A novel lab-scale solar reactor for kinetic analysis of non-volatile metal oxides thermal reductions

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Abstract

Thermal reduction of metal oxides is of primary interest within the R&D field of solar driven thermochemistry, because it is frequently involved in processes such as thermochemical cycles for hydrogen production or in thermochemical energy storage systems for solar thermal power plants. A lab-scale solar reactor has been designed to test and analyze solar-driven reduction of non-volatile metal oxides arranged in a packed bed. The test bed allows monitoring of oxygen evolution to determine the reaction rate. Experimental tests with Mn$_2$O$_3$, Mn$_3$O$_4$ and CeO$_2$ have been carried out and the performance of each reaction has been analyzed. Total conversion is obtained for Mn$_2$O$_3$ reduction. However, only some zones of the Mn$_3$O$_4$ and CeO$_2$ samples achieve reaction temperature. Different types of sample-holders have been used to hold the particles packed-bed, in order to enhance the conversion. The high influence of the irradiance distribution on the sample surface is demonstrated by a testMn$_3$O$_4$ reduction.

Keywords: Non-volatile metal oxides; solar reactor; solar thermochemistry; kinetic analysis.

1. Introduction

Solar thermochemistry is a promising long term prospect for commercially developing clean, efficient and sustainable energy systems [1]. Thermochemical processes carried out using concentrated solar energy have been widely demonstrated [2, 3] being the production of synthetic fuels, thermochemical storage and hydrogen generation the most investigated processes. Metal oxides reductions are involved in thermochemical processes and represent one of the most critical stages because they take place at the highest temperature of the process. Most of them usually occur at the temperature range of 1100-2300 K that is typically obtained at solar tower systems. Because of that, thermal reductions of metal oxides are very interesting as processes to be carried out by concentrated solar power. To develop them, different configurations of solar reactors have been conceived [4]. A solar reactor should ensure the optimal
operating conditions to enhance the chemical reaction and also provide a tool to get a deep understanding of reaction features. Particularly, reaction rates including chemical kinetics are often a major concern. Most of the studies for kinetic determinations have been done employing non-solar techniques such as thermogravimetry [5-7]. Some solar devices have been also used to determine kinetics at high radiation fluxes. The thermal decomposition of ZnO in a 45-kW concentrating solar furnace was studied at PSI (Paul Scherrer Institute, Villigen, Switzerland) [8,9] in a cavity-type solar reactor and a solar-driven thermogravimeter. The kinetic parameters were calculated from the sample mass loss. A revised version of the same solar thermogravimenter setup has been successfully applied for analyzing the kinetics of non-volatile metal oxides at PSI’s 50-kWth high flux solar simulator [10]. The chemical kinetics was also determined from carrier gas composition analysis at reactor downstream for the TREMPER reactor [11] at PSI’s solar furnace and spherical transparent reactors [12] in a vertical solar furnace at CNRS-PROMES, Odeillo, France. In both cases, the sample was enclosed in a transparent sealed cover to keep controlled atmosphere during operation.

In this work, the experimental reduction of some non-volatile oxides under high flux of radiation is presented. Non-volatile metal oxides facilitate the recovery the solid product obtained after the thermal treatment and also simplify the separation of oxygen released, avoiding the use of quenching or other complex separation processes. Particularly, manganese oxides, Mn$_2$O$_3$, Mn$_3$O$_4$ and cerium oxide, CeO$_2$ are studied. Manganese oxides reductions are involved in the thermochemical cycle proposed by Sturzenegger [13] and they occur according to this mechanism or chemical route:

\[
6 \text{Mn}_2\text{O}_3 \rightarrow 4 \text{Mn}_3\text{O}_4 + \text{O}_2
\]  
\[
2 \text{Mn}_3\text{O}_4 \rightarrow 6 \text{MnO} + \text{O}_2
\]  

A background on the work previously done on these oxides reduction is found in [14]. In relation to cerium oxide, Abanades et al. [15] proposed a two-step thermochemical cycle based on CeO$_2$/Ce$_2$O$_3$. Thermodynamical studies indicated the reduction gave rise to non-stoichiometric species:

\[
\text{CeO}_2 \rightarrow \text{CeO}_{2-x} + x/2\text{O}_2
\]  

where 0<x<0.5. A complete thermochemical cycle to water and CO$_2$ splitting was then developed by Chueh et al. [16]. Regarding reduction step, they concluded the oxygen evolution kinetics was limited predominantly by the heating rate.

In the present work, reductions are carried out in a novel solar reactor where reactants are arranged in a packed-bed.

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$X_a$</td>
<td>Conversion of reactant “a”</td>
</tr>
<tr>
<td>$m_a$</td>
<td>Initial mass of reactant “a”</td>
</tr>
<tr>
<td>$PM_a$</td>
<td>Molecular weight of reactant “a”</td>
</tr>
<tr>
<td>$[O_2]$</td>
<td>Oxygen concentration</td>
</tr>
</tbody>
</table>
2. Experimental

2.1. Solar reactor and experimental set-up

The main device is a lab-scale cavity-type solar reactor. A cross section of the reactor and photograph are depicted in Fig. 1. The radiation source is a high-flux solar simulator (total radiation power of 2 kW onto focal area, peak flux of 2.5 kW/m², and a rim angle of 26º) installed at IMDEA Energy Institute, Spain.

Fig. 1. (a) Schematic section of the solar reactor prototype. 1: Gas inlets; 2: Gas outlet; 3: Sample holder; 4: Quartz window; 5: Thermocouples ducts; 6: Alumina cavity; 7: Insulation; 8: Window water cooling circuit; and 9: Stainless steel housing;(b) Reactor placed on test bed.

The solar reactor consists of an alumina cavity surrounded by an insulating lining to reduce conduction heat losses. Concentrated solar radiation enters the cavity receiver through a water-cooled, transparent quartz window and 30 mm diameter aperture. Samples are horizontally placed at the middle of the cavity. K type thermocouples are used to measure temperature at the sample, gas, window and reactor walls. The flow pattern of the reactor can be approached to a plug flow [17]. Accordingly to that pattern, the oxygen delivered by the sample is evaluated from the carrier gas at the outlet [17]. More details about solar reactor and experimental setup have been described in [14,17].

2.2. Experimental procedure

The experimental samples consisted of a packed bed of reactant held into an alumina crucible (Al₂O₃; 99% purity; inner diameter, 20 mm; outer diameter, 30 mm; inner length, 18 mm; outer length, 23 mm). The crucible is perforated at the bottom to introduce the thermocouples. For some of the experimental cases, another sampler-holder was employed. This is a manually-fabricated crucible made of a soft material.
(enough for pricking the thermocouples) with 80% Al₂O₃-20% SiO₂. Its dimensions are inner diameter, 45 mm; outer diameter, 50 mm; inner length, 3.5 mm; outer length, 23 mm. Fig. 2 shows a photograph of both crucibles employed.

![Crucibles](image)

Fig. 2. Sample-holders employed for the experimental runs.

The starting chemicals are Mn₂O₃ powder 99 % purity and -325 meshes; Mn₃O₄ powder 97 % purity and -325 meshes from Sigma-Aldrich and CeO₂ powder 99.9 % purity from Acros. Samples were prepared by mixing the oxide powder with water in order to obtain a thick paste. The proportion oxide/water employed in each case is showed in Table 1.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Oxide (g)</th>
<th>Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₂O₃</td>
<td>1</td>
<td>0.25</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>CeO₂</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 1. Proportion oxide/water employed for preparing the samples.

The paste is introduced inside the sample holder and dried at 120 °C for 1 hour. As a result, particles form a consistent packed bed. The referenced temperature is measured by a K-type thermocouple that is centered in the sample through the hole at the bottom of the sample-holder (or through the wall in case of soft sample-holder) to ensure firm contact with the reactant. For some experiments, two or three thermocouples were placed at different depths.

Once the sample is inside the cavity and the reactor is closed, the reactor chamber is purged with argon. Gas flow rate is maintained constant with values of 9 l/min during the experimental run. The solar simulator is switched on to start heating the sample. Composition of the gas outlet and thermocouples and mass loss data are monitored and recorded. The radiation source is turned off once the oxygen concentration returns close to zero. Crystallographic phases in the solid products were identified by powder X-ray diffractometry (X-Pert, PANalytical B.V.)
3. Results

A 2 cm in diameter sample-holder was employed to carry out a first campaign of experimental reductions, by starting with Mn$_2$O$_3$, Mn$_3$O$_4$ and CeO$_2$ as examples of non-volatile metal oxides. Fig. 3 shows a typical oxygen release curve and temperature measurements for each type of oxide.

A common behaviour for all cases is the detection of a maximum peak of the oxygen production just immediately after starting radiation. Then, the production rate is gradually decreased. Different slopes have been identified for the drop of the oxygen releasing curve, mainly depending on the material features. Temperature measured at the sample is useful to provide a reference value at the middle of the packed bed. Additionally, in some experimental runs three thermocouples were distributed at
different depths in the sample, revealing temperature gradients of more than 500 °C in a length shorter than 2 cm. The low thermal conductivity of these metal oxides, typical of the ceramic materials, is reduced even more due to the porosity of the packed bed [18]. Thus, the reaction temperature at every point of the sample volume presents an uncertainty and cannot be employed to develop direct analytical kinetic studies as it has been done previously for volatile metal oxides [9, 19]. Reaction temperature under inert atmosphere for thermal reduction of Mn$_2$O$_3$ is established in the range of 900-1100 °C [20], while reduction of Mn$_3$O$_4$ is not observed until the reaction temperature exceeds 1400 °C. Reduction of cerium oxide to a non-stoichiometric species has been reported to occur at around 1600 °C [16], while the theoretical beginning of Ce$_2$O$_3$ production takes place at 2500 °C [15]. According to that, total conversion is achieved in case of Mn$_2$O$_3$ to Mn$_3$O$_4$ reduction, while only a fraction of the sample is reduced for Mn$_3$O$_4$ to MnO and CeO$_2$ reductions. Actually, MnO has been also found on the sample surface after reducing Mn$_2$O$_3$, although it has been proven that its presence has not an important contribution on the shape of oxygen evolution curve. Conversion for the reduction of a reactant “a” is defined as:

$$X_a = \frac{\int_0^t [O_2]}{2PM_a} \cdot \frac{m_a}{P_{M_{O_2}}}$$

(4)

As a reference, the evolution reaction is terminated when the oxygen concentration has dropped to 10 % of the maximum peak value. Therefore, a conversion of 35.1 % is obtained for the most favorable Mn$_3$O$_4$ reduction and only 8.6 % of the stoichiometric oxygen corresponding to the CeO$_2$ reduction into Ce$_2$O$_3$. The active area corresponds to the sample surface that is directly irradiated and those other regions of the packed bed that are able to achieve the reaction temperature while the duration of the experiment. However, the center and the bottom of the packed bed remain inactive because the maximum temperature reached is not enough, as it is showed in Fig. 3. It has been ascertained that the initial oxygen rise comes from the reduction of a specific area of the sample surface. There, the incident flux is high enough to allow the reactant particles to reach rapidly the reaction temperature. The heat flux is successively transferred to the rest of the sample where temperature is increased, although only in small areas it rises up the reaction temperature. According to this procedure, the sample was modified to increase the proportion of particles located at the surface in direct contact to the radiation. A new sample holder with larger diameter and smaller thickness is used keeping the packed bed total volume. The initial peak increases its amplitude and the total conversion for the Mn$_3$O$_4$ reduction is enhanced up to 41.7 %. However, this improvement does not take place in case of CeO$_2$ reduction. For CeO$_2$ experiments, the sample holder was placed at the focus of the solar simulator where the radiation power has the maximum concentration. Due to the fact that the spot area at this plane is smaller than the front surface of the first packed bed, an increment on the superficial active region is not observed in case of CeO$_2$, as demonstrated in Fig.4.

![Fig. 4. Reduced CeO$_2$ samples with different-diameter sample holder showing active areas of similar size.](image)
Fig. 5 shows an example of Mn$_3$O$_4$ reduction that was terminated after 250 seconds of heating. The chromatic change suggests that the reduction has partially occurred at indicated area. The shape and position of the active area match the map of irradiance distribution at the working plane. The oxygen evolution of that experiment shows a long and narrow peak as the initial one observed for longer experiments. After standard duration experiments it was found a mix of Mn$_3$O$_4$ and MnO at the sample surface (grey-green area) by XRD characterization (Fig. 6). As expected, Mn$_3$O$_4$ was only found at the middle and bottom of the sample corresponding to the regions remaining brown. XRD patterns are also presented for the product obtained from de Mn$_2$O$_3$ reduction and CeO$_2$ reduction. While the first one reveals total conversion even at the bottom of the sample, apparently, all patterns obtained for the cerium oxide samples, match only the reactant patterns. This might be explained assuming that all reduced product is re-oxidized as soon as it is in contact with the atmospheric oxygen. Regarding the reaction rate, it is important to note that it is influenced not only by the chemical process, but also by heat transfer and oxygen diffusion. Actually, all the evidences explained before support the hypothesis that heat transfer is the limiting factor in the oxygen release. A numerical model reproducing the sample thermal behavior is proposed as a necessary tool in order to distinguish the set of physical and chemical phenomena occurring during the experimental run and the influence of the material properties as well as the irradiance distribution and radiation power onto the sample surface.

**Fig. 5.** Comparison of the irradiance distribution map on the working plane with the surface of a sample of Mn$_3$O$_4$ after 250 s of thermal treatment. The shape of the highest irradiance area match the mark appeared on the sample surface with different color, due to the transformation into MnO.
Fig. 6. XRD pattern of some of the post-treated samples: (a) Sample of Mn$_3$O$_4$, top and center; (b) Sample of Mn$_2$O$_3$, top; (Sample of CeO$_2$, top)

4. Conclusions

Thermally activated reductions have been carried out in a solar reactor powered by a high flux solar simulator. Mn$_2$O$_3$, Mn$_3$O$_4$ and CeO$_2$ have been the initial reactants and all of them have showed a common behavior at the beginning of the thermal treatment, giving rise to an abrupt peak of delivered oxygen. It has been observed the main factor influencing the reaction rates is the irradiance distribution.
onto the sample surface and low thermal conductivity of the material. For Mn$_2$O$_3$ reduction, total conversion has been achieved. In case of Mn$_3$O$_4$ and CeO$_2$ reductions, only some areas of the sample became reduced, and they were those directly irradiated with higher flux.

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References


