

Methane production by mechanochemical processing of MgH₂-Li₂CO₃ as sources of H₂ and CO₂ at room temperature

Questa è la versione Post print del seguente articolo:

Original

Methane production by mechanochemical processing of MgH₂-Li₂CO₃ as sources of H₂ and CO₂ at room temperature / Grasso, M. L.; Fernandez Albanesi, L.; Garroni, S.; Mulas, G.; Gennari, F. C. - In: JOURNAL OF CO₂ UTILIZATION. - ISSN 2212-9820. - 40:(2020), p. 101209. [10.1016/j.jcou.2020.101209]

Availability:

This version is available at: 11388/239571 since: 2020-11-11T10:28:16Z

Publisher:

Published

DOI:10.1016/j.jcou.2020.101209

Terms of use:

Chiunque può accedere liberamente al full text dei lavori resi disponibili come "Open Access".

Publisher copyright

note finali coverpage

(Article begins on next page)

This is the Author's accepted manuscript version of the following contribution:

Methane production by mechanochemical processing of MgH₂-Li₂CO₃ as sources of H₂ and CO₂ at room temperature / Grasso, M. L.; Fernandez Albanesi, L.; Garroni, S.; Mulas, G.; Gennari, F. C.. - In: JOURNAL OF CO₂ UTILIZATION. - ISSN 2212-9820. - 40:(2020), p. 101209. [10.1016/j.jcou.2020.101209]

The publisher's version is available at:

<https://dx.doi.org/10.1016/j.jcou.2020.101209>

When citing, please refer to the published version.

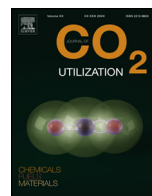


ELSEVIER

Contents lists available at ScienceDirect

Journal of CO₂ Utilization

journal homepage: www.elsevier.com/locate/jcou



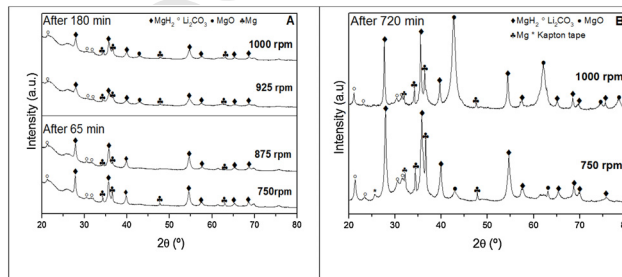
Graphical abstract



Methane production by mechanochemical processing of MgH₂-Li₂CO₃ as sources of H₂ and CO₂ at room temperature

María L. Grasso*, Luisa Fernández Albanesi, Sebastiano Garroni, Gabriele Mulas, Fabiana C. Gennari

Journal of CO₂ Utilization xxx (2019) pp. xxx–xxx



UNCORRECTED

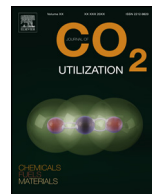


ELSEVIER

Contents lists available at [ScienceDirect](https://www.sciencedirect.com)

Journal of CO₂ Utilization

journal homepage: www.elsevier.com/locate/jcou



Highlights

Methane production by mechanochemical processing of MgH₂-Li₂CO₃ as sources of H₂ and CO₂ at room temperature

Journal of CO₂ Utilization xxx (2019) pp. xxx–xxx

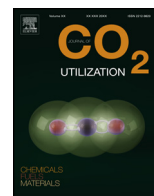
María L. Grasso*, Luisa Fernández Albanesi, Sebastiano Garroni, Gabriele Mulas, Fabiana C. Gennari

- CH₄/H₂ fuel mixture is obtained by mechanical milling of MgH₂-Li₂CO₃ at room temperature.
- Mechanochemical process occurs without catalyst and with high selectivity to methane.
- Analyses of the gas-product evolution evidences the absence of CO₂ or CO during milling.
- Methane generation is kinetically restricted by the high stability of Li₂CO₃.
- Solid products are reused as CO₂ absorbers for the exhaust gases treatment of power plants.

UNCORRECTED PROOF



Contents lists available at ScienceDirect

Journal of CO₂ Utilizationjournal homepage: www.elsevier.com/locate/jcou

Methane production by mechanochemical processing of MgH₂-Li₂CO₃ as sources of H₂ and CO₂ at room temperature

Q2 María L. Grasso^{a,b,*}, Luisa Fernández Albanesi^{a,c}, Sebastiano Garroni^d, Gabriele Mulas^d,
Q3 Fabiana C. Gennari^{a,c,e}

^a Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), R8402AGP, S. C. de Bariloche, Río Negro, Argentina

^b Universidad Nacional de Cuyo (UNCuyo), Facultad de Ciencias Exactas y Naturales, M5502JMA, Ciudad de Mendoza, Mendoza, Argentina

^c Centro Atómico Bariloche (CAB-CNEA), R8402AGP, S.C. de Bariloche, Río Negro, Argentina

^d Dipartimento di Chimica e Farmacia and INSTM, Università degli Studi di Sassari, 07100, Sassari, Italy

^e Universidad Nacional de Cuyo (UNCuyo), Instituto Balseiro, Av. Bustillo 9500, R8402AGP, Bariloche, Río Negro, Argentina

ARTICLE INFO

Article history:

Received 7 May 2020

Received in revised form 29 May 2020

Accepted 6 June 2020

Available online xxx

Keywords:

CO₂ conversion

Alkaline carbonates

Light metal hydrides

Methane

Hydrogen

ABSTRACT

The reutilization of CO₂ to produce valuable chemical fuels is an attractive approach to reduce the greenhouse effect and global warming. In this work, the room temperature production of CH₄/H₂ fuel mixtures via mechanochemical activation of Li₂CO₃-MgH₂ system was explored. The CH₄/H₂ fuel mixtures were obtained by a free-catalyst reaction, with high selectivity and using Li₂CO₃ and MgH₂ as solid portable sources of CO₂ and H₂, respectively. The effect of processing parameters on both the evolution of the solid phases and the production of CH₄/H₂ fuel mixtures was studied using X-ray diffraction, spectroscopic techniques, electron scanning microscopy and gas chromatography. Thermodynamic calculations predict the complete CO₂ reduction to CH₄, with simultaneous formation of MgO and Li₂O. Experimental evidence supports the progressive formation of MgO and the appearance of Li₂O. The presence of H₂ simultaneously with CH₄ in the gas phase was due to kinetic restrictions. Based on experimental results and equilibrium composition calculations, the reaction mechanism was proposed. The kinetic analysis reveals that the rate limiting CH₄ production is the nucleation of MgO/Li₂O in the surroundings of Li₂CO₃, while the H₂ release is controlled by the reaction interface between MgH₂/Mg or MgH₂/MgO.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon dioxide gas (CO₂) is considered one of the main contributors to global warming and climate change because of its role in the greenhouse effect. Human activities, such as combustion of fossil materials (coal, oil, natural gas), industrial processes, changes in land use and deforestation, are considered to be the main responsible for the growing CO₂ atmospheric concentration, from 280 ppm in the pre-industrial era to 415 ppm in 2019 [1], with an increase of 0.8 °C in global planet temperature. Intergovernmental Panel on Climate Change (IPCC) has estimated that by the end of the century, CO₂ concentration would reach 700 ppm and the average temperature would increase up to 5 °C, with devastating and irreversible climate changes [2]. For these reasons,

a current and urgent challenge is to find a sustainable way to reduce CO₂ concentration in the atmosphere. Unfortunately, the continuous increase in energy demand due to a growing population and life-style quality implies more CO₂ atmospheric emissions [3].

Carbon dioxide capture and utilization (CCU) is a very promising strategy to mitigate CO₂ emissions, having at the same time a benefit related to the production of value-added products. Here, CO₂ acts as a carbon source to synthesize products such as alcohols, polymers and synthetic fuels. Also, there are direct applications of the captured CO₂: in carbonated drinks, as dry-ice, in fire extinguishers or in algae farms for photosynthesis [3,4]. Among synthetic fuels to be produced from CO₂, methane is the hydrocarbon with the highest hydrogen to carbon ratio. Its gravimetric heat is greater (55.5 MJ/kg) than butane (49.5 MJ/kg), diesel (44.8 MJ/kg) and methanol (22.7 MJ/kg) [5]. In addition, CH₄ is compatible with our current storage and distribution network. Based on its good properties, methane is considered an attractive and alternative fuel. Interestingly, the addition of H₂ to CH₄ produces a fuel-gas mixture with improved properties for its

* Corresponding author at: Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de Cuyo (UNCuyo), Facultad de Ciencias Exactas y Naturales, Av. Bustillo 9500, R8402AGP, Bariloche, Río Negro, Argentina.
E-mail address: maria.grasso@cab.cnea.gov.ar (M.L. Grasso).

use in stationary applications like heaters, boilers and turbines or in mobile applications like internal combustion engines and gas turbines [6,7]. In fact, the wide ignition limits and high flame speed of hydrogen have a positive impact on the combustion, improving the energy density of natural gas on the operation conditions. In addition, mixtures of H₂ with CH₄ allow a substantial reduction of the CO₂ emissions. These hydrogen-enriched mixtures (up to 20 %) can be distributed by the mid-pressure natural gas network or stored under pressure using conventional methane storage technologies without substantial technical modifications [8].

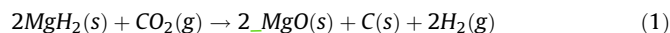
In the search for alternative methods of CO₂ hydrogenation, our working group has recently reported the use of Mg-Fe and Mg-Ni complex hydrides with a dual function: as promoters of the CO₂ conversion and as hydrogen sources [9,10]. CO₂ methanation was promoted by the presence of Fe, Ni and/or Mg-Ni alloys obtained during decomposition of the Mg₂FeH₆ and Mg₂NiH₄ hydrides, while its conversion depended on the nature of the hydride, the experimental conditions and the H₂:CO₂ molar ratio [9]. The global mechanism for both hydrides includes the reversed water-gas shift reaction followed by CO methanation in presence of steam. However, in the case of Mg₂NiH₄, the direct reduction of CO₂ by MgH₂/Mg₂NiH_x hydrides takes an important role in the whole process. Refinement of the Mg₂NiH₄ microstructure to the nanometric scale modifies the CO₂ methanation mechanism [10] and it proceeds by adsorption of C and direct solid gasification toward CH₄ formation.

In this context, the development of simple methods for CO₂ conversion into valuable chemicals or energy carriers under soft conditions (mild pressure and temperature) is a topic of interest in the scientific community. In this respect, the mechanochemical synthesis is considered a manufacturing technology that is simple, efficient, cheap, scalable, low-waste, and solvent-free for the production of chemicals at room temperature [11,12].

Mechanochemical activation of different solids was applied to promote CO_x storage and/or its conversion via different solid-gas reactions [13–17]. Mulas et al. studied the mechanochemical hydrogenation of CO over FeCo and Mg₂Ni-based catalysts [13]. Chemical transformations were promoted by mechanical treatment at the interface of solid-gas systems at mild conditions. The CO₂ conversion to CH₄ obtained via FeCo catalysts at room temperature and atmospheric pressure is similar to the corresponding one occurring in thermally activated conditions, which requires high temperature and pressure. In addition, a recent investigation reported the production of CH₄ and light hydrocarbons by milling of the olivine (a magnesium silicate mineral) and water under CO₂ atmosphere [14]. Energetic ball milling promotes the olivine-water activation, releasing H₂ and allowing the hydrogenation of CO₂ by the in situ formation of magnetite-based catalysts [15]. The mechanism of the whole process is complex, and competitive processes such as the precipitation of carbonate phases were also detected as dependent on the CO₂/H₂O ratio. These investigations exhibit the potential of mechanochemical processing to promote gas-solid reactions in the presence of catalysts and under mild conditions.

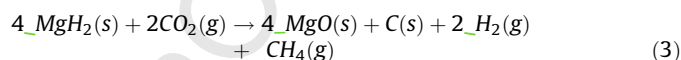
In this line, two recent investigations reported the mechanochemical conversion of CO₂ to produce CH₄-H₂ mixtures using light metal hydrides (LiH, NaH, MgH₂ and CaH₂) as hydrogen source at room temperature and without any catalyst [16,17]. Dong et al. were the first to produce CO_x-free mixtures of CH₄-H₂ through a solid-gas mechanochemical reaction. The yield of CH₄ was dependent on the nature of the light metal hydride, rate and duration of ball milling, and CO₂ pressure. The selectivity also depends on these parameters, detecting CO formation at high CO₂:H₂ ratios. Experimental results indicated that the mechanism of

CO₂ reduction using MgH₂ (or LiH) involves the production of amorphous carbon followed by a hydrogenation step:

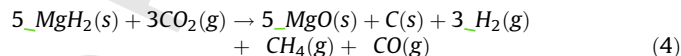


The reaction between carbon and H₂ produced *in situ* during mechanochemical processing is responsible for the CH₄ formation.

Using a similar strategy, Pu et al. investigated the effect of different H₂:CO₂ ratios on the conversion efficiency of CO₂ to CH₄ by mechanochemical reduction with light metal hydrides. According to the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) data, the following reaction mechanism was proposed for H₂:CO₂ molar ratio lower than 2:1:



As the concentration of CO₂ was increased, CO formation was observed. For H₂:CO₂ ratio of 7:5, the solid products formed were MgO, MgCO₃ and C, and the global reaction can be described by:



These investigations demonstrated that the mechanism of CO₂ reduction by light metal hydrides depends on several factors. In general, LiH and MgH₂ hydrides, contrary to NaH, favor the reduction of CO₂ to CH₄.

Recently, Dong et al. studied the interaction between metal hydrides and alkaline carbonates as sources of H₂ and CO₂, respectively [18]. This study consisted in following the reactivity of MH-M₂CO₃ systems (where M = Mg or Ca) during mechanical milling at room temperature under catalyst-free conditions. The authors reported a highly selective method to CO₂ conversion and to synthesize CO_x free H₂/CH₄ blends. Different parameters such as prolonged milling times of 48 h, high ball milling rates (450–550 rpm), and high H₂:CO₂ ratios promote the formation of CH₄ as the only hydrocarbon product. The analysis of the gas and solid products show that the methanation reaction occurs between the H₂ released from the hydride and amorphous carbon produced by carbonate reduction. This reaction mechanism is similar to the one proposed by the same research group during mechanochemical reduction of CO₂ gas using light metal hydrides [17].

On the basis of previous knowledge, the replacement of gaseous CO₂ and H₂ by solid alkaline carbonates and hydrides to carry out the CO₂ conversion process, presents some advantages. From the point of view of materials manipulation, inorganic carbonates are inexpensive, abundant, and easy to handle under air atmosphere. As an extra advantage, some carbonates are the main product obtained after CO₂ capture by absorbents like Li₄SiO₄ or Na₂ZrO₃ [19–23], then their use as CO₂ source could allow the recycling of degraded absorbents after long operation periods. Also, the use of CO₂ and H₂ storage materials eases transportation and storage. Finally, the reduction of inorganic carbonates reinforces the aim of reusing CO₂ as a feedstock in other chemical processes [24–26]. However, despite the recent advances reported in the current literature, the light carbonates-hydrides mixtures have been poorly explored.

In this work, Li₂CO₃ and MgH₂ were chosen, for the first time to the best of our knowledge, as CO₂ and H₂ portable storage materials to evaluate the direct methanation reaction promoted by

high-energy mechanochemical activation. Specifically, the selection of Li₂CO₃ gives the possibility to reuse final products obtained from deteriorated CO₂ absorbents. In addition, the formation kinetics of both CH₄ and H₂ was investigated using theoretical models to fit the time-dependent experimental conversion data. In order to clarify the reaction mechanism of the MgH₂-Li₂CO₃ reaction system, a combination of different techniques for structural, microstructural and chemical characterization of the solids was used and complemented by thermodynamic calculations.

2. Experimental

2.1. Materials preparation

Commercial MgH₂ (Rockwood Lithium, 99.8 %) and Li₂CO₃ (Alfa Aesar, 99 %) powders were used as precursor reagents. Mixtures with different molar ratio of MgH₂:Li₂CO₃, 4:1 and 2:1 were prepared by ball milling (BM). For each mixture, a total amount of 1 g was used, corresponding to 0.59 g MgH₂-0.41 g Li₂CO₃ and 0.42 g MgH₂-0.58 g Li₂CO₃ for 4:1 and 2:1 M ratio, respectively. The procedure for the mechanical treatment consisted in sealing each reagent mixture in a vial and ball milling by using a Spex mixer/mill model 8000 adapted for milling at different rotation speeds. The vial and the ball used are made of stainless steel. The ball milling conditions were: ball mass to powder mass ratio of 1–4, room temperature, an argon pressure of 0.98 atm and rotation speed of 750, 875, 925 and 1000 rpm. The milling was stopped each 5 min, avoiding temperature increase in the milling system.

Because of the air sensitivity of the powders, sample handling was performed under a high-purity argon atmosphere inside a glove box device (MBraun) with oxygen and water levels below 1 ppm.

2.2. Characterization techniques

The structural and morphological properties of the materials were analyzed by X-Ray Powder Diffraction (XRPD) using a Rigaku DMax diffractometer with CuK α radiation tube, Scanning Electron Microscopy (SEM, ZEISS Crossbeam 340 microscope and SEM, FEI Inspect S50) with Energy-Dispersive X-ray Spectroscopy (EDXS) and solid state FTIR (Perkin Elmer Spectrum Series 400). To prevent the sample oxidation during XRPD measurements, an airtight sample holder with Kapton dome was used. A wide peak at lower angle was observed due to kapton contribution. Using the Scherrer equation [27], the crystallite size of the phases before and after milling was calculated using the following peaks: MgH₂ (2 θ : 27.9°), Mg(OH)₂ (2 θ : 18.6°), Li₂CO₃ (2 θ : 21.3°), MgO (2 θ : 42.9°) and Mg (2 θ : 36.6°). Considering that the area of the main peak of each phase is proportional to the amount of that phase in the crystalline sample, estimations of the proportion of X phase respect to the rest of phases all containing Mg were performed. The proportion (P, percent) of MgH₂, Mg, or MgO in the starting material and after mechanochemical milling were calculated from XRPD measurements, using the following equation:

$$P_X = \frac{I_X}{I_{MgH_2} + I_{MgO} + I_{Mg}} \cdot 100 \quad (6)$$

where X is the specie of interest and I is the integrated intensity of the most intense reflections of MgH₂ (2 θ : 27.9°), MgO (2 θ : 42.9°) and Mg (2 θ : 36.6°).

For the morphological observations and elemental mapping, powder samples were dispersed on a carbon based tape and coated with gold to improve electrical conductivity. In the case of solid-state FTIR spectroscopy measurements, the powders were mixed

with dry KBr and pressed to pellets under air conditions. The presence of carbon-based solids on the final products was investigated by Raman spectroscopy with a confocal microscope (LabRAM HR Evolution Raman microscope) at room temperature using the laser wavelength of 514 nm.

The gaseous phase was followed by gas-chromatography (GC). Hydrogen (H₂), methane (CH₄) and other hydrocarbons were detected using both a Perkin Elmer 8500 and a Fisons 8000 apparatus equipped with a flame ionization (FID) and thermal conductivity (TCD) detectors, respectively. Suitable gas standard mixtures were used to quantify the hydrocarbons production during milling at different times. The conversion values (α) for the gas products CH₄ and H₂ were calculated as follows:

$$\alpha_{CH_4} = \frac{n_{CH_4}}{n_{CO_2}} \quad (7)$$

$$\alpha_{H_2} = \frac{n_{H_2}}{n_{MgH_2}} \quad (8)$$

where n_{CH_4} =moles of CH₄ produced, n_{CO_2} =moles of CO₂ supplied from Li₂CO₃, n_{H_2} = moles of H₂ produced and n_{MgH_2} =moles of MgH₂ supplied.

2.3. Thermodynamic calculations

The equilibrium compositions for MgH₂-Li₂CO₃ system as a function of the pressure were calculated using HSC Chemistry Windows, 6.1 version [28]. When all species in a reaction system are given (reactants and products), the software determines the distribution of the products where the Gibbs free energy of the system reaches its minimum at constant temperature. For calculations, H₂:CO₂ molar ratio of: 4MgH₂:Li₂CO₃; 2MgH₂:Li₂CO₃; 3.64MgH₂:Li₂CO₃:0.36 Mg and 1.82MgH₂:Li₂CO₃:0.18 Mg were taken into account as initial reagents; it was supposed room temperature condition. For these reaction system, the following phases were considered: Ar, CO₂, H₂, CO, O₂, CH₄, C₂H₄, C₂H₆ and H₂O in the gas phase, and Li₂O, LiOH, Li₂CO₃, Li₂C₂, MgH₂, Mg, MgO, Mg(OH)₂, MgCO₃ and carbon as possible solid products.

3. Results

3.1. Ball milling of MgH₂-Li₂CO₃ system: structural and microstructural analyses

XRPD patterns of the MgH₂-Li₂CO₃ system after milling for different times show the structural and microstructural evolution of the solid phases (Fig. 1). For all cases, a broadening of the peaks was observed due to a gradual modification of microstructural features induced by the mechanical processing. For comparison, the structural study of the reagents before milling shows the high crystallinity of MgH₂, with minor amounts of Mg, and Li₂CO₃ (Fig. S1A). Independently on the milling time and the rotation speed, a remnant of the reactants MgH₂ and Li₂CO₃ as crystalline phases as well as free Mg was identified during mechanochemical processing (Fig. 1A). At higher rotation speeds such as 925 rpm, it is possible to recognize the most intense diffraction peaks of MgO at 42.92° and 62.31°. Progressive formation of MgO was confirmed with the increment of the milling time at 1000 rpm (Fig. 1B); simultaneously Li₂CO₃ and MgH₂ were detected, indicating their incomplete transformation. Other Li-containing phases were not detected with this technique.

The solids obtained after milling of MgH₂-Li₂CO₃ for 720 min using 750 and 1000 rpm were analyzed by FTIR and Raman (Fig. 2). The FTIR results confirm the presence of Li₂CO₃ phase in both samples (Fig. 2A), in agreement with XRPD technique. The bands at

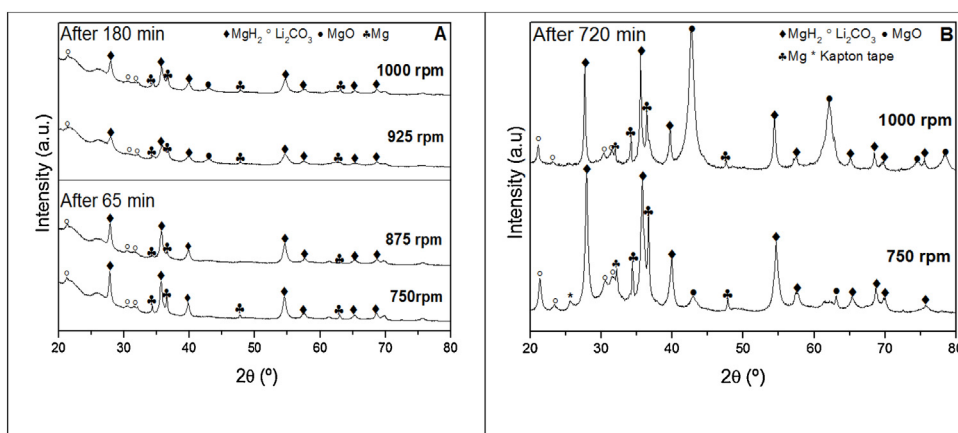


Fig. 1. XRPD patterns after milling of the 4MgH₂-Li₂CO₃ system at different milling times (A) and rotation speeds (B).

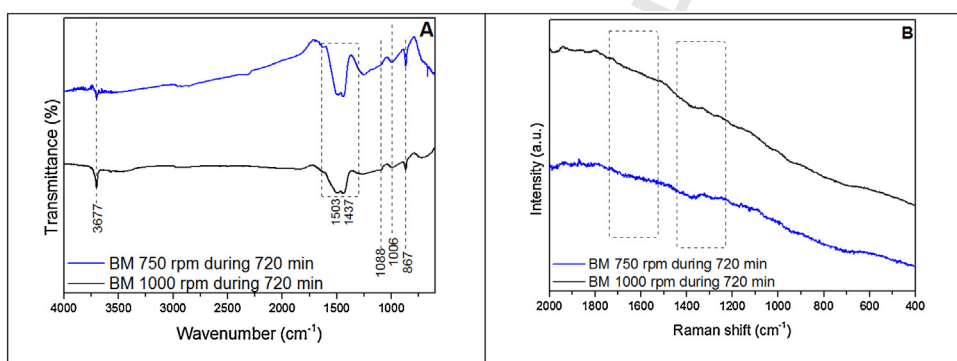


Fig. 2. Solid-state FTIR (A) and Raman spectra (B) of 4MgH₂-Li₂CO₃ after milling at 750 rpm and 1000 rpm during 720 min.

867, 1503 and 1437 cm⁻¹ due to the bending and asymmetric stretching vibrations of Li₂CO₃ were observed simultaneously with a small band at 1088 cm⁻¹ due to the stretching vibration [29]. The band identified at 3677 cm⁻¹ is related with OH⁻ onto Li⁺ and it is ascribed to partial hydroxylation of the sample. Its presence can be interpreted as a result of the reaction between Li₂O with moisture from the air, in agreement with previous work [30]. No evidence of MgO hydroxylation was observed, as it can be inferred by the absence of the stretching vibration at 3699 cm⁻¹ [31]. This result is in accordance with the minor ΔG° value obtained for hydrolysis of Li₂O (-88.1 kJ/mol [28]) respect to MgO (-35.7 kJ/mol [28]) at room temperature, suggesting that Li₂O reacts easily with H₂O from a thermodynamic point of view.

This constitutes an evidence that mechanochemical processing of the MgH₂-Li₂CO₃ mixture for long milling times induces the formation of Li₂O. In addition, Raman measurements were performed to clarify if amorphous carbon was formed as an intermediate of the reaction, as it was observed in similar systems [18]. The Raman spectra shows the absence of both G and D peaks in the region near 1600 and 1350 cm⁻¹, which are ascribed to graphite and defects in carbonaceous solid respectively (Fig. 2B) [32].

The crystallite sizes of the reagents and products were calculated before and after milling using the Scherrer equation (Fig. 3). The values evidence a trend to decrease in grain size with the time and milling rotation speed for the reagents and associated phases (Mg). On the contrary, the phase MgO shows an increment in the grain size during milling probably due to its partial crystallization during mechanical processing.

The morphological characterization of starting powders reveals a uniform distribution of MgH₂ agglomerates with an average size of 180 μm, while for Li₂CO₃ powders display a broad distribution size between 60 and 700 μm (Figs. S1B and S1C, respectively). In both cases, their agglomerates have faceted edges; in particular, partial agglomerate disaggregation was observed for Li₂CO₃. Mechanical milling of the MgH₂-Li₂CO₃ mixture introduces relevant morphological modifications in the starting materials. The size distribution of the agglomerates goes from 40 to 60 microns. The as-milled MgH₂-Li₂CO₃ powders at 750 rpm for 65 and 720 min show agglomerates with sponge-type shape (Figs. 4A and B, respectively). The surface of each agglomerate was analyzed by EDXS element mapping evidencing uniform distribution of magnesium, oxygen and carbon due to a well mixing grade of the initial reagents. In particular, after 65 min of milling, there are smooth particles (red circles) with a chemical composition corresponding to Mg. Long times of milling (720 min) favor the uniform distribution of all elements to sizes lower than 1 μm.

3.2. Gas evolution during milling: Kinetic analysis of the CH₄ and H₂ production

The release of the gaseous species inside the milling chamber was followed by gas chromatography analysis (Fig. 5), taking samples at different reaction times. From short milling times and independently of the energetic conditions, the main products formed by milling of the MgH₂-Li₂CO₃ system were methane (Fig. 5A) and hydrogen (Fig. 5B). Signals corresponding to other hydrocarbons such as ethylene and acetylene were found after

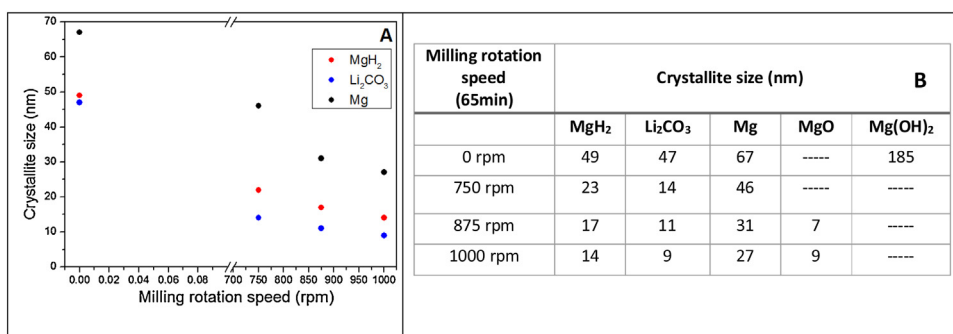


Fig. 3. Change in the crystallite size as a function of milling rate after 65 min of milling. Plot for the starting reagents (A) and table of all the crystalline species observed (B).

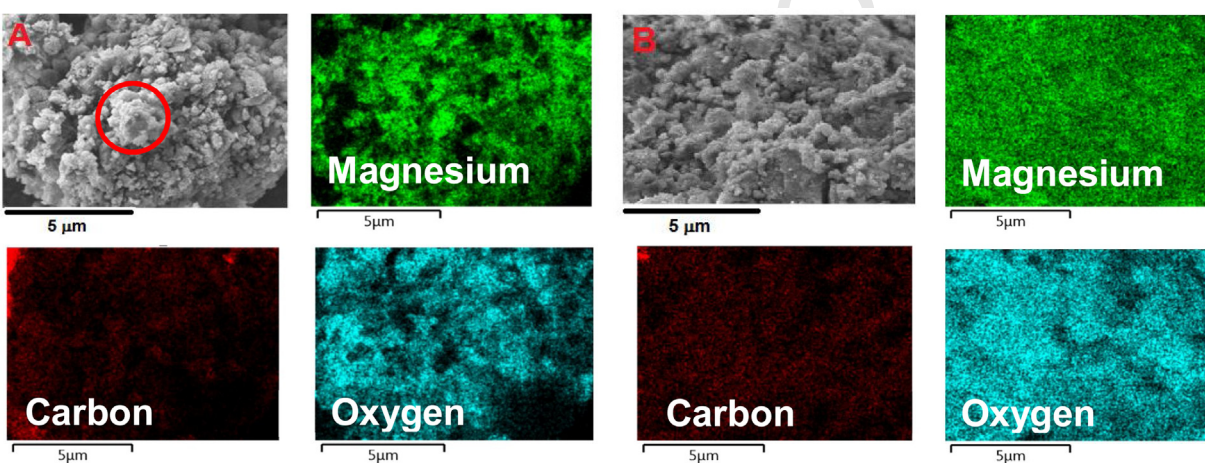


Fig. 4. SEM photographs and elemental mapping after milling of the 4MgH₂-Li₂CO₃ system at 750 rpm during 65 min (A) and 720 min (B).

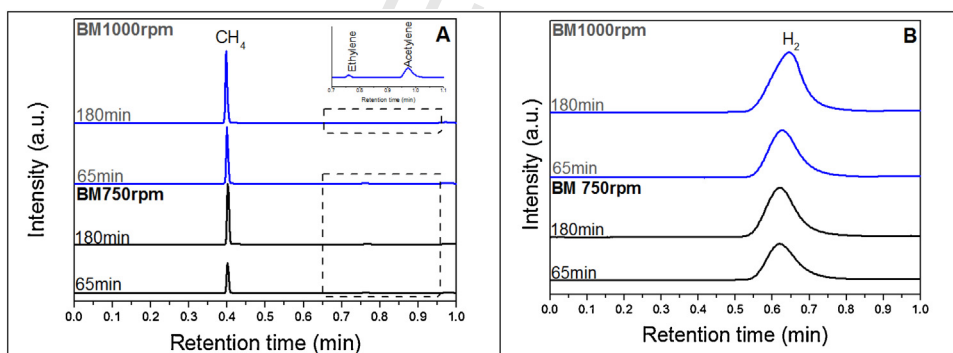


Fig. 5. Chromatograms of the gas products collected during milling of 4MgH₂-Li₂CO₃ system at 750 rpm and 1000 rpm for different times.

milling at 1000 rpm promoted by high-energy milling conditions. The ethylene and acetylene concentrations were below 1 % for all milling rotation speeds. The presence of CO₂ or CO in the gas phase was not detected in any experimental condition.

Evolution of the moles of CH₄ and H₂ as function of milling time at different speeds (Figs. 6A and B) shows that the amounts of CH₄ and H₂ increase with both parameters. The curves of CH₄ show a quadratic dependence with the milling time increase, while H₂ moles grow following an approximately linear behavior from the beginning of the mechanical processing. In both cases, the moles of H₂ formed at a fix milling time and milling rotation speed are at least two times the moles of CH₄ detected.

To study the influence of H₂:CO₂ molar ratio in the reactivity of the MgH₂-Li₂CO₃ system, the most energetic conditions (1000 rpm) were selected to compare the amount of gas produced with the milling time increase (Fig. S2 and Table S1). The shapes of the curves for methane and hydrogen in the plot look similar. In fact, the amount of H₂ (available in the gas phase) increased due to the rise in the H₂:CO₂ molar ratio and did not have a clear impact on the moles of the CH₄ formed. This result suggests that the mechanism controlling the global process is the same independently of the starting H₂:CO₂ mol ratio.

To analyze the possible mechanism that controls the reaction between MgH₂ and Li₂CO₃ during mechanochemical processing,

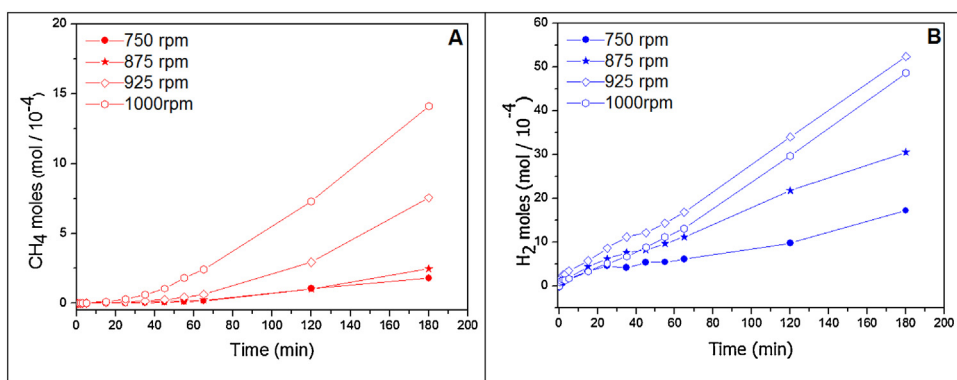


Fig. 6. Moles of CH₄ (A) and H₂ (B) produced during milling of the 4MgH₂-Li₂CO₃ system for different milling rotation speeds and milling times.

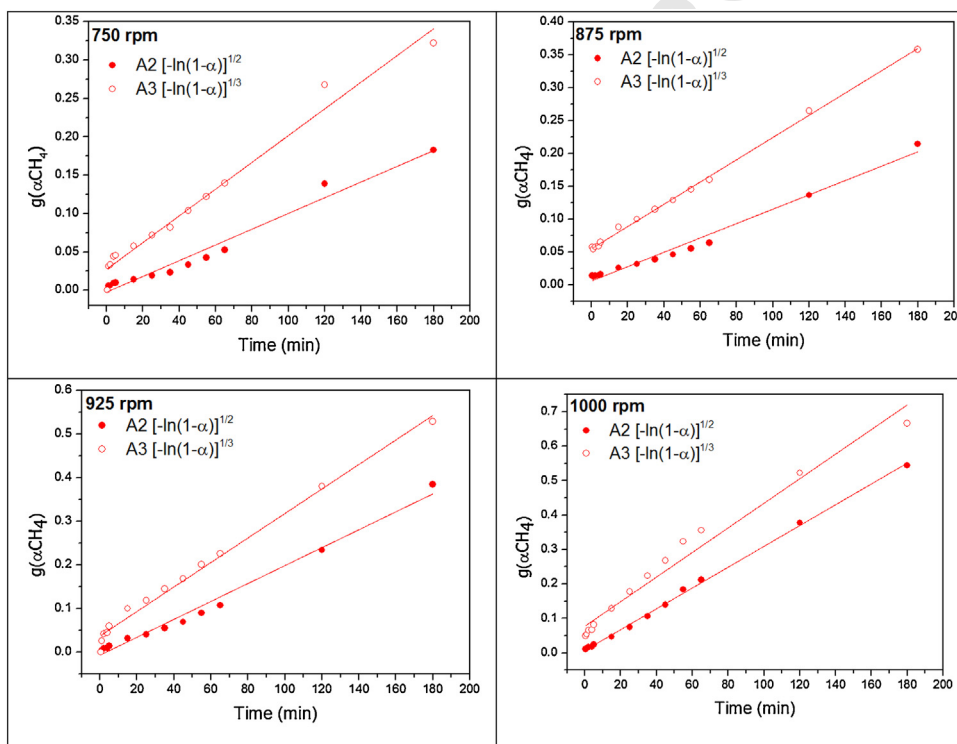


Fig. 7. Fitting of the experimental data for methane conversion using Avrami-Erofev models.

the conversion of CH₄ and H₂ was calculated using equations (8), (9) and data from Fig. 6 (Fig S3). These experimental data were fitted using theoretical models (Figs. 7 and 8), i.e. g(α) linearized functions developed for solid state reaction such as Avrami-Erofev, Power law and diffusion models (Table 1). These models assume that the solid-state reaction occurs in a single step; however, in many cases, intermediate phases are experimentally observed, indicating a complex reaction mechanism.

In this analysis, the value R² (squared correlation coefficient) was chosen as a goodness of fit parameter. R² parameter was obtained by fitting the whole range of milling time (up to 180 min). The average value of R² parameter for each model proposed by Flanagan et al. [33] is shown in Fig. S4. From this figure it is possible to notice that the rate controlling mechanism for methane and hydrogen production is different. The conversion values (α) for methane adjust well with nucleation models such as Avrami-Erofev and Power law (Fig. 7), with R² between 0.97 and 0.998.

However, Power law is simply a numerical model without a specific association with the physical mechanism. In contrast, the Avrami-Erofev exponent describes the feasibility of nucleation and usually provides information about the rate-limiting step and the dimensionality of the growth process.

On the other hand, the geometrical contraction models (R2 and R3) are the most accurate to describe the hydrogen gas formation, with R²=0.995 (Fig. 8). These models assume that nucleation occurs rapidly on the surface of the particle, and all particles are equivalent in shape and size. The reaction is usually controlled by the resulting reaction interface progressing toward the center of the particles.

The values of the kinetic rate constant as a function of milling rotation speed obtained from Figs. 7 and 8 are displayed in Table 2. The trend shows that the kinetic rate constant for each model increases with milling rotation speed, showing an enhancement of the conditions for CH₄ and H₂ gas production.

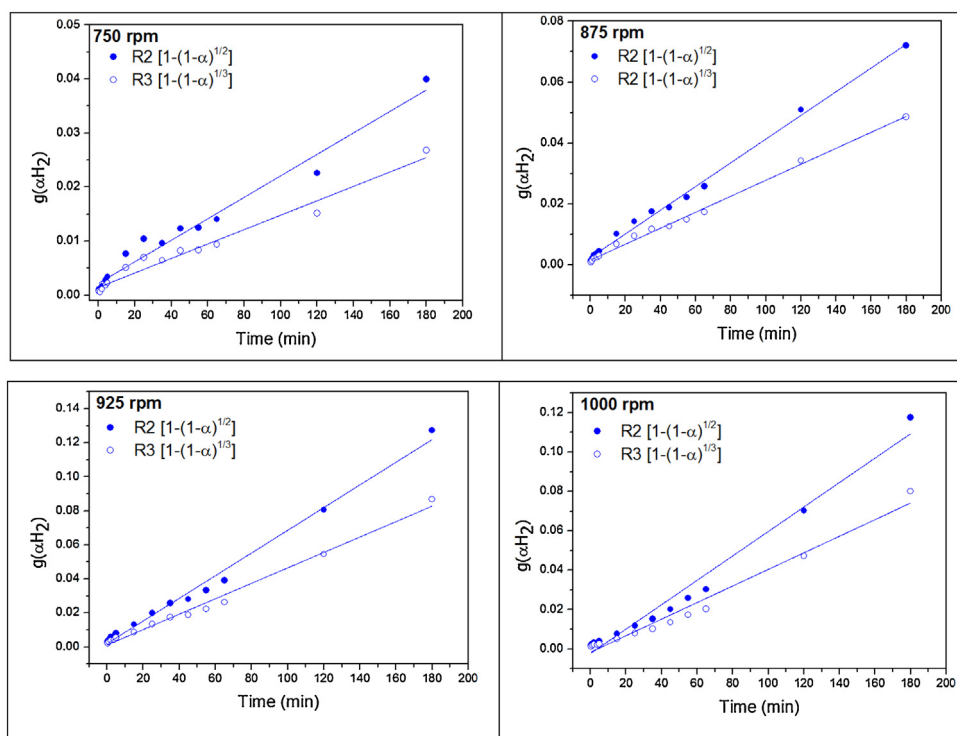


Fig. 8. Fitting of the experimental data for hydrogen conversion using geometrical contraction models.

Table 1

Kinetic models and rate equations used for fitting the conversion of CH₄ and H₂ experimental data. α=conversion (eqs. 8 and 9), k=kinetic rate constant, t= time(s).

Model	Integral form g(α)=kt
Nucleation models	
Power law (P2)	α ^{1/2}
Power law (P3)	α ^{1/3}
Power law (P4)	α ^{1/4}
Avrami-Erofeyev (A2)	[-ln(1-α)] ^{1/2}
Avrami-Erofeyev (A3)	[-ln(1-α)] ^{1/3}
Geometrical contraction models	
Contracting area (R2)	[1-(1-α) ^{1/2}]
Contracting volume (R3)	[1-(1-α) ^{1/3}]
Diffusion models	
1D diffusion (D1)	α ²
2D diffusion (D2)	[(1-α)ln(1-α)] + α
3D diffusion-Jander equation (D3)	[1-(1-α) ^{1/3}] ²
Reaction zero-order	
Zero-order (F0)	α
First-order (F1)	-ln(1-α)
Second-order (F2)	(1-α) ⁻¹ -1
Third-order (F3)	0.5[(1-α) ⁻² -1]

4. Discussion

The reaction between MgH₂ and Li₂CO₃ occurs at room temperature promoted by high-energy milling. Its progress is demonstrated by the gradual formation of both the MgO in the solid phase (Fig. 1) and the mixture CH₄-H₂ in the gas phase (Fig. 4). As an unexpected result, long milling times (720 min) and high energetic conditions (1000 rpm) are not enough to completely consume the reagents. In fact, both MgH₂ and Li₂CO₃ starting materials were identified as crystalline phases after reaction under the most energetic conditions (Fig. 1B). Moreover, after a prolonged milling of 720 min, MgH₂, Mg and MgO are the preponderant phases containing Mg detected by XRPD (Fig. 1); while the presence of LiOH detected by FTIR is an indication of the Li₂O formation during extended high-energetic milling conditions (Fig. 2B).

The thermodynamic calculations for the MgH₂-Li₂CO₃ system at different H₂-CO₂ mol ratio (2:1 and 4:1) were performed to determine the equilibrium composition (Figs. 9A and B). These Figures show the equilibrium composition of the gaseous and solid state species as a function of gas pressure at room temperature. Similar results were obtained in both approaches. It can be noted

Table 2

Reaction rate constants obtained for the CH₄ and H₂ formation using Avrami-Erofeyev model and geometrical contraction model, respectively.

Milling rotation speed	Reaction rate constant (s ⁻¹), k for CH ₄ data	Reaction rate constant (s ⁻¹), k for H ₂ data
750 rpm	1.66.10 ⁻⁵ (A2)	3.3.10 ⁻⁶ (R2)
	3.33.10 ⁻⁵ (A3)	2.21.10 ⁻⁶ (R3)
875 rpm	1.66.10 ⁻⁵ (A2)	4.8.10 ⁻⁶ (R2)
	3.33.10 ⁻⁵ (A3)	4.37.10 ⁻⁶ (R3)
925 rpm	3.33.10 ⁻⁵ (A2)	1.11.10 ⁻⁵ (R2)
	5.10 ⁻⁵ (A3)	7.55.10 ⁻⁵ (R3)
1000 rpm	5.10 ⁻⁵ (A2)	1.0.10 ⁻⁵ (R2)
	6.67.10 ⁻⁵ (A3)	7.03.10 ⁻⁵ (R3)

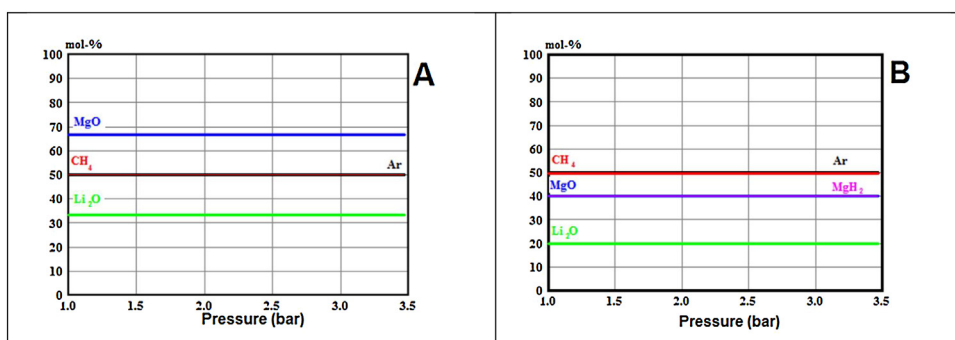
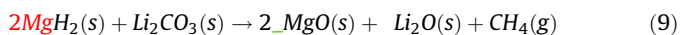


Fig. 9. Equilibrium composition (mol %) as a function of pressure of 2MgH₂-Li₂CO₃ (A) and 4MgH₂-Li₂CO₃ (B).

that MgO and Li₂O are stable in the condensed phase in the entire range of pressure investigated, while CH₄ appears as the only product in gas phase (Fig. 9). The equilibrium composition of these phases was constant and independent of the total gas pressure of the system at room temperature. As it was seen for MgH₂-Li₂CO₃ with 2:1 ratio, whole oxidation of MgH₂ to MgO is predicted (Fig. 9A), while for 4:1 ratio, free MgH₂ remains without reacting (Fig. 9B). The global reaction based on these thermodynamic calculations can be expressed for the 2:1 ratio as:



In the case of the 4:1 ratio, it is expected the presence of 2 mol of unreacted MgH₂ in the solid products. For thermodynamic calculations performed considering that the starting MgH₂-Li₂CO₃ mixture contains a molar ratio minor than 2:1 or 4:1 due to partial decomposition of MgH₂ to Mg in the starting mixture (Figs. S5A and S5B, respectively), the formation of C or Li₂C₂ was predicted. From Raman measurements no evidence of the appearance of C (bands at about 1580 and 1340 cm⁻¹) and/or Li₂C₂ (band at 1873 cm⁻¹, [34]) was obtained.

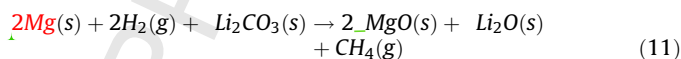
The formation of H₂ in the gas phase was not predicted from thermodynamic calculations independently of the starting MgH₂-Li₂CO₃ molar ratio (Figs. 9 and S5). Its detection during milling of the MgH₂-Li₂CO₃ mixture (Fig. 5) could be related with some kinetic restrictions operating in the reaction system, which hinder its consumption to form CH₄. In fact, the amount of H₂ available in gas phase exceeds the necessary quantity to produce an extra amount of CH₄ (Fig. 6), suggesting that its availability is not a limiting factor. Milling of pure MgH₂, using the same experimental mechanochemical conditions applied to the 2MgH₂-Li₂CO₃ mixture, demonstrates that H₂ is formed by direct MgH₂ decomposition (Fig. S6):



In contrast, no evidence of CO or CO₂ formation was observed after milling pure Li₂CO₃. Moreover, when MgH₂ was milled simultaneously with Li₂CO₃ in the same experimental conditions, H₂ release is promoted (Fig. S6) from the beginning of the reaction. Among the possible reasons, one is that the presence of a second phase with different mechanical properties (Li₂CO₃) modifies the milling conditions, affecting the energy transfer during fracturing and cold working phenomena of the powders. Other possible explanation is that the presence of Li₂CO₃ modifies the stability of MgH₂ by superficial oxidation and favors its decomposition.

Reaction (10) explains the presence of H₂ measured by GC but not envisaged from thermodynamic calculations. As it was previously shown, the amount of H₂ formed exceeds at least in a factor of 2 that corresponding to CH₄ (Fig. 6). According to kinetic studies (Fig. 8), the hydrogen release is controlled by the reaction

interface between MgH₂/Mg or MgH₂/MgO. The formation of Mg via reaction (10) allows its reaction with Li₂CO₃ to produce CH₄ in a H₂ rich environment:



Reaction (11) is thermodynamically favored at room temperature [34]. The combination of reactions (10) and (11) gives the global reaction (9), predicted from thermodynamic calculations. Considering that rate constant for the contracting volume is proportional to the rate constant of the interface-controlled reaction and inversely proportional to the particle length [35], the increment in the rate constant with the milling rotation rate (Table 2) can be attributed to the improvement of the microstructure refinement of the Mg based phases (Figs. 3 and 4).

Considering that reaction (10) is a fast process and that it does not control the global reaction rate, reactions (9) and (11) could occur simultaneously to produce CH₄. An inspection of the relative change of the MgH₂ and Mg amounts with the milling time for 750 rpm and 1000 rpm (Table S2) shows that the amount of MgH₂ decreases, while the Mg amount increases. This behavior demonstrates that reaction (10) is actually occurring, justifying the detection of H₂ in the gas phase and the increment in the relative amount of Mg with the milling time. In addition, the amount of MgH₂ decreases due to its consumption by direct reaction (9) or combination of reactions (10) and (11). The formation of CH₄ seems to be kinetically restricted by the high stability observed for Li₂CO₃ under mechanochemical processing. In fact, experimental results demonstrate the absence of CO and CO₂ in the gaseous phase as a carbon source. Moreover, no alternative carbon source in the solid phase, such as amorphous carbon or Li₂C₂, were detected (Figs. 1 and 2). Then, kinetic constrains for CH₄ production involve the formation of Li₂O and MgO through reaction (9) and/or (11). The transfer of oxygen atoms from Li₂CO₃ toward two different oxides is necessary and can possibly be the rate-controlling process. In this context, the nucleation and growth models are suitable to describe the reaction mechanism (Fig. 7).

Finally, in this study it was demonstrated for the first time that Li₂CO₃ and MgH₂ can be used as CO₂ and H₂ sources to effectively produce a CH₄/H₂ fuel mixture at room temperature (see Fig. 10). All resulting products of the mechanochemical treatment of Li₂CO₃ and MgH₂ are used: the CH₄-H₂ mixture as fuels in internal combustion engines /gas turbines; and the Mg-Li oxides as absorbers of CO₂ for the treatment of exhaust gases of a power plant. In the whole cycle process, only MgH₂ is consummated. The new addition of MgH₂ allows starting the cycle again by the reaction with Li carbonate (or Mg carbonate).

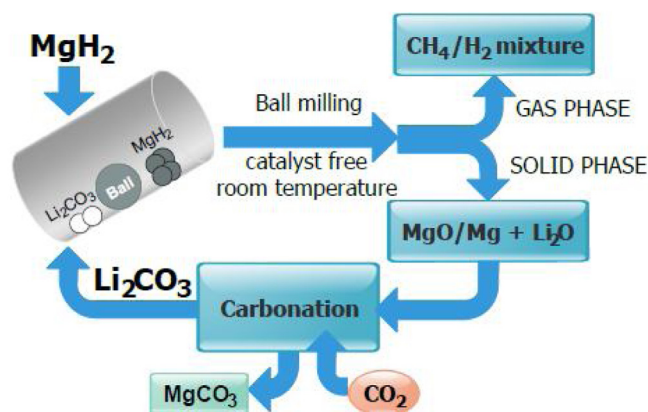


Fig. 10. Schematic representation of the mechanochemical reaction between Li_2CO_3 and MgH_2 and their integration.

By comparison of our mechanochemical processing of MgH_2 - Li_2CO_3 with alternative processes to produce CH_4 , different advantages emerge. Traditional CO_2 hydrogenation is a process with significant kinetic constraints due to the high stability of CO_2 molecule. Therefore, it requires the utilization of active and selective catalysts to favor this reaction and produce mainly CH_4 , avoiding the formation of CO as intermediate product. Even though, CO_2 hydrogenation involves high temperatures, atmospheric pressure and a $4\text{H}_2:1\text{CO}_2$ molar ratio [36,37]. Another process involves MgH_2 to reduce CO_2 without the use of catalysts, but requires 48 h at 450°C [38]. Although mechanochemical reaction between MgH_2 and CO_2 gas occurs at room temperature, long milling times (24 h) are required to obtain yields lower (6% and 15% at 450 rpm and 550 rpm, respectively) [16] than those obtained in this work (3 h of milling, yield of 25% at 1000 rpm, Table S1). Reaction of magnesite (MgCO_3) as CO_2 source with H_2 needs 475 – 505°C for the CH_4 production, with simultaneous formation of CO [26].

Recently, the use of dual function materials for CO_2 capture and catalytic conversion to CH_4 allows the temperature to be reduced to about 200°C , but the use of noble metals is required [39]. Taking advantage of the mechanochemical processing as a simple, efficient and scalable technology, in this work the CO_2 contained in Li_2CO_3 was reduced using MgH_2 to produce CH_4/H_2 fuels at room temperature with high selectivity, avoiding the use of catalyst and/or solvents, minimizing the generation of waste.

5. Conclusions

In this work, the production of the CH_4/H_2 fuel mixtures by high-energy mechanochemical activation of the Li_2CO_3 - MgH_2 system at room temperature was studied for the first time. The products were obtained through a free-catalyst reaction, with high selectivity and using Li_2CO_3 and MgH_2 as solid portable sources of CO_2 and H_2 , respectively. The analyses done by X-ray diffraction, FTIR and Raman spectroscopies, electron scanning microscopy and gas chromatography techniques to study the evolution of the Li_2CO_3 - MgH_2 system during milling was complemented with thermodynamic calculations. Theoretical calculations predict the complete CO_2 reduction to CH_4 , with simultaneous formation of MgO and Li_2O . Experimental evidence supports the progressive formation of MgO , MgH_2 consumption and the appearance of Li_2O when milling time increases. The presence of H_2 in the gas phase was due to the high Li_2CO_3 stability and the consequent kinetic restrictions in the CH_4 formation. The conversion of MgH_2 - Li_2CO_3 to CH_4/H_2 mixtures depends on the milling time, rotation speed and H_2/CO_2 molar ratio.

The experimental data of CH_4 and H_2 conversion were fitted using theoretical kinetic models with R^2 as a goodness of fit parameter. The best kinetic model for describing the CH_4 evolution was found to be the JMA (Johnson-Mehl-Avrami) model. It can be associated with MgO and Li_2O nucleation and their three-dimensional growth along the interface between Li_2CO_3 and Mg/MgH_2 . In the case of H_2 release, the contracting volume model fits very well the experimental data and the process is controlled by the reaction interface between MgH_2/Mg or MgH_2/MgO .

Therefore, the combination of carbonates and metal hydrides are promising portable systems for the *in situ* preparation of CH_4/H_2 mixture fuels. The use of Li_2CO_3 as a CO_2 source allows for recycling exhausted absorbents from the post-combustion technologies and to reuse CO_2 efficiently producing *in situ* fuels with high added value. Currently we are developing alternative methods and innovative explorations to improve the rate of the aforementioned reactions, keeping selectivity and the mild experimental conditions.

CRediT authorship contribution statement

María L. Grasso: Data curation, Validation, Visualization, Formal analysis, Investigation, Writing - original draft. **Luisa Fernández Albanesi:** Data curation, Validation, Investigation, Writing - review & editing. **Sebastiano Garroni:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision. **Gabriele Mulas:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision. **Fabiana C. Gennari:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The present work is part of the CO2MPRISE, “ CO_2 absorbing Materials Project- RISE”, a project that has received funding from the European Union’s Horizon 2020 research and innovation programme, under the Marie Skłodowska-Curie Grant Agreement No 73487. The work was also supported by CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), ANPCyT (Agencia Nacional de Promoción Científica y Tecnológica), CNEA

(Comisión Nacional de Energía Atómica) and UNISS (Università degli Studi di Sassari). The authors also thank Bernardo Pentke (Departamento Fisicoquímica de Materiales /CAB- CNEA) for the SEM micrographs and Sebastián Anguiano for the Raman measurements (Laboratorio de Fotónica y Foelectrónica /CAB-CNEA).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2020.101209>.

References

- [1] NASA Global Climate Change, (2020) . <https://climate.nasa.gov/vital-signs/carbon-dioxide/> (Accessed 07 April 2020).
- [2] R.K. Pachauri, L. Meyer (Eds.), Climate Change 2014: Synthesis Report, IPCC, Geneva, Switzerland, 2014, pp. 151.
- [3] A. Rafiee, K.R. Khalilpour, D. Milani, M. Panahi, Trends in CO₂ conversion and utilization: a review from process systems perspective, *J. Environ. Chem. Eng.* 6 (2018) 5771–5794, doi:<http://dx.doi.org/10.1016/j.jece.2018.08.065>.
- [4] H. Sun, Y. Zhang, Z. Guan, J. Huang, C. Wu, Direct and highly selective conversion of captured CO₂ into methane through integrated carbon capture and utilization over dual functional materials, *J. CO₂ Util.* 38 (2020) 262–272, doi:<http://dx.doi.org/10.1016/j.jcou.2020.02.001>.
- [5] NIST Chemistry WebBook, (2018) . <https://webbook.nist.gov/chemistry/> (Accessed 30 March 2020).
- [6] S. Specchia, S. Tacchino, V. Specchia, Facing the catalytic combustion of CH₄/H₂ mixtures into monoliths, *Chem. Eng. J.* 167 (2–3) (2011) 622–633, doi:<http://dx.doi.org/10.1016/j.cej.2010.10.051>.
- [7] Y. Yu, W. Lin, L. Li, Z. Zhang, Effects of hydrogen addition on the combustion characteristics of diesel fuel jets under ultra-high injection pressures, *Int. J. Hydrogen Energy* 45 (17) (2020) 10592–10601, doi:<http://dx.doi.org/10.1016/j.ijhydene.2019.08.242>.
- [8] M. Muradov, Chapter 8. transition to low- and zero- carbon energy and fuels, *Liberating Energy From Carbon: Introduction to Decarbonization*, first ed., Springer, New York, 2014, pp. 279–323.
- [9] M.L. Grasso, J. Puszkiel, L. Fernández Albanesi, M. Dornheim, C. Pistidda, F.C. Gennari, CO₂ utilization for methane production via catalytic promoted by hydrides, *Phys. Chem. Chem. Phys.* 21 (2019) 19825–19843, doi:<http://dx.doi.org/10.1039/C9CP03826D>.
- [10] M.L. Grasso, J. Puszkiel, C. Pistidda, A. Santoru, M. Dornheim, F.C. Gennari, CO₂ reactivity with Mg₂NiH₄ synthesized by in situ monitoring mechanical milling, *Phys. Chem. Chem. Phys.* 22 (2020) 1944–1952, doi:<http://dx.doi.org/10.1039/C9CP05697A>.
- [11] C. Bolm, J.G. Hernández, Mechanochemistry of gaseous reactants, *Angew. Chem. Int. Ed. Engl.* 58 (11) (2019) 3285–3299, doi:<http://dx.doi.org/10.1002/anie.201810902>.
- [12] P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J.M. Criado, F. Delogu, E. Dutková, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskaia, K. Wiczorek-Ciurowa, Hallmarks of mechanochemistry: from nanoparticles to technology, *Chem. Soc. Rev.* 42 (2013) 7571–7637, doi:<http://dx.doi.org/10.1039/C3CS35468G>.
- [13] G. Mulas, R. Campesi, S. Garroni, F. Delogu, C. Milanese, Hydrogenation of Carbon monoxide over nanostructured systems: mechanochemical approach, *Appl. Surf. Sci.* 257 (2011) 8165–8570, doi:<http://dx.doi.org/10.1016/j.apsusc.2011.03.024>.
- [14] V. Farina, N.S. Gamba, F. Gennari, S. Garroni Sebastiano, F. Torre, A. Taras, S. Enzo, G. Mulas, CO₂ hydrogenation induced by mechanochemical activation of olivine with water under CO₂ atmosphere, *Front. Energy Res.* 7 (2019) 107–117, doi:<http://dx.doi.org/10.3389/fenrg.2019.00107>.
- [15] F. Torre, V. Farina, A. Taras, C. Pistidda, A. Santoru, J. Bednarcik, G. Mulas, S. Enzo, S. Garroni, Room temperature hydrocarbon generation in olivine powders: effect of mechanical processing under CO₂ atmosphere, *Powder Technol.* 364 (2020) 915–923, doi:<http://dx.doi.org/10.1016/j.powtec.2019.10.080>.
- [16] B.-X. Dong, L.-Z. J. Zhao, Y.-L. Wang, W.-L. Teng, L. Liu, ME Wang, Mechanochemical synthesis of COx-free hydrogen and methane fuel mixtures at room temperature from light metal hydrides and carbon dioxide, *Appl. Energy* 204 (2017) 741–748, doi:<http://dx.doi.org/10.1016/j.apenergy.2017.07.088>.
- [17] K. Pu, Y. Yang, X.Q. M. Gao, Y. Liu, H. Pan, Room temperature conversion of Carbon Dioxide into fuels gases by mechanochemically reacting with metal hydrides, *Chem. Select.* 2 (2017) 5244–5247, doi:<http://dx.doi.org/10.1002/slct.201700834>.
- [18] B.-X. Dong, L. Wang, J. Zhao, Y.-L. Teng, C. Ping, W. Zhu, H.-B. Chen, W.-L. Liu, Highly selective room-temperature catalyst-free reduction of alkaline carbonates to methane by metal hydrides, *Energy Technol.* 7 (2019) 1800719, doi:<http://dx.doi.org/10.1002/ente.201800719>.
- [19] M.L. Grasso, M.V. Blanco, F. Cova, J.A. González, P. Arneodo Larochette, F.C. Gennari, Evaluation of the formation and carbon dioxide capture of Li₄SiO₄ using in situ synchrotron powder X-ray diffraction studies, *Phys. Chem. Chem. Phys.* 20 (2018) 26570–26579, doi:<http://dx.doi.org/10.1039/c8cp03611>.
- [20] X. Yan, Y. Li, X. Ma, J. Zhao, Z. Wang, Performance of Li₄SiO₄ material for CO₂ capture: a review, *Int. J. Mol. Sci.* 20 (2019) 928–950, doi:<http://dx.doi.org/10.3390/ijms20040928>.
- [21] Y. Zhang, Y. Gao, H. Pfeiffer, B. Louis, L. Sun, D. O'Hare, Q. Wang, Recent advances in lithium containing ceramics based sorbents for high-temperature CO₂ capture, *J. Mater. Chem. A Mater. Energy Sustain.* 7 (2019) 7962–8005, doi:<http://dx.doi.org/10.1039/C8TA08932A>.
- [22] D. Peltzer, J. Múnera, L. Cornaglia, Operando Raman spectroscopic studies of lithium zirconates during CO₂ capture at high temperature, *RSC Adv.* 6 (2016) 8222–8231, doi:<http://dx.doi.org/10.1039/C5RA21970A>.
- [23] I. Alcérreca-Corte, E. Fregoso-Israel, H. Pfeiffer, CO₂ absorption on Na₂ZrO₃: a kinetic analysis of the chemisorption and diffusion processes, *J. Phys. Chem. C* 112 (2008) 6520–6525, doi:<http://dx.doi.org/10.1021/jp710475g>.
- [24] D. Jagadeesan, M. Eswaramoorthy, C.N.R. Rao, Investigations of the conversion of inorganic carbonates to methane, *Chem. Sus. Chem.* 2 (2009) 878–882, doi:<http://dx.doi.org/10.1002/cssc.200900152>.
- [25] S. Lux, G. Baldauf-Sommerbauer, M. Siebenhofer, Hydrogenation of inorganic metal carbonates: a review on its potential for carbon dioxide utilization and emission reduction, *Chem. Sus. Chem.* 11 (2018) 3357–3375, doi:<http://dx.doi.org/10.1002/cssc.201801356>.
- [26] G. Baldauf-Sommerbauer, S. Lux, W. Aniser, M. Siebenhofer, Reductive calcination of mineral magnesite: hydrogenation of carbon dioxide without catalysts, *Chem. Eng. Technol.* 39 (11) (2016) 2035–2041, doi:<http://dx.doi.org/10.1002/ceat.201600094>.
- [27] L. Alexander, P.H. Klug, Determination of crystalline size with the X-Ray spectrometer, *J. Appl. Phys.* 21 (1950) 137–147, doi:<http://dx.doi.org/10.1063/1.1699612>.
- [28] H.S.C. Outokumpu, Chemistry For Windows, Version 6.1, Outokumpu Research Oy, Finland, 2009.
- [29] P. Pasierb, S.K. ornicki, M. Rokita, M. Rekas, Structural properties of Li₂CO₃-BaCO₃ system derived from IR and Raman spectroscopy, *J. Mol. Struct.* 596 (1–3) (2001) 151–156, doi:[http://dx.doi.org/10.1016/S0022-2860\(01\)00703-7](http://dx.doi.org/10.1016/S0022-2860(01)00703-7).
- [30] G. Weber, E. Sciora, J. Guichard, F. Bouyer, I. Bezverkhyy, Investigation of hydrolysis of lithium oxide by thermogravimetry, calorimetry and in situ FTIR spectroscopy, *J. Therm. Anal. Calorim.* 132 (2) (2018) 1055–1064, doi:<http://dx.doi.org/10.1007/s10973-017-6943-7>.
- [31] A. Ansari, A. Ali, M. Asif, Shamsuzzaman, Microwave-assisted MgO NPs catalyzed one-pot multicomponent synthesis of polysubstituted steroidal pyridines, *New J. Chem.* 42 (2018) 184–197.
- [32] J. Hong, M.K. Park, E.J. Lee, D.E. Lee, D.S. Hwang, S. Ryu, Origin of new broad raman d and g peaks in annealed graphene, *Sci. Rep.* 3 (2012) 2700.
- [33] A. Khawam, D. Flanagan, Solid state kinetic models: basics and mathematical fundamentals, *J. Phys. Chem. B* 110 (2006) 17315–17328, doi:<http://dx.doi.org/10.1021/jp062746a>.
- [34] N. Tian, C. Hua, Z. Wang, L. Chen, Reversible reduction of Li₂CO₃, *J. Mater. Chem. A Mater. Energy Sustain.* 3 (2015) 14173–14177, doi:<http://dx.doi.org/10.1039/C5TA02499D>.
- [35] Y. Pang, Q. Li, A review on kinetic models and corresponding analysis methods for hydrogen storage materials, *Int. J. Hydrogen Energy* 41 (2016) 18072–18087, doi:<http://dx.doi.org/10.1016/j.ijhydene.2016.08.018>.
- [36] B.C. Sempuga, Y. Yao, CO₂ hydrogenation from a process synthesis perspective: setting up process targets, *J. CO₂ Util.* 20 (2017) 34–42, doi:<http://dx.doi.org/10.1016/j.jcou.2017.05.004>.
- [37] S. Saeidi, N.A.S. Amin, M.Reza Rahimpour, Hydrogenation of CO₂ to value-added products-A review and potential future developments, *J. CO₂ Utilization* 5 (2014) 66–81, doi:<http://dx.doi.org/10.1016/j.jcou.2013.12.005>.
- [38] J. Zhao, Y.-F. Wei, Y.-L. Cai, L.-Z. Wang, J. Xie, Y.-Lei. Teng, W. Zhu, M. Shen, B.-X. Dong, Highly selective and efficient reduction of CO₂ to methane by activated alkaline earth metal hydrides without a catalyst, *ACS Sustain. Chem. Eng.* 7 (2019) 4831–4841, doi:<http://dx.doi.org/10.1021/acssuschemeng.8b05177>.
- [39] M.S. Duyar, S. Wang, M.A. Arellano-Treviño, R.J. Farrauto, CO₂ utilization with a novel dual function material (DFM) for capture and catalytic conversion to synthetic natural gas: an update, *J. CO₂ Util.* 15 (2016) 65–71, doi:<http://dx.doi.org/10.1016/j.jcou.2016.05.003>.