



Mechanochemical synthesis of CO_x-free hydrogen and methane fuel mixtures at room temperature from light metal hydrides and carbon dioxide



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HIGHLIGHTS

- The mechanochemical reactions of light metal hydrides with CO₂ were investigated.
- Mechanochemical reduction of CO₂ to CH₄ by light metal hydrides is highly selective.
- CO_x-free H₂-CH₄ fuel mixtures have been successfully generated by these reactions.
- The yield and mole fraction of CH₄ were examined under various condition.
- The work provides a new and simple method for *in situ* preparation of H₂-CH₄ fuel.

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ABSTRACT

In this work, we report a novel, simple and convenient method for CO₂ methanation and synthesis of hydrogen and methane fuel mixtures at room temperature. CO_x-free hydrogen and methane fuel mixtures have been successfully generated for the first time in one pot at room temperature through the solid/gas mechanochemical reactions of selected light metal hydrides with CO₂. It is noted that methane is the sole hydrocarbon product in the mechanochemical reactions of selected light metal hydrides with CO₂, which suggests that the mechanochemical reduction of CO₂ by light metal hydrides is highly selective. The yield and mole fraction of methane in the gas product depend mainly on the species of light metal hydride, rate and duration of ball milling, and CO₂ pressure.

1. Introduction

Over the past several decades, increasing levels of carbon dioxide (CO₂) in the atmosphere have become a major contributing factor to global warming and climate change [1,2]. However, CO₂ can also be considered to be a cheap, nontoxic, and abundant C-1 feedstock [3], especially if future fossil fuel-based power stations require carbon sequestration [4]. The use of CO₂ for the production of fuels and chemicals has attracted considerable attention given the current situation of fossil resource depletion and increase in CO₂ emissions. However, the activation of CO₂ remains one of the biggest challenges in chemistry, as CO₂ is a highly thermodynamically stable molecule.

Among all hydrocarbons, methane exhibits the highest hydrogen-to-carbon ratio and generates the smallest amount of CO₂ for each unit of heat that is released. Moreover, its gravimetric heat of combustion (55.7 MJ kg⁻¹) is greater than that of gasoline (46.4 MJ kg⁻¹) [5]. Given these merits, methane is considered a strong candidate as an alternative fuel [6]. However, a methane-powered vehicle is

unattractive because methane's poor combustion efficiency results in a narrow flammability range, slow burning speed, and high ignition temperature, which, in turn, result in an intensive energy requirement for ignition [7]. Interestingly, the disadvantages of methane as a fuel can be overcome by the addition of H₂ to produce hythane, a mixture of hydrogen and methane [8]. First, the flame speed of methane is greatly increased by the addition of hydrogen, ultimately reducing combustion duration and improving heat efficiency. Second, the addition of hydrogen also reduces the quenching distance of methane, thereby making the fuel easier to ignite with less energy input [9]. Therefore, hythane is considered one of the important fuels involved in achieving the transition of technical modes from a fossil fuel-based society to a terminal hydrogen-based society. Currently, hythane has been used commercially as vehicle fuel in the USA and India and has also received much attention from many individual companies. The large-scale application of hydrogen and methane fuel mixtures requires the development of a safe and efficient *in situ* preparation technology with a competitive volumetric energy density.

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Since CO₂ methanation technology was first proposed by the French chemist, Paul Sabatier [10,11], the reduction of CO₂ under mild conditions (mild temperature and pressure) has been extensively studied biologically [12], electrochemically [13,14], and photochemically [15–17]. Despite this, satisfactory levels of desired products have not been achieved because reaction rates for processes that lead to these valuable products require further improvement, while avoiding by-products such as CO, NO, and NH₃. In addition, detailed reduction mechanisms have not been established in most cases [1]. Although these CO₂ reduction technologies can be performed under mild conditions, expensive equipment is required and both the operating methods and reaction mechanisms are complicated for these technologies. Therefore, the development of simple methods that effectively and conveniently convert CO₂ into valuable hydrocarbon fuels under mild conditions is clearly an interesting international research priority. Mechanochemical syntheses are simple, efficient, inexpensive, and easily accessible methods for the preparation of compounds at room temperature [18,19]. In recent years, mechanochemical syntheses using ball milling and involving solid-gas reactions have been widely used [20]. However, little attention has been devoted to converting CO₂ into valuable chemicals or hydrocarbon fuels utilizing these mechanochemical methods.

As a type of ionic compounds with strong reducibility and low density [21], light metal hydrides are often used as reductants. They have also been combined with other materials into high-energy and high-density storage systems that are convenient and safe for hydrogen storage and transport. For example, a composite made from a light metal hydride (LiH, NaH, MgH₂, or CaH₂) and a light metal amide (LiNH₂ or Mg(NH₂)₂) has been recognized to be a good solid-state hydrogen storage system, because it offers relatively high gravimetric storage capacity (greater than 5.5 wt% of hydrogen can be released) [22,23]. Moreover, recent studies have also demonstrated that light metal hydrides can efficiently reduce small gas molecules such as NH₃ under mechanical ball milling conditions to produce H₂-containing fuels [24–26]. Inspired by these results, we expected light metal hydrides to be capable of reacting with CO₂ to generate hydrocarbon fuels under mechanical ball milling conditions at room temperature.

In this study, we, for the first time, demonstrate that CO₂ can be effectively reduced by selected light metal hydrides to exclusively produce CO_x-free mixtures of methane and hydrogen fuels through solid/gas mechanochemical reactions at room temperature. The experimental results indicate that the mechanochemical reduction of CO₂ to methane by light metal hydrides is highly selective. The yield and mole fraction of methane in the gas products depend mainly on the species of light metal hydrides, as well as the mechanical milling intensity and conditions. This study provides a new, simple and convenient method for CO₂ methanation and *in situ* preparation of CO_x-free hydrogen and methane fuel mixtures under mild conditions.

2. Material and method

2.1. Sample preparation

Lithium hydride (LiH) (98%, J & K Chemical Ltd., China), sodium hydride (NaH) (98%, Alfa Aesar), magnesium hydride (MgH₂) (98%, Alfa Aesar), calcium hydride (CaH₂) (98%, Alfa Aesar), and CO₂ (99.999%) were used in the following experiments. A weighed amount of LiH, NaH, MgH₂, or CaH₂ and 30 steel balls (6 mm diameter, about 27 g) were placed into a steel milling vessel with inner volume of about 70 cm³. The ball-to-powder weight ratio is approximately 30–260:1. CO₂ (0.1–1.0 MPa) was introduced into the milling vessel at room temperature, ensuring the molar ratio of LiH (or NaH)/CO₂ = 4 or MgH₂ (or CaH₂)/CO₂ = 2. Ball milling then was performed at 350–550 rpm for 1–48 h using a planetary ball milling apparatus (QM-3SP4). To minimize temperature fluctuations of the samples, the milling process was paused for 30 min for every hour of milling. All

samples were handled in an Ar-filled (> 99.999%) glove box (Mikrouna, China) equipped with a circulating purification system, in which typical H₂O/O₂ levels were below 0.1 ppm.

2.2. Estimation of the reaction yields and mol% of CH₄

To estimate the reaction yields and mol% of CH₄ in the gas products after the reactions of the various metal hydrides with CO₂, the gases produced were analyzed by an on-line gas chromatograph (SP-6890) using a 5 Å molecular sieve column connected to a TCD detector. Standard curves (Fig. S1) for H₂ and CH₄ were constructed by plotting GC peak area vs different inject partial pressure for quantification. The reaction yields and mol% of CH₄ in each sample were calculated by the standard curve method. The yield of CH₄ and mole percent of methane were calculated as follows: yield of CH₄ = moles of CH₄ produced/moles of CO₂ supplied, and mole percent of CH₄ = moles of CH₄ produced/moles of gas produced.

2.3. Structural and morphological characterizations

The gas produced from each reaction was characterized by gas Fourier transform IR spectroscopy (FTIR) (Vertex 70 v, Bruker, German) in transmission mode. The morphologies of the solid products from the various mechanochemical reactions were characterized by scanning electron microscopy (S-4800II, Japan). The structural characteristics of the solid composites produced were examined by X-ray diffraction (XRD) measurements (AXS D8 ADVANCE, Bruker, German) and Fourier transform IR spectrometer (FTIR) (TENSOR 27, Bruker, Canada) in transmission mode. Samples pellets were prepared by cold pressing a mixture of the sample powder and potassium bromide (KBr) powder at a weight ratio of 1:20. Each spectrum was created from 16 scans averaged with a scan resolution of 4 cm⁻¹. The samples were covered with a polyimide sheet to protect them against oxidation during XRD measurements. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 VersaProbe system using monochromatic Al Kα radiation (1486.6 eV) at an accelerator power of 15 kW.

3. Results and discussion

3.1. The mechanochemical reactions of alkali metal hydrides with CO₂

The mechanochemical reactions of alkali metal hydrides with CO₂ were initially investigated because these metal hydrides have higher reaction activities than those of other light metal hydrides. LiH or NaH was ball milled for 24 h under a 0.25 MPa CO₂ atmosphere with a mol ratio of MH(M = Li or Na)/CO₂ = 4 at 350–550 rpm. The gas products were characterized by GC and FTIR. Fig. 1a shows the GC profiles of the gas products obtained after 24 h from the mechanochemical reactions of LiH with CO₂ at 350, 450, and 550 rpm. In addition to GC peak corresponding to H₂ with a retention time of around 0.53 min, there is an obvious GC signal corresponding to CH₄, with a retention time of around 2.15 min (Fig. 1a). When the rate of ball milling is above 350 rpm, which is indicative of through mechanical ball milling, CO₂ is effectively reduced by lithium hydride to produce CH₄ and H₂. The relative proportions of CH₄ in the gases produced by the mechanochemical reactions of LiH with CO₂ at 350, 450, and 550 rpm are different (Fig. 1a), indicating that the composition of the gas products depends on the rate of ball milling. Fig. 1b depicts the gas FTIR spectra of the gas products obtained after 24 h from the mechanochemical reactions of LiH with CO₂ at 350, 450, and 550 rpm. Absorptions due to CH₄ at 3084, 3013, 2936, 1344, 1300, and 1266 cm⁻¹ dominate the FTIR spectra of the products obtained from these mechanochemical reactions at 350–550 rpm, further confirming the formation of CH₄. Moreover, absorptions expected for CO₂ and CO are absent in the FTIR spectra corresponding to reactions carried out at 450 and 550 rpm, indicating that CO₂ was completely consumed and that no CO

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