Development of a high-pressure thermobalance working under constant rate thermal analysis

Antonio Perejón[1,2], Pedro E. Sánchez-Jiménez[1], José Manuel Criado[1], Luis A. Pérez-Maqueda[1]

[1]Instituto de Ciencia de Materiales de Sevilla (C.S.I.C.-Universidad de Sevilla). C. Américo Vespucio 49, Sevilla 41092, Spain.
[2]Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, Sevilla. 41071, Spain.

Abstract

A thermogravimetric instrument that works at high pressure of different gases has been designed and assembled. The instrument has been devised to work in a temperature range from room temperature to 1000 ºC in various controlled pressures of selected gas up to 15 bar, and under conventional rising temperature and Constant Rate Thermal Analysis (CRTA) modes. CRTA method allows an intelligent control of the reaction temperature using a feedback system that monitors the mass gain or mass loss of the sample in such a way that the reaction rate is maintained constant all over the process at a preselected value. CRTA method provides a significant advantage for studying processes under high pressure as it reduces heat and mass transfer phenomena that are very relevant under these high-pressure experimental conditions. The thermal oxidation of Ni at 8 bar of pure oxygen has been used for testing the performance of the instrument under both linear heating rate and CRTA conditions.

Keywords: constant rate thermal analysis; thermogravimetry; high-pressure; thermal oxidation; nickel

1. Introduction

Gas pressure is a key parameter in the kinetics and thermodynamics of gas-solid processes. Experiments under high gas pressure allow obtaining information under realistic conditions of application, separating overlapping thermal events, or accelerating the processes.[1-5] Nevertheless, the acceleration induced by the gas pressure might produce significant heat and mass transfer gradients and, therefore, the experimental results might not be representative of the process.[6-9] Additionally, if the amount of heat released or absorbed by a reaction is significant, it could cause significant self-heating of self-cooling of the sample, especially if the process takes place over a short period of time. Taking into consideration all these limitations, obtaining reliable experimental data for performing kinetic or thermodynamic analysis under high gas pressure is quite challenging for many processes. Conventional studies are based on either heating the sample under controlled linear heating rate conditions or increasing sharply the temperature up to a selected value and maintaining it constant during the entire experiment (isothermal conditions). Combinations of linear heating and isothermal steps are also quite common. Nevertheless, in all these cases, the sample temperature is controlled according to the preset program while the mass gain or mass loss of the sample is monitored as a function of temperature and time. A much less conventional approach is using a signal related to the process for determining the temperature profile in a sample controlled thermal analysis (SCTA) fashion.[10-15] This type of smart program is based on a feedback method that uses a signal related to the evolution of a process for controlling the sample temperature.[12, 16-18] The most common SCTA method is constant rate thermal analysis (CRTA), in which the reaction rate of the process is maintained at a programed constant value all over the process. Advantages of CRTA for studying gas-solid reactions have been stressed in literature. [18-23] Thus, CRTA minimizes heat and mass transfer phenomena, improves the discrimination of the kinetic model followed by solid-state reactions as compared with conventional linear heating rate method, and provides better discrimination for overlapping processes.[24-28]

In this work, a thermogravimetric instrument that works at high gas pressure has been designed and assembled. The instrument works under conventional rising temperature and Constant Rate Thermal Analysis (CRTA). The CRTA method has been implemented in the thermobalance by means of a feedback control system that uses the thermogravimetric (TG) integral signal for controlling the sample temperature. The instrument performance has been tested with the oxidation of Ni under 8 bar of pure oxygen.

2. Instrumental setup

A microbalance (Gravimetric Sensor Type 202, Scientech, USA) equipped with an analogical output of TG signal was used for assembling the instrument, which is capable of measuring masses up to 35 g with a precision of 0.01 mg. Figure 1 shows the configuration of the microbalance and sample holder. For the measurements at high pressure, the microbalance was placed in a cylindrical aluminum housing sealed with a viton O-ring. An open KF-40 flange was used for the top of the microbalance housing to introduce the sample holder. An alumina rod (260 mm in length and 3 mm in diameter) was used as the sample holder and loaded on the microbalance. The sample crucible (16 mm in inner diameter and 30 mm in depth) was placed on the top end of the sample holder. The sample holder was surrounded by an alumina tube (11 mm in inner diameter, 2 mm in thickness, and 250 mm in length) for improving the stability of the TG signal.

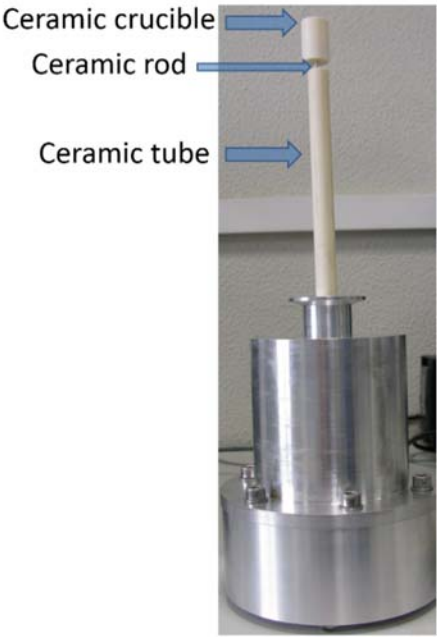

Figure 1. Microbalance covered by the cylindrical aluminum enclosure, with the sample holder attached and the aluminum crucible.

Figure 2 shows a picture of the overall instrumental setup. The system becomes hermetically closed after attaching the reactor in the KF-flange, what permits to control the pressure and the flow rate of any inert or reactive gas through the sample. A wall feedthrough inserted in the cylindrical aluminum enclosure connects electrically the microbalance to the control unit (Figure 2).

The reactor is a cylindrical stainless steel chamber (Figure 2), that withstands the high pressure required to perform the experiments. Inside the reactor, a homemade furnace consisted of an electrical nickel-chrome resistance surrounding a quartz tube, is inserted. The resistance is fixed to the quartz tube by means of a ceramic cement. The furnace is thermally isolated by means of alumina fiber placed between the furnace and the metallic wall of the reactor to prevent the wall of the metallic reactor from reaching high temperatures; in fact, it remained below 80ºC during all the tests performed with the instrument. Moreover, this furnace arrangement allows a fast and precise control of the sample temperature, as required for a proper CRTA control.

An electrical feedthrough in the stainless steel chamber connects the resistance to the control system. The temperature of the furnace is controlled by placing a thermocouple underneath the sample crucible, which also serves for measuring the temperature of the sample. The recirculation of the flowing gases through the system is achieved by two wall feedthroughs, inserted in the reactor chamber and the aluminum enclosure of the balance, which serve as gas inlet and gas outlet, respectively (Figure 2). The system is directly connected to a gas cylinder and the pressure is selected in the gas cylinder pressure regulator. The gas outlet is connected to a rotameter with an integrated needle valve for the adjustment of the flow through the reactor during the experiments.

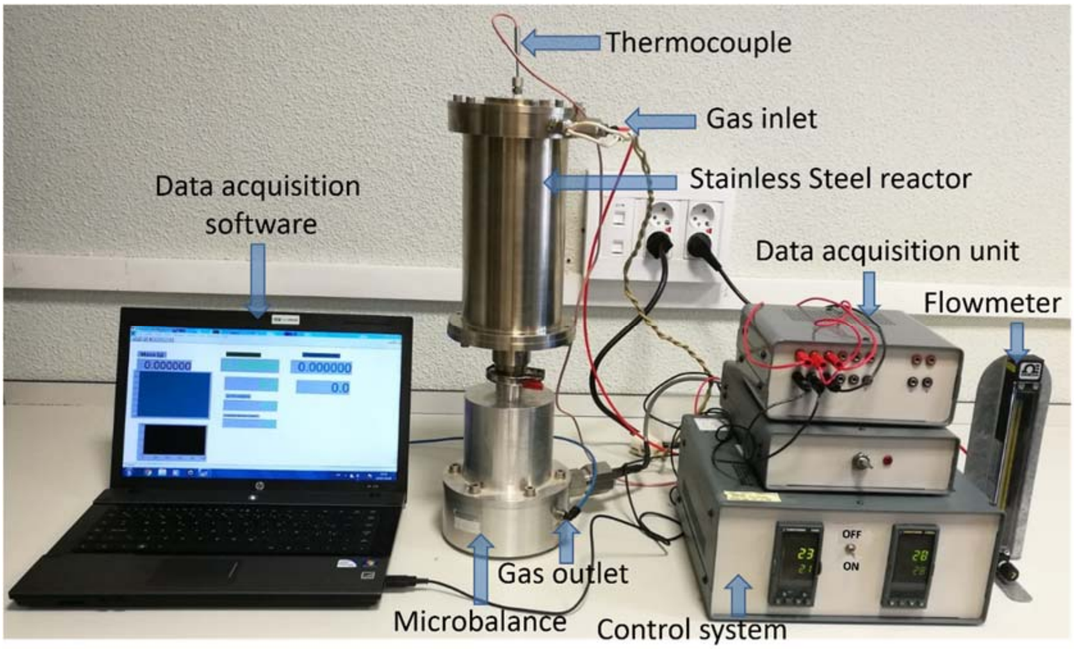

Figure 2. High-pressure setup.

This design permits controlling the temperature and pressure under isothermal and linear heating rate conditions from room temperature up to 1000ºC, and working at pressures up to 15 bar. Moreover, a control of the temperature at a desired Constant Reaction Rate is attained by means of two Eurotherm programmers/controllers.[29, 30] A diagram of the control system is shown in Figure 3. The temperature programmer measures the analog signal of the thermocouple and commands the temperature under isothermal or linear heating/cooling conditions. The thermogravimetric-signal controller measures and programs the analog signal of the mass from the microbalance.

Both programmers are needed for working under CRTA conditions, since one programmer by its self is not able to control the temperature in such a way that the mass signal provided by the microbalance follows a preset linear trend as a function of time (i.e., a preset constant reaction rate). This is because the proportional integral differential (PDI) control used by the programmers needs a reversible control parameter (the mass in this case), whose values depend on the parameter that is controlled (the temperature in this case). This condition cannot be satisfied by an integral signal such as the mass, which is not always reversible. For instance, for a mass gain experiment the mass increase recorded at a certain temperature during the reaction cannot be reversed by decreasing the temperature. For this reason, the reaction rate is controlled by connecting the control relay of the thermogravimetric-signal controller to the digital input of the temperature programmer (Figure 3). Thus, a command in the digital input of the temperature programmer moves the temperature from a preset heating rate when the mass control relay is closed, to a preset cooling rate when the mass control relay is open, as described elsewhere.[29, 30]

This control system allows increasing the temperature if the mass gain value is lower than the programmed mass gain at a time t, and decreasing the temperature if the mass gain value is higher than the programmed mass gain. In the case of an experiment where a mass decrease takes place, such as for example in a thermal decomposition of a solid, a reverse program should be used.

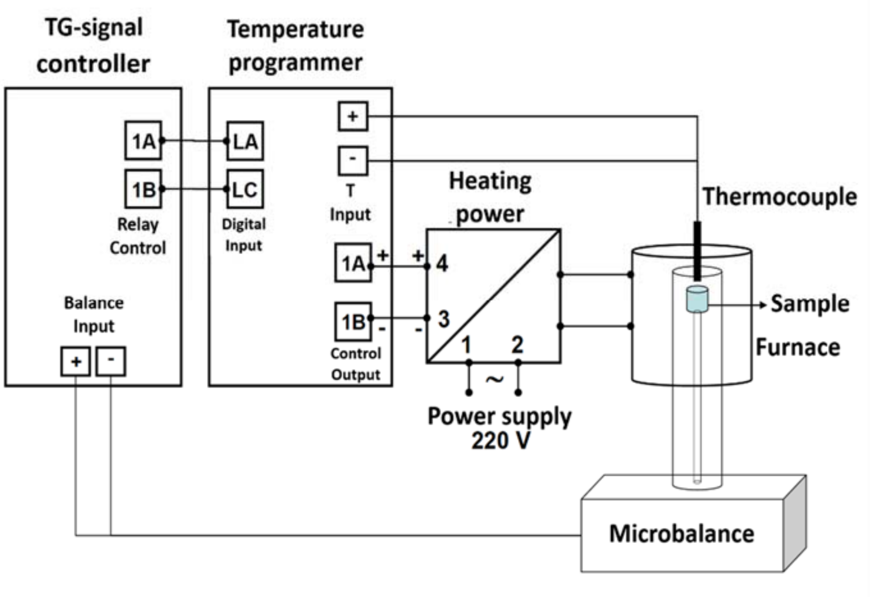

Figure 3. Scheme of the control system used to perform the experiments under constant rate thermal analysis. The temperature of the process is controlled using the input supplied by the microbalance.

The mass calibration of the system was performed using a set of calibration masses, ranging from 1 mg to 30 g. Calcium oxalate decomposition reaction was used to calibrate the temperature of the high-pressure setup. The three mass loss stages of this standard served to define three points of calibration. Buoyancy effects were corrected by registering blank curves using alumina powder as a standard.

3. Experimental

Nickel powder was purchased from Sigma-Aldrich, St. Louis, MO, USA (product number 266981-500G). The mass employed for the linear heating rate and CRTA experiments was about 52 mg.

X-Ray diffractograms were registered in a PANanlytical X’Pert PRO diffractometer working at 45 kV and 40 mA. The instrument uses a CuKα radiation, an X'Celerator detector and a graphite diffracted beam monochromator

4. Results and discussion

The performance of the high-pressure thermobalance was tested with the thermal oxidation of nickel under a high pressure of pure oxygen, which takes place according to the following reaction:

$$Ni + \frac{1}{2}O_2 \;\rightarrow\; NiO$$

Two experiments were carried out, under 8 bar of oxygen with a flow of 100 cm^3 min^{-1}: conventional linear heating rate at 5 ºC min^{-1} and constant rate thermal analysis. Figure 4 shows the evolution of the mass, the mass gain rate and temperature as a function of time for both tests.

A precise control of the temperature was achieved in the system for the experiment performed at 5 ºC min^{-1} (Figure 4a), with the thermocouple placed near the sample crucible, as can be seen in the temperature-time profile. The mass increases from low temperatures, indicating that the oxidation starts from the beginning of the heating process up to 740 ºC, where the process finishes. The total mass% increase is in agreement with the stoichiometric value for the oxidation of Ni to NiO. Moreover, the mass%-time curve presents a sigmoidal shape, which is characteristic of experiments carried out under linear conventional rising temperature conditions. The reaction rate curve (dotted line) indicates that the mass gain rate is low up to 340 ºC, which corresponds to the first 60 min of the test. From this temperature, a rapid mass gain, with a maximum reaction rate of 0.6 mg min^{-1} at 550 ºC, is recorded.

Figure 4b presents the experiment performed under CRTA conditions. The reaction rate was set at 7.5 × 10^{-2} mg min^{-1}, taking into account the mass increase corresponding to the full oxidation of nickel (~27.3%) and that the starting mass was 52 mg. The process rate was controlled employing heating and cooling rates of 5 ºC min^{-1}. The temperature of the process was linearly increased by the system at 5 ºC min^{-1} from room temperature up to 270 ºC. From this temperature, the control of the reaction rate started, which can be noticed first in a decrease of the heating rate. Thus, the system maintains constant the reaction rate by automatically controlling the temperature during the entire process, as can be seen in Figure 4b that shows how the mass gain% describes a linear increase with time while the d(mass%)/dt is maintained constant in the preselected value. It may be seen that the reaction rate at the final part of the reaction is controlled by linearly increasing the temperature at the selected maximum heating rate (5 ºC min^{-1}).

It should be highlighted that the reaction rate has been precisely controlled during the entire experiment working at a constant pressure of 8 bar of oxygen, and up to a temperature of 700 ºC.

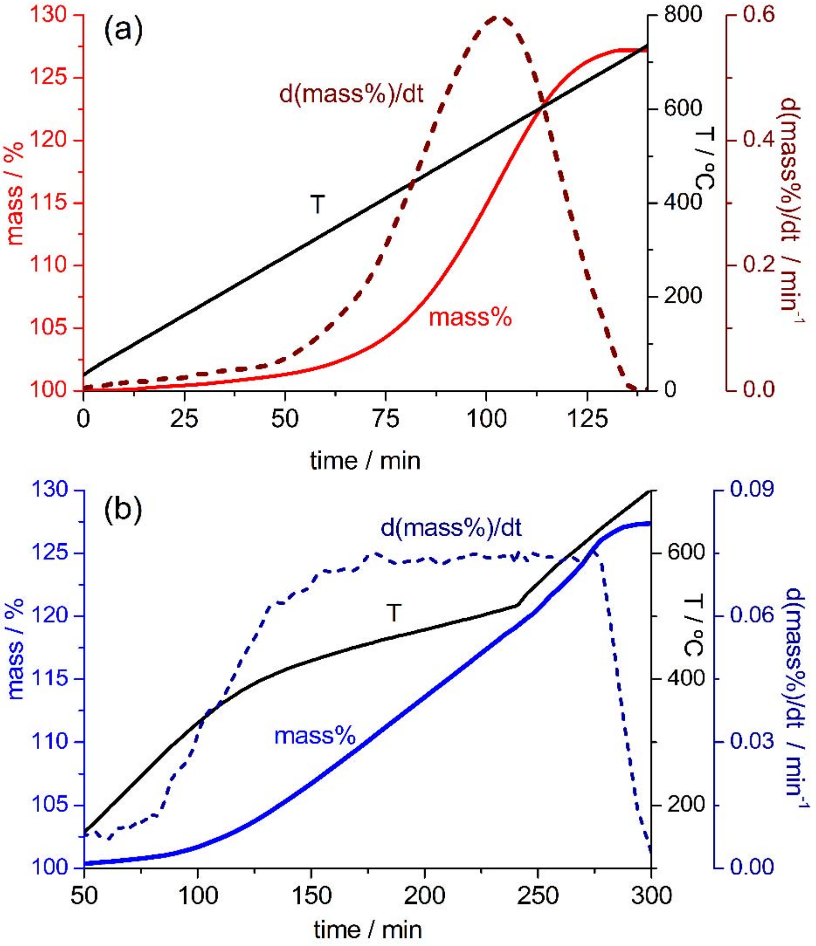

Figure 4. Mass%, mass gain rate and temperature as a function of time for the thermal oxidation of nickel powder under 8 bar of oxygen. (a) Experiment performed at a heating rate of 5 ºC min^{-1}. (b) Experiment carried out under CRTA conditions (7.5 × 10^{-2} mg min^{-1}).

Figure 5 presents the corresponding XRD patterns of the samples after the linear heating rate experiment and the CRTA test. All the diffraction peaks can be indexed in the rhombohedral cell (space group R-3m) of NiO, confirming that the nickel sample was fully oxidized in both experiments.

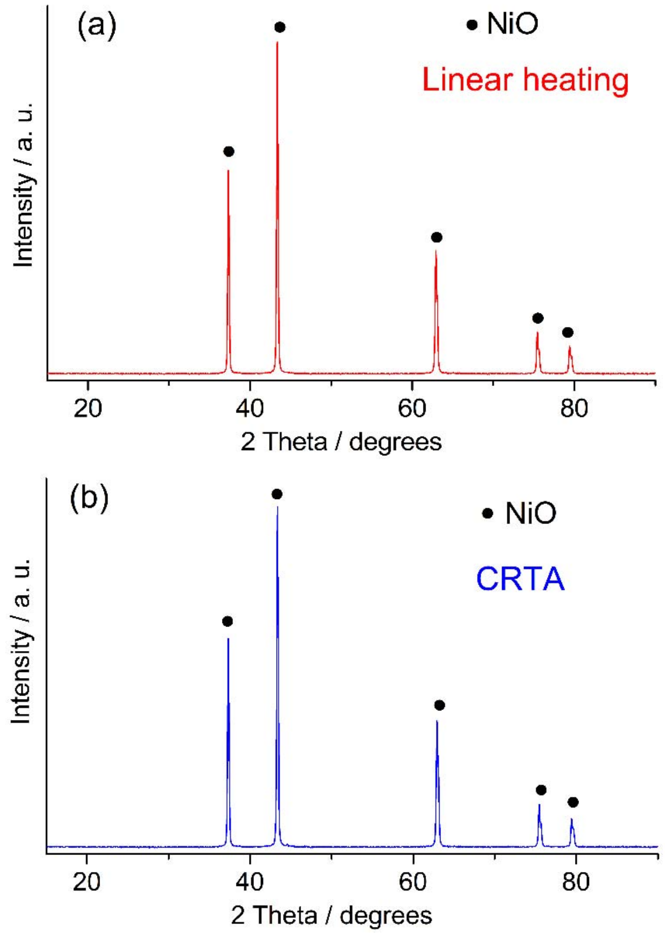

Figure 5. XRD patterns collected after the oxidation treatments. (a) Experiment performed at a heating rate of 5 ºC min^{-1}. (b) Experiment carried out under CRTA conditions (7.5×10^{-2} mg min^{-1}).

Figure 6 illustrates the higher resolution power of the CRTA experiment as compared to the conventional linear heating one. Thus, while the conventional experiment shows only a very broad mass gain-temperature profile where it is hard to discriminate different steps, the CRTA trace clearly show two processes. This is in agreement with previous studies that suggest that the oxidation of metallic nickel particles is a complex process dominated by the reaction on the surface and the inner oxide layer formation by diffusion of oxygen. However, the mechanisms of this latter process is still under debate [31-33]

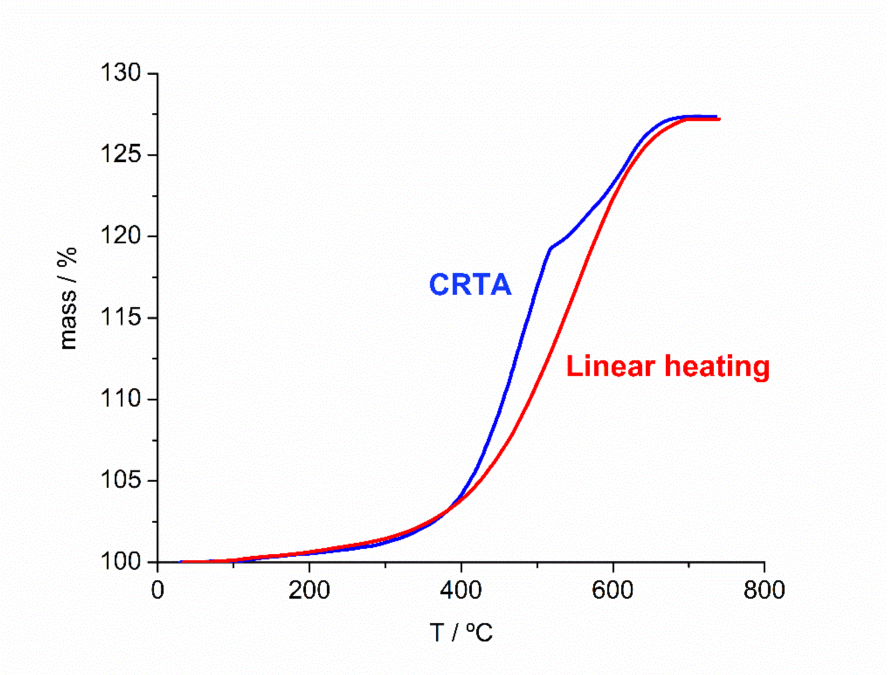

Figure 6. Mass% as a function of temperature for the thermal oxidation of nickel powder under 8 bar of oxygen and under linear heating rate and CRTA conditions.

4. Conclusions

In this work, a high-pressure thermobalance has been designed and constructed. The thermobalance is composed of a microbalance and a cylindrical stainless steel reactor in which a homemade furnace is inserted. The microbalance is able to measure masses up to 35 g with a precision of 0.01 mg and is placed in a sealed cylindrical aluminum enclosure. The high-pressure sealing of this setup allows performing experiments under pressures up to 15 bar. The control of the temperature is achieved by using a commercial temperature programmer, for temperatures up to 1000 ºC.

The system has been equipped for working under Constant Rate Thermal Analysis conditions (CRTA) conditions using the analog output of the mass signal of the microbalance as control signal. The instrument has a TG-signal programmer connected to the temperature programmer. The TG-programmer commands the temperature programmer in order to maintain constant the reaction rate in the preselected value. Thus, for an experiment in which mass gain is expected, the temperature is increased if the TG-signal is lower than the programmed setpoint and decreased if the TG-signal is higher than the setpoint. In the case of a reaction where mass loss is expected the behavior will be the other way around.

The performance of the instrument has been tested by studying the thermal oxidation of nickel powder under 8 bar of oxygen pressure using a linear heating rate and a CRTA experiment. It has been demonstrated that precise measurement and control of the mass and temperature are attained in both experiments. Nevertheless, CRTA has shown better resolution power for overlapping processes and two stages could be clearly discriminated for the oxidation of nickel.

5. Acknowledgements

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6. References

1. Siriwardane R V, Shen M-S, Fisher E P, Losch J. Adsorption of CO_2 on Zeolites at Moderate Temperatures. Energy Fuels 2005;19:1153-59.

2. Chłopek K, Frommen C, Léon A, Zabara O, Fichtner M. Synthesis and properties of magnesium tetrahydroborate, $Mg(BH_4)_2$. J. Mater. Chem. 2007;17:3496-503.

3. Roberts D G, Harris D J. Char Gasification with O_2, CO_2, and H_2O: Effects of Pressure on Intrinsic Reaction Kinetics. Energy Fuels 2000;14:483-89.

4. Yang H, Chen H, Ju F, Yan R, Zhang S. Influence of Pressure on Coal Pyrolysis and Char Gasification. Energy Fuels 2007;21:3165-70.

5. Perejon A, Sanchez-Jimenez P E, Criado J M, Perez-Maqueda L A. Magnesium hydride for energy storage applications: The kinetics of dehydrogenation under different working conditions. J. Alloy. Compd. 2016;681:571-79.

6. Perejon A, Sanchez-Jimenez P E, Soria-Hoyo C, Valverde J M, Criado J M, Perez-Maqueda L A. Sample-Controlled analysis under high pressure for accelerated process studies. J. Am. Ceram. Soc. 2019;102:1338-46.

7. Sarrion B, Sanchez-Jimenez P E, Perejon A, Perez-Maqueda L A, Valverde J M. Pressure Effect on the Multicycle Activity of Natural Carbonates and a Ca/Zr Composite for Energy Storage of Concentrated Solar Power. ACS Sustain. Chem. Eng. 2018;6:7849-58.

8. Dali Y, Tupin M, Bossis P, Pijolat M, Wouters Y, Jomard F. Corrosion kinetics under high pressure of steam of pure zirconium and zirconium alloys followed by in situ thermogravimetry. J. Nucl. Mater. 2012;426:148-59.

9. Lang A J, Vyazovkin S. Effect of pressure and sample type on decomposition of ammonium perchlorate. Combust. Flame 2006;145:779-90.

10. Rouquerol J. A general introduction to SCTA and to rate-controlled SCTA. J. Therm. Anal. Calorim. 2003;72:1081-86.

11. Criado J M, Perez-Maqueda L A. Sample controlled thermal analysis and kinetics. J. Therm. Anal. Calorim. 2005;80:27-33.

12. Charsley E L, Laye P G, Parkes G M B, Rooney J J. Development and applications of a sample controlled DSC system. J. Therm. Anal. Calorim. 2011;105:699-703.

13. Pérez-Maqueda L A, Criado J M, Subrt J, Real C. Synthesis of acicular hematite catalysts with tailored porosity. Catal. Lett. 1999;60:151-56.

14. Valverde J M, Sanchez-Jimenez P E, Perejon A, Perez-Maqueda L A. Constant rate thermal analysis for enhancing the long-term CO_2 capture of CaO at Ca-looping conditions. Appl. Energy 2013;108:108-20.

15. Pérez-Maqueda L A, Criado J M, Real C, Šubrt J, Boháček J. The use of constant rate thermal analysis (CRTA) for controlling the texture of hematite obtained from the thermal decomposition of goethite. J. Mater. Chem. 1999;9:1839-45.

16. Perejon A, Sanchez-Jimenez P E, Criado J M, Perez-Maqueda L A. A Promising approach to the kinetics of crystallization processes: The sample controlled thermal analysis. J. Am. Ceram. Soc. 2017;100:1125-33.

17. Sanchez-Jimenez P E, Perez-Maqueda L A, Perejon A, Criado J M. Combined kinetic analysis of thermal degradation of polymeric materials under any thermal pathway. Polym. Degrad. Stabil. 2009;94:2079-85.

18. Perez-Maqueda L A, Criado J M, Gotor F J. Controlled rate thermal analysis commanded by mass spectrometry for studying the kinetics of thermal decomposition of very stable solids. Int. J. Chem. Kinet. 2002;34:184-92.

19. Nishikawa K, Ueta Y, Hara D, Yamada S, Koga N. Kinetic characterization of multistep thermal oxidation of carbon/carbon composite in flowing air. J. Therm. Anal. Calorim. 2017;128:891-906.

20. Koga N, Goshi Y, Yamada S, Perez-Maqueda L A. Kinetic approach to partially overlapped thermal decomposition processes. J. Therm. Anal. Calorim. 2013;111:1463-74.

21. Yamada S, Tsukumo E, Koga N. Influences of evolved gases on the thermal decomposition of zinc carbonate hydroxide evaluated by controlled rate evolved gas analysis coupled With TG. J. Therm. Anal. Calorim. 2009;95:489-93.

22. Koga N, Yamada S. Influences of product gases on the kinetics of thermal decomposition of synthetic malachite evaluated by controlled rate evolved gas analysis coupled with thermogravimetry. Int. J. Chem. Kinet. 2005;37:346-54.

23. Criado J M, Ortega A, Rouquerol J, Rouquerol F. Influence of pressure on the shape of tg and controlled transformation rate thermal-analysis (CRTA) traces. Thermochim. Acta 1994;240:247-56.

24. Dawson E A, Parkes G M B, Barnes P A, Chinn M J. An investigation of the porosity of carbons prepared by constant rate activation in air. Carbon 2003;41:571-78.

25. Koga N, Criado J M. The influence of mass transfer phenomena on the kinetic analysis for the thermal decomposition of calcium carbonate by constant rate thermal analysis (CRTA) under vacuum. Int. J. Chem. Kinet. 1998;30:737-44.

26. Koga N, Criado J M, Tanaka H. A kinetic aspect of the thermal dehydration of dilithium tetraborate trihydrate. J. Therm. Anal. Calorim. 2002;67:153-61.

27. Sanchez-Jimenez P E, Perez-Maqueda L A, Crespo-Amoros J E, Lopez J, Perejon A, Criado J M. Quantitative Characterization of Multicomponent Polymers by Sample-Controlled Thermal Analysis. Anal. Chem. 2010;82:8875-80.

28. Criado J M, Ortega A, Gotor F. Correlation between the shape of Controlled-Rate Thermal-Analysis curves and the kinetics of solid-state reactions. Thermochim. Acta 1990;157:171-79.

29. Criado J M, Perez-Maqueda L A, Dianez M J, Sanchez-Jimenez P E. Development of a universal constant rate thermal analysis system for being used with any thermoanalytical instrument. J. Therm. Anal. Calorim. 2007;87:297-300.

30. Dianez M J, Perez-Maqueda L A, Criado J M. Direct use of the mass output of a thermobalance for controlling the reaction rate of solid-state reactions. Rev. Sci. Instrum. 2004;75:2620-24.

31. Haugsrud R. On the high-temperature oxidation of nickel. Corrosion Sci. 2003;45:211-35.

32. Song P, Wen D, Guo Z X, Korakianitis T. Oxidation investigation of nickel nanoparticles. Phys. Chem. Chem. Phys. 2008;10:5057-65.

33. Karmhag R, Niklasson G A, Nygren M. Oxidation kinetics of small nickel particles. J. Appl. Phys. 1999;85:1186-91.