

**STUDY OF THE HYDROGEN PRODUCTION STEP OF THE Mn_2O_3/MnO
THERMOCHEMICAL CYCLE**

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Abstract

In this work, a complete study of the second step of the $\text{Mn}_2\text{O}_3/\text{MnO}$ thermochemical cycle for solar hydrogen production has been performed. It includes a complete thermodynamic calculation of the equilibrium phases between MnO , NaOH and H_2 , which shows that the reaction takes place theoretically at temperatures above $75\text{ }^\circ\text{C}$. However, the experimental results demonstrate that it is necessary at least $450\text{ }^\circ\text{C}$ to achieve a satisfactory reaction rate. It indicates a dramatic influence of chemical kinetics and diffusion process, displacing the reaction to higher temperatures than those predicted by thermodynamics. The resultant solid of the reaction exhibits a phases distribution highly dependent on the temperature and the $\text{NaOH}:\text{MnO}$ ratio and this is of great influence in the overall rate of the process. The kinetic study shows that the overall process involves not only the chemical reaction between MnO and NaOH , but also a number of physical processes (heat and mass transfer) and solid phase transformations. The apparent activation energy calculated is a composite value determined by the activation energies of those elementary processes.

Keywords: Thermochemical water splitting, Hydrogen production, Manganese oxide, Thermodynamics, Kinetics

1. Introduction

The worldwide increasing energy demand and the need to reduce greenhouse gases emissions have promoted the study of alternative fuels and energy sources [1, 2]. As a promising energy carrier, hydrogen could be a solution to store and transport renewable energy in a chemical form, helping to solve the problem of some greenhouse gases emissions and releasing the world from the current fossil fuel dependence. However 95 % of hydrogen production is mainly derived from fossil fuels while only about 5 % is produced from renewable energy [1, 2]. It must be taken into account that only a massive hydrogen use is reasonable if renewable energy sources are used for its production. At this point the ideal process would be the water thermolysis driven by solar energy concentrated into a chemical reactor where the dissociation of water into H₂ and O₂ occurs. However the high temperature required to reach reasonable values of dissociation (above 4250 °C) and the need to separate H₂ and O₂ at high temperatures, to avoid recombination or explosive mixtures, have hindered the development of this process. For these reasons, water splitting by solar-driven thermochemical cycles that overcome those limitations represents a promising technology for this purpose [3].

The viability of a thermochemical cycle is based on different factors such as the number of reactions involved in the process, the required temperatures, the availability and cost of reactants, the corrosive power of the species involved in the process, etc. The most important features of a thermochemical cycle to be considered interesting are [4, 5]: i) $\Delta G_r = 0$ in a achievable range of temperatures; ii) minimum number of steps; iii) each step should be a fast reaction, without secondary reactions to avoid slow steps that slow the process down; and, iv) easily manageable intermediate species and minimum energetic requirement in any separation needed.

In recent years research has mainly focused on two-step metal oxide thermochemical cycles because of their simplicity and high efficiencies. However despite the advantages presented by these cycles, difficulties associated to the still high temperatures required for the process (1900-2200 °C) have diverted attention to other alternatives. Thus, new modified materials and operational conditions have been developed and proposed as alternatives for traditional two-steps cycles [5]. Besides that, thermochemical cycles based on more than two steps, which require lower temperatures, have been proposed attractive to be combined with

concentrated solar energy [3]. In these cycles the direct reduction of water with the reduced oxide is not thermodynamically possible so a better oxidizing compound such as NaOH or KOH must be used for hydrogen production. Then, the oxidizing species and the initial oxide are recovered by reaction of the mixed oxide obtained in the hydrogen production step with water at low temperatures.

Sturzenegger and Nüesch proposed in 1999 a manganese-oxide-based cycle for the production of solar hydrogen [6]. This cycle consists of three steps (reactions 1-3).



The influence of different variables and the kinetics of the high-temperature reduction of Mn_2O_3 to MnO have been previously studied in detail [7, 8]. However, the hydrogen production step has been studied less thoroughly. From a theoretical point of view, Charvin et al. [9] couldn't developed the thermodynamic study for hydrogen production from MnO and NaOH due to the lack of thermodynamic data for NaMnO_2 . Nevertheless they carried out the study for the production of hydrogen from Fe_3O_4 and NaOH and they saw that an excess of NaOH in the initial mixture (10 mol NaOH /1 mol Fe_3O_4) is enough to enhance the hydrogen production reaction, which is completed in the range of 100-1000 $^\circ\text{C}$.

Experimentally, Sturzenegger et al. [10] proposed that hydrogen production from MnO and NaOH could be completed within ca. 75 minutes at temperatures of ca. 700 $^\circ\text{C}$ under reduced pressure. Kreider et al. [11] observed a full conversion after 3 h using a nitrogen purge, but only 30 min were required under vacuum at 850 $^\circ\text{C}$. During those experiments vaporized sodium compounds reacted with the walls of the reactor (quartz or inconel metal alloy) and formed thermodynamically stable sodium silicate resulting in visible corrosion [9, 11].

For these reasons the aim of this work is to carry out a thermodynamic study of the hydrogen production step in order to get knowledge about the system behavior and be able to compare with experimental results since predictions from thermodynamic data can be obviously limited by kinetics. Optimal operation conditions of the second step of the manganese-oxide thermochemical cycle will be determined to overcome all the difficulties reported in the

literature (corrosion, high reaction times) and enhance and maximize the production of hydrogen.

2. Materials and methods

The hydrogen formation by reaction of MnO with NaOH was studied in a high temperature furnace as shown in Figure 1. A Pt/Rh (90/10) crucible, resistant to NaOH corrosion and temperatures above 1300 °C, was placed inside as support for the MnO/NaOH mixtures. Stoichiometric MnO/NaOH mixtures and also an excess of twice NaOH respect to the stoichiometry of reaction 2 were studied. The reactants were milled before the reactions to homogenize the reactant mixture. The temperature was increased up to 1300 °C with different heating rates, from 2 to 20 °C/min. The H₂ released from the reaction between MnO and NaOH was continuously removed with a purge of nitrogen (50 L/h). The gas flow from the reactor goes through a moisture trap in order to remove traces of condensed water that could interfere in the hydrogen detection. Then, part of the gas flow was released to the environment (Figure 1, purge) whereas the other part was conditioned to a proper pressure (Figure 1, pump and recirculation) for the analysis of the hydrogen in an Emerson Xstream analyser based on the thermal conductivity measurement principle and working at 50 °C. Since the hydrogen produced in the reaction is carried out from the reactor to the analyzer with a nitrogen flow of 50 L/h, the response of the analyzer is obtained as percentage of hydrogen in the flow with time. Integration of the graph obtained, taking into account the gas flow in the reactor (50 L/h plus the contribution of the hydrogen release during the reaction) and the simplification of the mixture as a perfect gas, allows the transformation of the response in total volume of hydrogen produced and the corresponding hydrogen mass. A standard gas mixture of 0.5% in H₂ was used for the calibration of the equipment. The resultant solid material obtained after the reaction was characterized by X-Ray diffractometry using a PW3040/00 X'Pert MPD/MRD equipment.

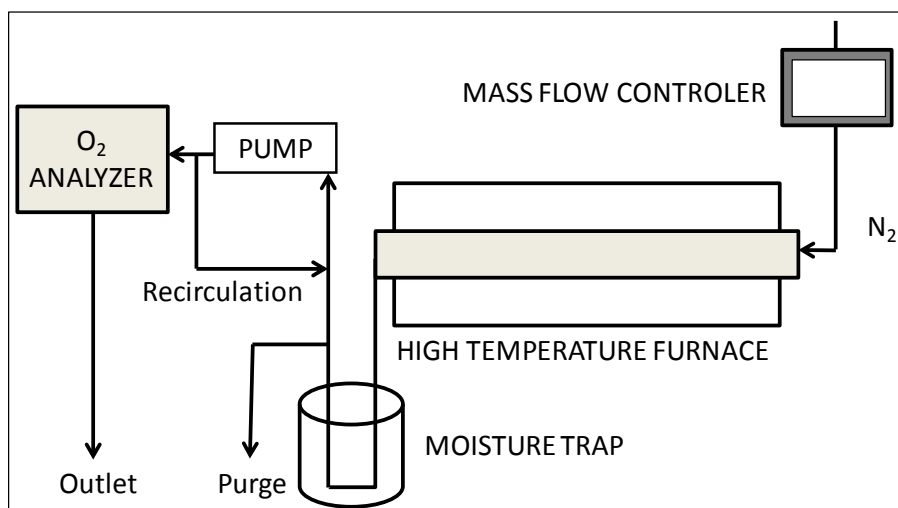


Figure 1. Schematic representation of the high temperature tubular furnace setup

3. Results and Discussion

3.1. Thermodynamic study

Some preliminary thermodynamic studies of the $\text{Mn}_2\text{O}_3/\text{MnO}$ thermochemical cycle have been already reported in the literature. However, the second step of hydrogen production has been hardly reported since thermodynamic data of the mixed oxides are not available [9]. Sturzenegger and Nuësch evaluated the thermodynamic feasibility of the cycle, concluding that the reaction between NaOH and MnO occurs at temperatures between 627 °C and 827 °C, being this range usually accepted in the reference literature [6]. Although the temperature is considerable lower than that required for the reduction of Mn_2O_3 (1300-1450 °C), problems of corrosion of the materials of the reactor derived from some of the gaseous compounds released during the reaction (Na_2O and NaOH) as has been reported previously [9].

In this work, a new thorough thermodynamic study of the process has been carried out following the method described elsewhere [7]. Equilibrium compositions as a function of temperature have been calculated following standard thermodynamic methods. Coefficients for the temperature dependence equation of specific heat at constant pressure (C_p) and values for the standard enthalpies of formation (ΔH_f°), standard entropies of formation (ΔS_f°), and the derived standard Gibbs energies of formation (ΔG_f°) of solids MnO and NaOH, liquid NaOH

and gaseous H₂ were obtained from the HSC6® database. The corresponding parameters for the NaMnO₂ were estimated by the calculation of the heat capacity at constant pressure and 25 °C for the NaMnO₂, using the Neumann-Kopp rule (NKR) for binary mixed oxides, following the procedure proposed by Bayón et al. [12]. After that, the parameters for the coefficients of the temperature dependence equation were obtained using the equations proposed by Kubaschewski and Ünal [13], applying a value of 1127 °C for the fusion temperature of the NaMnO₂. This temperature was selected by comparison with the analogous mixed metallic oxide NaFeO₂, due to the lack of data for the NaMnO₂ in the literature. From C_p data, calculus of ΔH_f^o was performed by a sensitivity analysis for the reaction between NaOH and MnO and taking into account that the value reported in literature for the enthalpy of the reaction at 900 K is -3 kJ/mol [6]. Finally, ΔS_f^o was evaluated from the value for the NaFeO₂, since the values of C_p obtained previously are very similar for both mixed metallic oxides. All the parameters are summarized in Table 1.

Table 1. Thermodynamic parameters for the chemicals involved in the hydrogen production with MnO and NaOH

Chemicals	Coefficients of the equation C _p (T) (J/mol·K) ^a				ΔH _f ^o (kJ/mol)	ΔG _f ^o (kJ/mol)	ΔS _f ^o (J/mol·K)
	A	B	C	D			
MnO	42.1	17.0	-2.4	-4.2	-385.2	-403.0	59.7
NaOH	90.5	-7.1	-1.1	0.4	-417.1	-439.6	75.5
H ₂	22.5	17.0	0.4	11.1	0.0	-39.0	130.7
NaMnO ₂	82.8	1.7	0.0	0.0	-770.7	-804.6	113.6

$$^a C_p = A + B \cdot (10^{-3}) \cdot T + C \cdot (10^5) \cdot T^{-2} + D \cdot (10^{-6}) \cdot T^2$$

The equilibrium constants (K_p) of the reactions at constant pressure as a function of temperature were calculated from the values of the Gibbs energy of reaction (ΔG_r), computed from ΔH_f^o and ΔS_f^o and the temperature dependence of the C_p of the species [7]. Figure 2 shows results of ΔG_r with the temperature for the generation of hydrogen by reaction of MnO and NaOH (reaction 2), confirming that the reaction could take place spontaneously for temperatures above 250 °C.

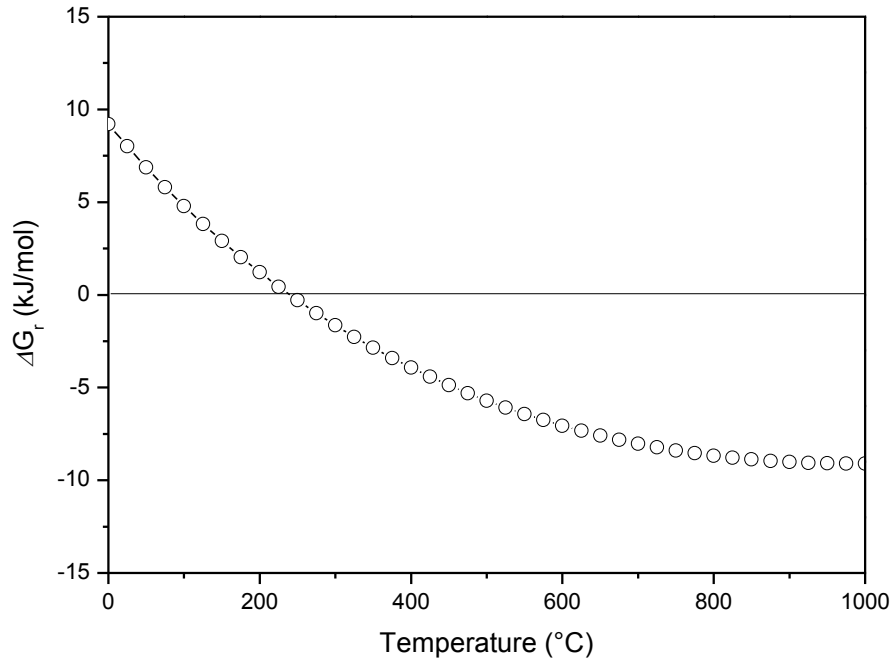


Figure 2. Gibbs free energy of the H₂ formation by reaction of MnO with NaOH

According to predicted equilibrium compositions (Figure 3), the reaction takes place completely between 50 and 175 °C, which is a much lower temperature range than that proposed experimentally in literature [6]. The reason is that those predictions establish the upper limit of conversion achievable at a certain temperature, but the results shown in Figure 3 correspond to thermodynamic equilibrium and it does not take into account if the temperatures allow suitable kinetics for the reaction.

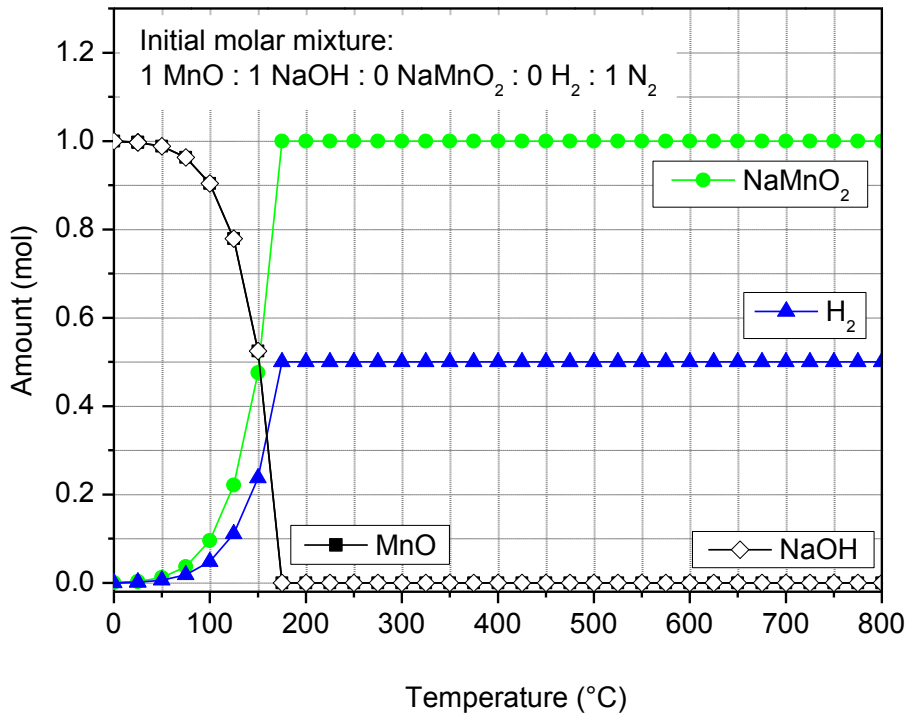


Figure 3. Influence of temperature on the thermodynamic equilibrium of the solid phases of the second step of the Mn₂O₃/MnO thermochemical cycle at 1 bar of total pressure and a ratio N₂/MnO of 1.

Equilibrium composition is strongly influenced by the operation variables. Figure 4 shows the influence of the total pressure on the process. It is clearly evident that the lower the pressure, the lower the required reaction temperature. Particularly, the required temperature for a 100 % conversion of MnO at 0.1 bar is 75 °C lower than that necessary at 1 bar. On the other hand a significant increase in that temperature up to values of ca. 375 °C is obtained at 10 bar. A similar behaviour has been reported in literature for the first step of the thermochemical cycle (Mn₂O₃ to MnO reduction) [7, 9], although the shift to higher temperatures at higher pressure was less significant than that for the hydrogen production. The reason is that both the stoichiometric coefficient and equilibrium constant of the hydrogen production are higher, so the reaction is more sensitive to the total pressure of the system.

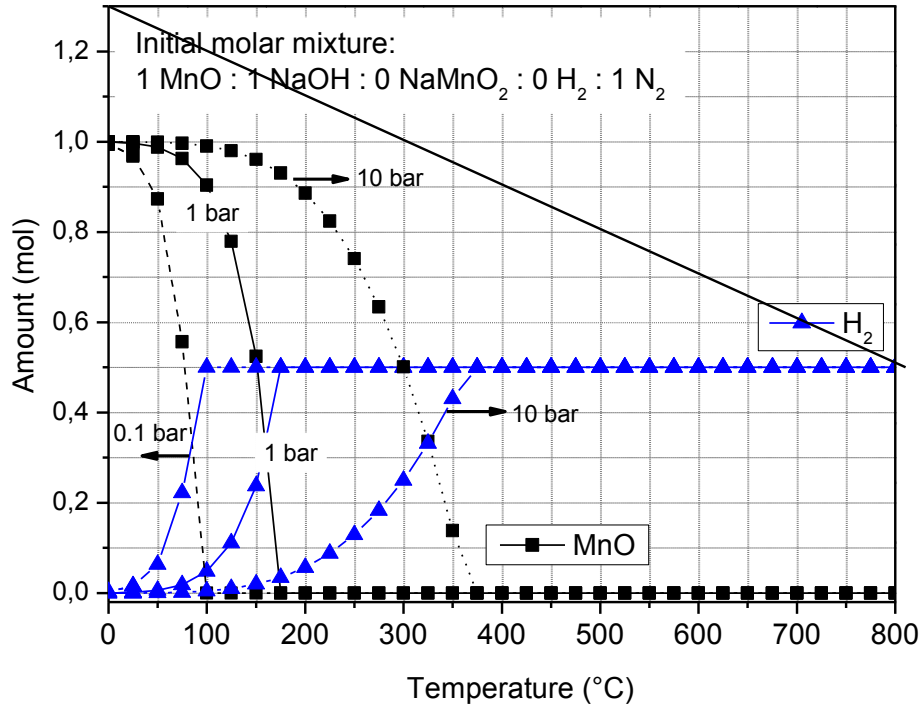


Figure 4. Effect of total pressure in the thermodynamic equilibrium of the solid phases of the second step of the Mn₂O₃/MnO thermochemical cycle at a ratio N₂/MnO of 1 (NaOH and NaMnO₂ not shown for clarity purposes).

The use of inert gas (commonly N₂ or Ar) is usually considered in the operation of thermochemical cycles as a carrier for the oxygen and the hydrogen generated in the first and second stage of the process, respectively. Thus the influence of the N₂/MnO molar ratio has been also studied by calculation of equilibrium composition corresponding to 1 mol of MnO and 1 mol of NaOH with 0.1, 1 and 10 mol of N₂, at 1 bar of total pressure (Figure 5). An increase of the inert gas/MnO molar ratio displaces the equilibrium ca. 50 °C to lower temperatures. On the contrary, a remarkable shift to higher temperatures (ca. 100 °C) is obtained lowering the N₂ proportion in the system. Nevertheless, the displacement to higher temperatures is less pronounced than that obtained by increasing the total pressure of the system (Figure 4). A similar behaviour has been reported in literature for the first step of the Mn₂O₃/MnO thermochemical cycle for hydrogen production [7]. According to this behaviour, in which a reduction of temperature is obtained by decreasing the pressure of the system or increasing the amount of inert gas, a technical and economical optimization considering both steps would be necessary to determine the combination of pressure and inert gas flow that

minimizes the total cost, considering the vacuum and energy requirements, and the production and recovery costs of the inert gas.

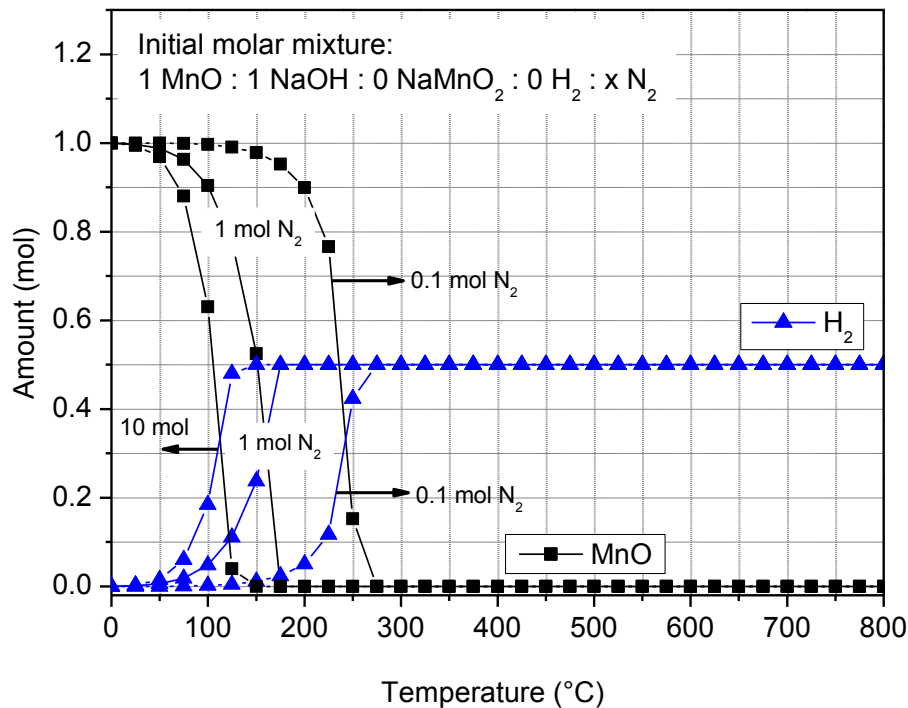


Figure 5. Influence of the gas/solid molar ratio in the thermodynamic equilibrium of the solid phases of the second step of the $\text{Mn}_2\text{O}_3/\text{MnO}$ thermochemical cycle at 1 bar of total pressure (NaOH and NaMnO_2 not shown for clarity purposes).

3.2. Validation of the thermodynamic calculations in an experimental high temperature furnace

Validation of the previous thermodynamic calculations has been carried out in a high temperature tubular furnace equipped with a hydrogen analyzer. According to previous studies regarding to the first step of the cycle [7, 8], the reaction has been carried out following a non-isothermal method by increasing the temperature with different heating rates up to $1300\text{ }^{\circ}\text{C}$ to ensure a complete conversion of solid reactants and the corresponding production of hydrogen. The results obtained are shown in Figure 6, in terms of hydrogen yield and MnO conversion (calculated from the amount of hydrogen produced respect to the theoretical for the initial MnO amount in the reaction). It can be observed that the reaction between MnO and NaOH starts around $400\text{ }^{\circ}\text{C}$ and it finishes at temperatures between $650\text{ }^{\circ}\text{C}$ and $1150\text{ }^{\circ}\text{C}$ depending on the heating rate. The higher the heating rate the shorter the time to carry out the reaction, being the total reaction time to reach $1300\text{ }^{\circ}\text{C}$ from initial $40\text{ }^{\circ}\text{C}$ of 630,

252, 126 and 63 min for heating rates from 2 to 20 °C/min. As it can be noticed, the experimental results are shifted to higher temperatures in comparison with the theoretical equilibrium. The increase in the experimental temperature required for the reaction can be related to the kinetics limitations that usually appear in solid-state reactions.

Surprisingly, the maximum conversion of MnO achieved was 85 %, with independency of the heating rate. Since stoichiometry of reaction 2 is 1:1 and the MnO is totally consumed but only a 85% of the theoretical hydrogen production is obtained, a loss of ca. 15% of NaOH can be estimated. A similar behaviour has been reported by Kreider et al. [11] in experiments performed at 850 °C, showing 1 total sodium loss of ca. 30 % under vacuum conditions (and below that value with a purge gas). Since NaOH is liquid from ca. 320 °C and the boiling point is around 1390 °C, it has a small, but not negligible, vapour pressure under the selected conditions. Consequently, losses of NaOH limit the total conversion of MnO when a stoichiometric amount of NaOH is used. Additionally, NaOH is a highly hygroscopic chemical, so the theoretical mass introduced in the reactor could be slight lower than the corresponding to stoichiometric MnO/NaOH ratio due to the presence of water in its structure.

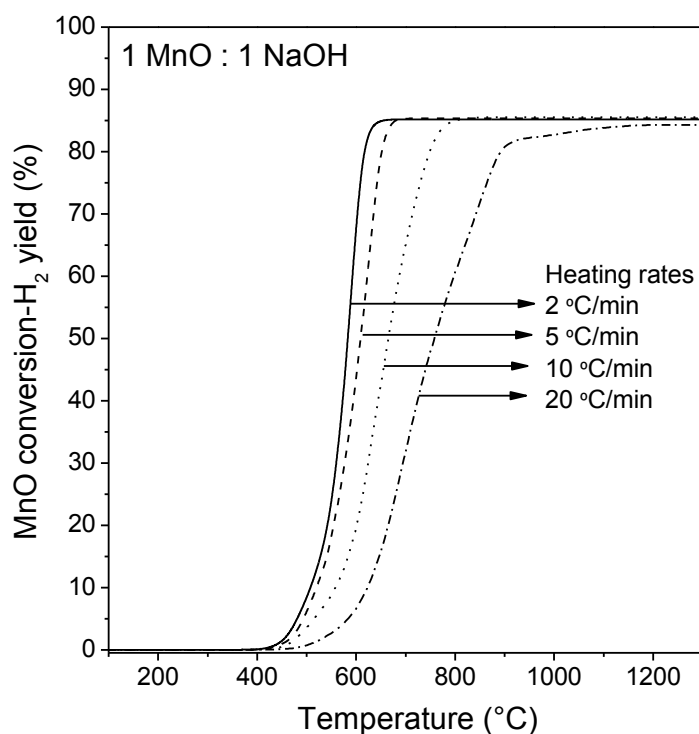


Figure 6. H₂ release as a function of the temperature for a mixture of 1 mol MnO : 1 mol NaOH (1 g and 0.6 g, respectively) at different heating rates.

In order to overcome the limitation in the maximum MnO conversion, experiments with an excess of NaOH (2 mol of NaOH per mol of MnO; 1.2 g and 1 g, respectively) were carried out. The comparison of the performance with both MnO/NaOH ratios for heating rates of 2 to 20 °C/min is shown in Figure 7 (straight and dot lines).

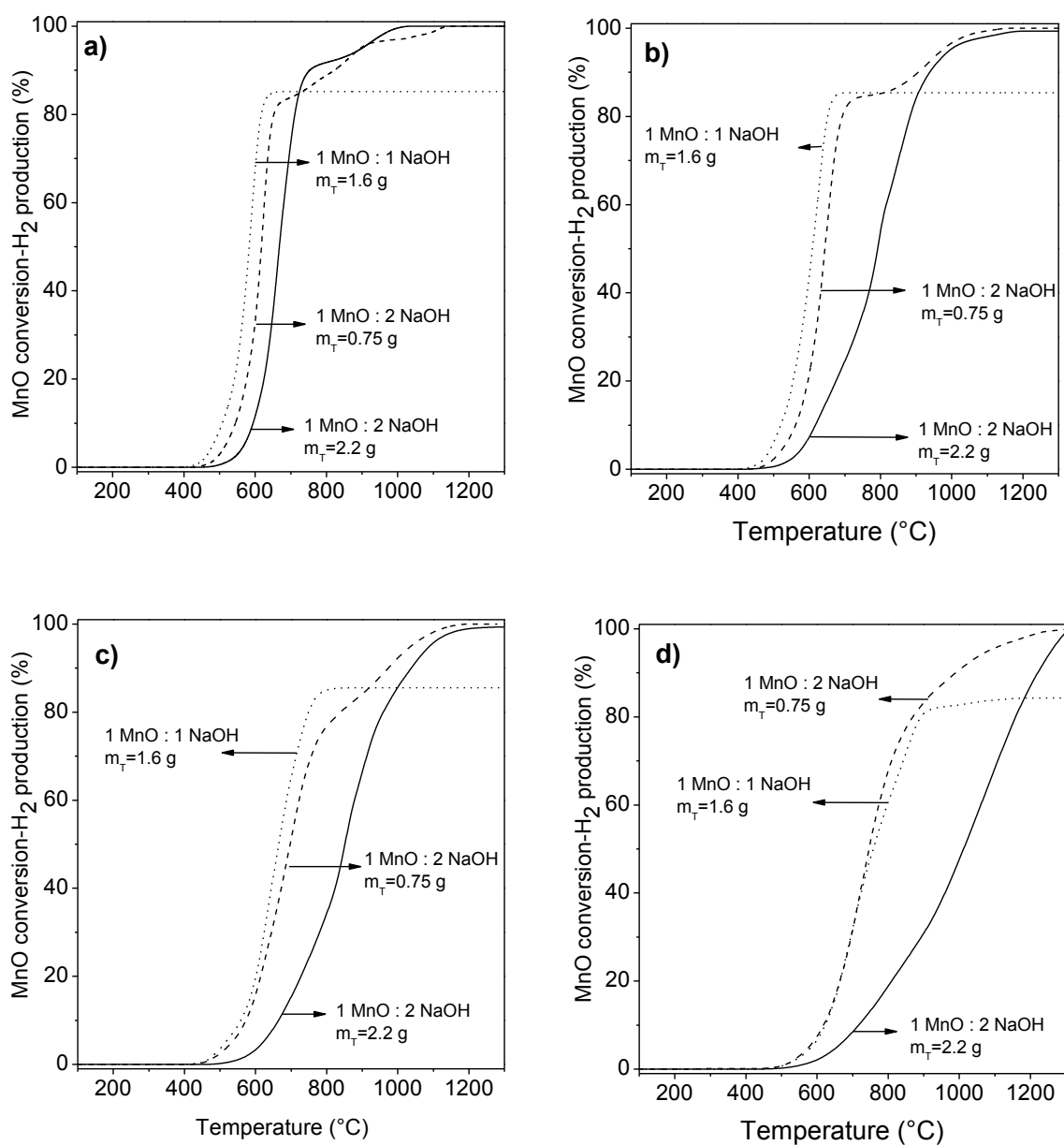


Figure 7. Hydrogen production with mixtures with MnO : NaOH ratios of 1 : 1 and 1 : 2 and different total mass. Heating rates: a) 2 °C/min, b) 5 °C/min, c) 10 °C/min, and d) 20 °C/min.

First of all, it must be noticed that when the experiment is performed with an excess of NaOH the release of hydrogen reaches the value corresponding to a 100 % of MnO conversion. However, the reaction rate seems to be slower than the one for the stoichiometric proportion process, showing a shift of ca. 200 °C in the final temperature required for full conversion at all the heating rates tested in this study. It should be remarked that an increase in the NaOH:MnO ratio produces an increase in the total mass of the initial solid. The slower reaction rate with the mixture 1:2 and 2.2 g of total mass as compared to the ratio 1:1 and total mass of 1.6 g could be related to the influence of both mass and heat transfer in the process. Thus, at increasing heating rates in the furnace, the actual temperature inside the MnO/NaOH bed is increasingly lower than the theoretical one. However, in the tubular furnace with 1.6 g, in which a thinner layer of particles is formed in the crucible, the effect of the heat transfer could be of lower influence. Additionally, taking into account that NaOH melts at a temperature of ca. 320 °C, a remarkable increase in the restrictions for the hydrogen diffusion can be considered in that case. Thus, the resultant reaction rate is actually controlled by diffusion phenomena instead of the chemical reaction kinetics.

In order to rule out the effect of mass and heat transfer, further experiments were performed using a mixture with a MnO:NaOH ratio of 1:2 but lowering the total mass of solid in the reactor to 0.75 g. According to previous experiences, this mass of solid allows a really thin layer of particles close to a monolayer in the bottom part of the crucible used as support inside the reactor. The results obtained demonstrated the great influence of the physical phenomena mentioned previously, that could be minimized by decreasing the total mass in the system (Figure 7, dash lines). Additionally, a decrease in the slope of the curves in Figure 7, related to a decrease in the reaction rate, was obtained at increasing heating rates (10 and 20 °C/min). It could be also related to influence of heat transfer under those conditions, as well as changes in phases composition of the resultant solid with temperature. Actually, the MnO/NaOH ratio has a critical influence in the phases equilibrium of the resultant Na-Mn-O system. It has been reported a number of phases for $\text{Na}_x\text{-MnO}_{(2-\delta)}$ ($x = 0.4, 0.5, 0.6, 0.7, 1.0$; $\delta = 0-0.3$) in literature, depending on the sodium content and reaction temperature during the synthesis of the Na-Mn-O system [14]. Bayón et al. [12] confirmed that the reaction of MnO and NaOH in the range of 600-700 °C produces mainly $\text{Na}_{0.70}\text{MnO}_{2.05}$, and $\text{Na}_{0.55}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$, whereas at higher temperatures, the predominant phase is $\text{Na}_{0.70}\text{MnO}_{2.0}$. Figure 8 shows the XRD of the solid resultant in reactions with different MnO:NaOH molar ratios (Figures 8a and b) and in

reactions stopped at 600 °C and 800 °C with a heating rate of 2 °C/min and MnO:OH ratios of 1:2 (Figure 8c).

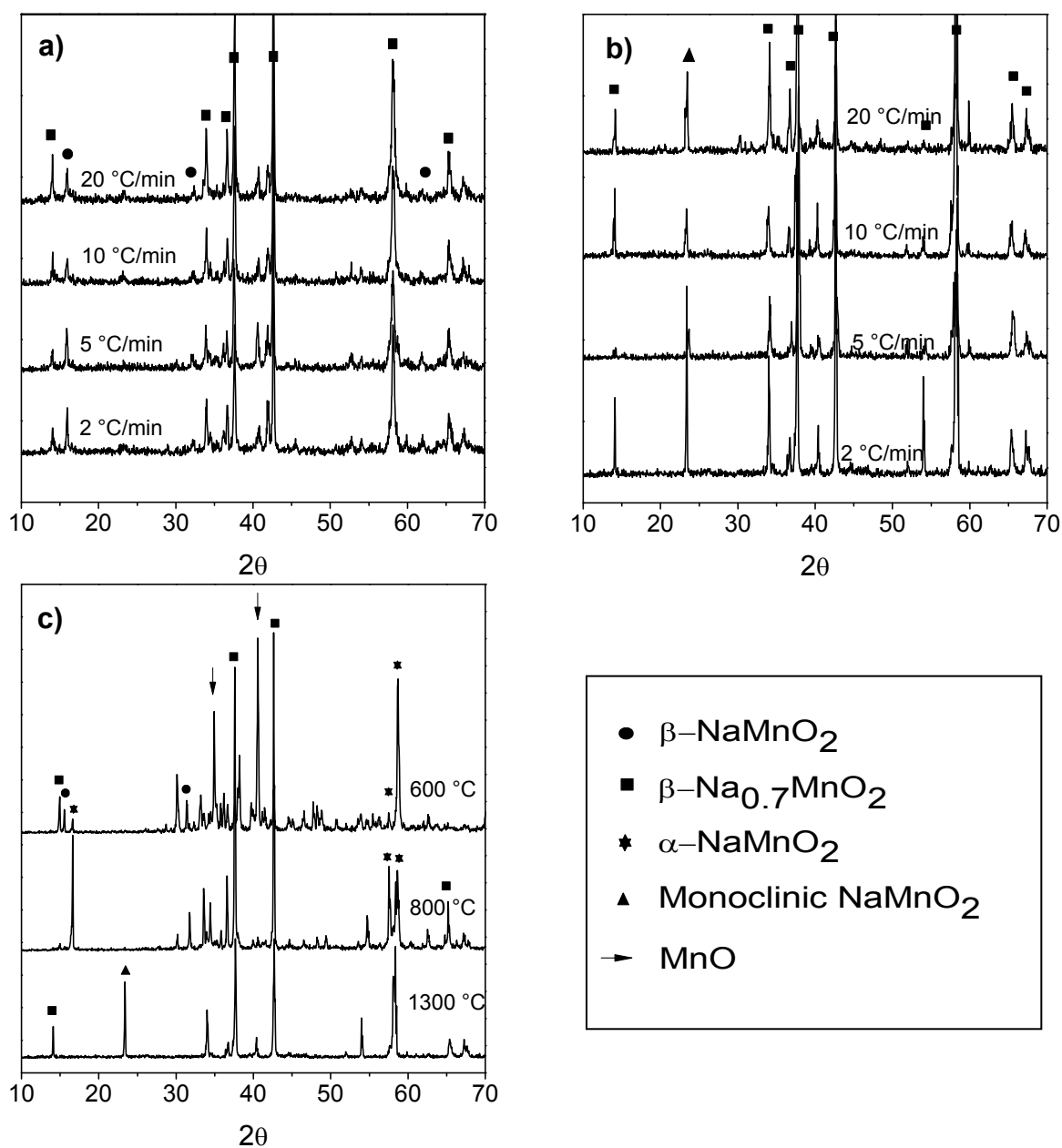


Figure 8. XRD patterns for the solid resultant in the reaction of MnO and NaOH; a) MnO:NaOH=1:1, b) MnO:NaOH=1:2, and c) at 2 °C/min and reactions performed at 600, 800 and 1300 °C and MnO:NaOH=1:2.

A remarkable shift of phases from β -NaMnO₂ and β -Na_{0.7}MnO₂ to α -NaMnO₂ and monoclinic NaMnO₂ is obtained by increasing the proportion of NaOH in the initial solid mixture. The

formation of the monoclinic NaMnO_2 occurs at temperatures higher than $800\text{ }^\circ\text{C}$ (Figure 8 c). Finally the formation of the $\alpha\text{-NaMnO}_2$ is clearly evident at $800\text{ }^\circ\text{C}$, although it is transformed to other phases at higher temperatures. In any case, XRD results confirm the complete disappearance of MnO , by the full conversion of the reaction.

3.3. Kinetic study of the reaction between MnO and NaOH for hydrogen production

In a previous work, the authors reported the combination of isoconversional methods for the estimation of realistic activation energy (E_a) values and a multivariate nonlinear regression procedure for the determination of the best kinetic model and pre-exponential factor of the reactions involved in the reduction of Mn_2O_3 to MnO , the first step of the $\text{Mn}_2\text{O}_3/\text{MnO}$ thermochemical cycle [8]. The results of amount of hydrogen release as a function of the corresponding temperature to the conversion of the MnO and the same method can be used for the determination of the kinetic parameters of the reaction of MnO with NaOH . The first part of the method involves the evaluation of E_a . It should be remarked that different values of the E_a can be estimated for each value of conversion (α) [15, 16], being the dependence of α on E_a characteristic of the elementary processes occurring in the system. Among the different isoconversional procedures reported in the literature, Ozawa [17] and Friedman [18] methods have been proposed for the calculation of E_a of solid reactions at high temperatures. Figure 9 shows the values calculated for E_a at incremental values of 0.5% for α using the method proposed by Ozawa [17].

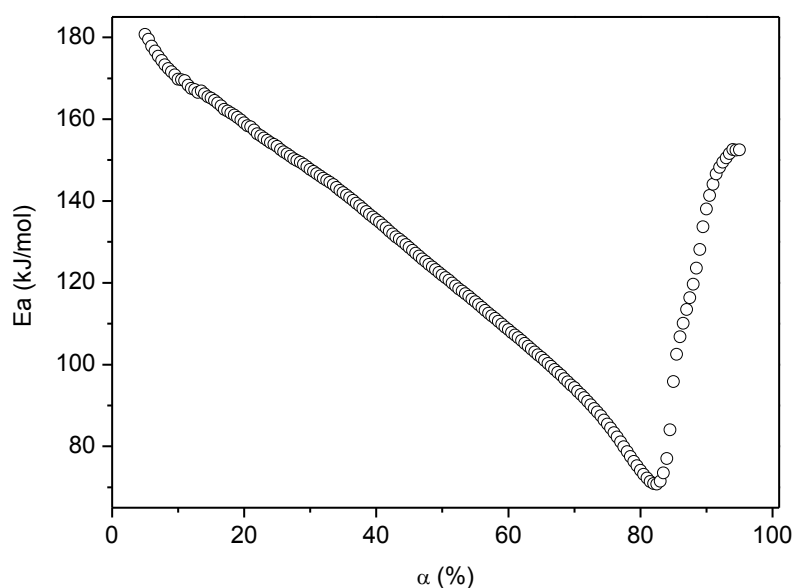


Figure 9. Influence of the conversion in the activation energy calculated by the method proposed by Ozawa [17].

It is clearly evident the great dependence of the apparent activation energy and the conversion. Thus, for α rising up to 80 % a decrease in E_a from 180 to 70 kJ/mol is clearly obtained, whereas from α of 80 %, a quick increase in that kinetic parameter reaching values of ca. 160 kJ/mol was obtained. Although the shape of the dependence of the E_a on α does not unequivocally identify the kinetic scheme of a process, the behavior shown in Figure 9 for α up to 80 % has been reported in solid state reactions influenced by diffusion phenomena [15, 19]. Thus, it could be associated with the reaction of NaOH and MnO which could be influenced with intra-particle diffusion and heat transfer processes due to the non isothermal reaction performed. On the other hand, a second process takes relevance for α higher than 80 %, being reported in literature a similar increasing dependence of the E_a on conversion for processes involving competing or consecutive reactions. This fact could be consequent with the solid phase transitions occurring at high temperatures and discussed previously.

Summarizing, the hydrogen production following the manganese oxide thermochemical cycle involves a chemical reaction between MnO and NaOH, a number of physical processes (heat and mass transfer) and solid phase transformations. Thus, the E_a is a composite value determined by the activation energies of those elementary processes. Nevertheless, averaged kinetic parameters and model for the overall process can be calculated by simultaneous fitting of MnO conversion vs. T curves obtained under different heating rates by a nonlinear programming formulation that minimizes the sum of quadratic residuals using a sequential quadratic programming method [8]. Among the different models with different mechanistic assumptions proposed in literature for solid-state reactions [20], the best fit was obtained for the first-order model, F_1 (Figure 10), in which the overall reaction rate is proportional to the remaining fraction of reactant [21]. Values of 130 kJ/mol and 4.43 min^{-1} were obtained for averaged parameters E_a and $\log A$, respectively. It is clearly evident that even the best fitting shown in Figure 10 exhibits a great difference between experimental and calculated data for heating rates of 10 and 20 °C/min. It is related to the physical processes, mainly the heat transfer rate, which is of critical influence especially at higher heating rates. Additionally, a remarkable shift between experimental and calculated data is obtained for lower heating rates when reaction reaches a α higher than 80 %. According to the results shown in Figure 9, the dependence of the E_a on conversion changes dramatically for values higher than 80 %, in

which the presence of competitive reactions between solid phase transitions, as well as the MnO / NaOH reaction could be governing the overall process rate.

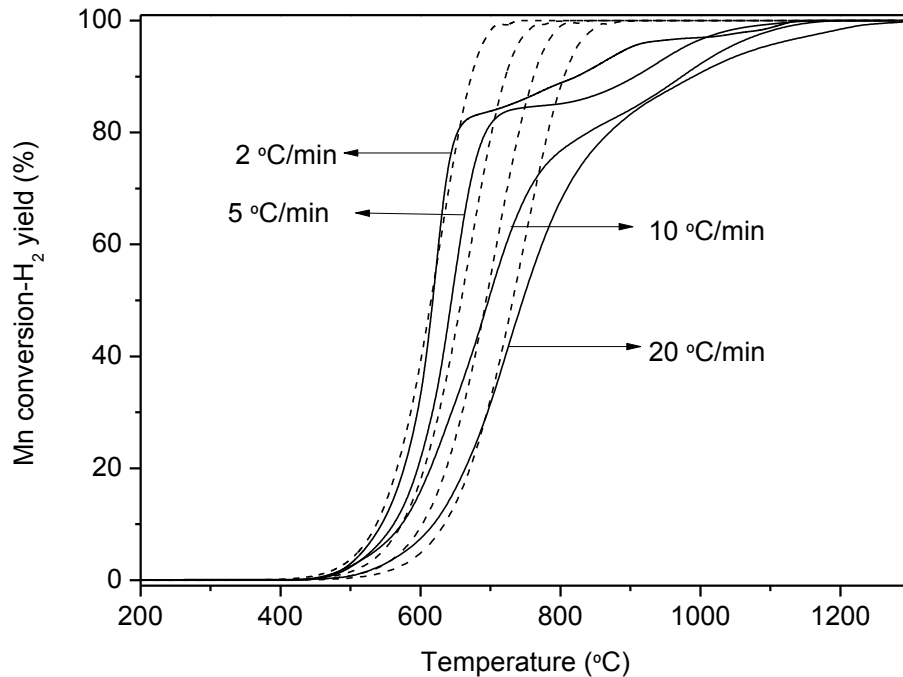


Figure 10. Experimental (straight lines) and calculated (dash lines) values for the hydrogen production reaction with mixtures with a MnO : NaOH ratio of 1 : 2 and a total mass of 0.75 g, according to first order model F_1

4. Conclusions

According to the thermodynamic study, the hydrogen production step of the Mn_2O_3/MnO thermochemical cycle can be completely finished at 175 °C, starting from 50 °C, at 1 bar of total pressure and N_2/MnO ratio of 1. Thermodynamic studies reveal a critical influence of the gas/solid ratio and pressure of the gas in the equilibrium of the second step of the thermochemical cycle. Thus, the higher the pressure of the system the higher the temperature needed to complete the reaction, whereas higher N_2/MnO ratios shift the system to lower temperatures. Experimental results in the tubular furnace have shown that the reaction starts above 400 °C and it finishes at temperatures between 650 and 1150 °C depending on the heating rate. Moreover, it is necessary to work with a NaOH excess to reach 100 % of MnO conversion in the hydrogen production since NaOH is partially vaporized during the process. However this over-stoichiometric ratio slows down the process not only because of diffusion

and heat transfer phenomena but also because of changes in the solid phase during the process. Finally, the kinetic study reveals a strong dependence of the E_a and α , which is related to the presence of diffusion phenomena and the presence of competitive reactions such as Na-Mn-O solid phase transformations. A first order reaction model with values of 130 kJ/mol and 4.43 min^{-1} for the averaged apparent kinetic parameters E_a and $\log A$, respectively, can be used for a partial description of the process, especially at low heating rates. However, this model cannot describe the mechanism governing the final part of the reaction when α reaches values higher than 80 %.

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