carbonate, and iron oxide. The powders were mixed in a ball mill, then annealed at 1100 °C for 20 h in an alumina crucible. The desired phase composition was verified via XRD. For the experiments, 4 mm spherical particles were prepared by mixing-spheronization using microcrystalline cellulose as binder.

Laboratory-Scale Proof of Concept

50 g of the synthesized beads were packed in a fixed bed reactor with an inner diameter of 20 mm that allowed for rapid heating and cooling via infrared radiation.

The bed was kept horizontal and heated in gas flows of synthetic air and nitrogen while the oxygen content of the outlet gas was monitored continuously. For the reduction process, the sample was heated under a flow of nitrogen of approximately 500 sccm to 800 °C. Reoxidation was performed under either synthetic air or 1% oxygen and 99% nitrogen flow at 350 °C.

Results

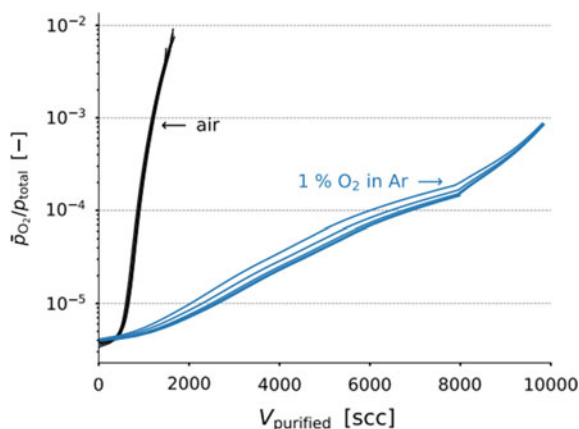
Laboratory-Scale Proof of Concept

The goal of the experiments was to prove that very low oxygen partial pressures can be reached during the reoxidation step performed in synthetic air. After the high temperature reduction step, when oxidation begins, the outlet oxygen concentration drops to a value of approximately 3×10^{-6} bar for some time, giving an outflow of purified nitrogen with low oxygen impurities, from the gas entering the system with 20% oxygen. As the oxidation progresses, the oxygen vacancies in the material become filled and it slowly loses capability to remove oxygen at low concentrations, so that the outlet concentration increases over time. The approximate residence time for the gas flow in the bed is calculated to be less than 5 s for the air flow through the bed. This highlights the very high kinetic activity of the oxidation reaction under plug flow conditions.

To investigate the cyclability of the material, five cycles were performed at identical thermal conditions of 800 °C reduction and 350 °C oxidation for air purification. Additional five cycles were performed at identical conditions but with an inlet gas of 1% oxygen in a 500 sccm nitrogen flow. This is of interest as the SrFeO₃ cycle alone would be a rather energy intensive route to producing nitrogen, but coupling it with an already established technology for producing low purity nitrogen, such as a pressure swing adsorption unit, could offer a very efficient route to removing the remaining trace oxygen and producing high purity nitrogen. The production versus purity relationships for each cycle is given in Fig. 1. The narrow grouping between curves of different cycles shows the excellent repeatability of the process and lack of degradation of the material, at least over the limited number of cycles performed.

When removing oxygen from air, the 48 grams of material produced 0.602–0.662 l of gas with less than 10 ppm of oxygen impurities. When removing oxygen from a semi-purified stream, the same amount of material produced 2.014–2.661 l of gas with the same purity.

Fig. 1 Production curves for five identical purification trials from both synthetic air and from a mixture with 1% O₂



20 kW Solar Reactor Design

SrFeO_{3-δ} is suitable for use in the form of particles, therefore a number of reactor designs may be considered, such as a fixed bed reactor, rotary kiln, fluidized bed reactor or moving bed reactor. During the first step of the selection process, the latter two were rejected due to their relatively complex design and operation with concentrated sunlight, and only the fixed bed reactor and the rotary kiln were considered during the continuing evaluation.

The use of a fixed bed reactor is a simple solution that is similar to the laboratory-scale technology demonstration in the IR furnace, but it only allows batch mode operation, and since the whole reactor has to be cooled for the oxidation reaction step, the overall efficiency would be lower. A more promising option is to use a rotary kiln that would allow the separation of the reduction and oxidation step to reach higher energy efficiency. The reduction of the redox material would take place at a higher temperature in the kiln heated by concentrated sunlight, then it would be transferred to another reactor, where after cooling the air separation would take place. The rapid kinetics of the redox reaction by using perovskites means that the rotary kiln could be given a high mass flow and a high input power, improving the reactor's thermal efficiency. Solar rotary-driven kilns were already demonstrated to work well in previous studies, also with continuous particle flow [5].

The proposed reactor scheme is shown in Fig. 2. The solar radiation enters through a quartz window that is fixed to the stainless steel crucible with a flange that ensures a gas-tight connection. The gas inlet and outlet pipes are welded to the back of the crucible. The inlet pipe reaches inside the crucible close to the focal point of the radiation, which allows the gas to preheat before entering the reactor area. In addition, it serves to separate the inlet and outlet flows. The oxygen concentration of the outlet flow is monitored by a zirconium oxide-based lambda-sensor.

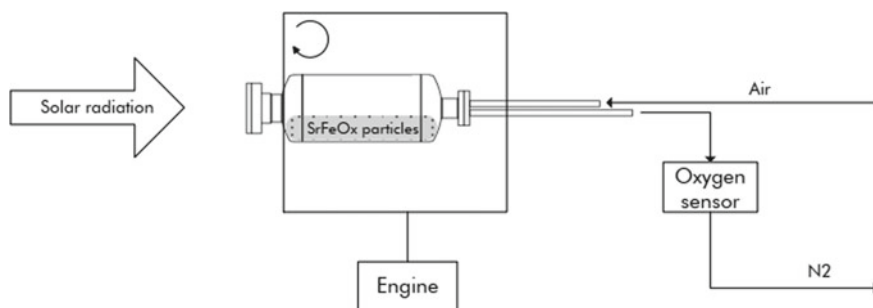


Fig. 2 Scheme of a solar rotary kiln for air separation

Process and CFD Simulation

Based on the thermochemical characterization of the redox material and the results from the laboratory-scale experiments, a CFD model of the solar rotary kiln (Fig. 2) is set up in order to investigate and understand the interaction of gaseous flow, chemistry of the redox processes and heat and mass transfer. Furthermore, the CFD model combines conventional CFD techniques with a discrete element modeling (DEM) approach, modeling the bed consisting of individual numerical model particles to account both for internal solid mixing of the bed as well as the fluid flow through the porous bed structures. The redox chemistry is included as heterogeneous surface reactions attached to the DEM particles. This model should also serve to optimize both the design and the operation of the solar rotary kiln and provide information about the reactor characteristics for a process model.

An overall process model is created to investigate the thermochemical feasibility of the process in general, as well as the related mass and energy balances in particular. It is based on process simulation software tools and components [6, 7] and the corresponding thermochemical substance data by GTT-Technologies, and can be used to investigate the effects of different operating conditions regarding the intended process design, thus also contributing to a comprehensive economic analysis.

Summary

Solar thermochemical air separation is a promising approach to provide nitrogen with the required purity to feed the Haber–Bosch process. Our current work focused on selecting a suitable redox material for the thermochemical cycle based on large-scale experimental screening aided by thermodynamic calculations. The viability of using the perovskite SrFeO_3 was verified by laboratory-scale experiments, where 50 g of

redox material particles produces ca. 600 ml purified nitrogen per cycle. Based on these results, a 20 kW solar rotary kiln design was proposed for the scaled-up process that was optimized by process simulation software tools.

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