

## GENERATION OF H<sub>2</sub> GAS FROM SOLID BASED POLYMER WASTES MECHANICALLY MILLED WITH Ni AND Ca

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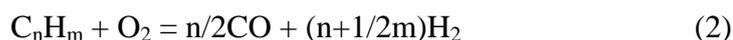
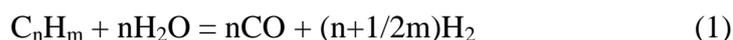
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**Abstract:** This paper discusses a process developed to produce high purity hydrogen gas from solid based hydrocarbons or polymers such as plastic wastes or biomass in a two-step process at temperatures below 600 °C. Polyethylene [–CH<sub>2</sub>–]<sub>n</sub> (PE), polyvinyl chloride [–CH<sub>2</sub>–CHCl–]<sub>n</sub> (PVC), Polystyrene [–CH<sub>2</sub>–CH(C<sub>6</sub>H<sub>5</sub>)–]<sub>n</sub>, Poly(vinyl alcohol) [–CH(OH)CH<sub>2</sub>–]<sub>n</sub>, cellulose C<sub>6</sub>(H<sub>2</sub>O)<sub>5</sub> as sample hydrocarbon based compounds were first prepared by milling with Ni(OH)<sub>2</sub> or Ni-doped LDH to provide Ni as catalyst for C–C bond rupture and Ca(OH)<sub>2</sub> or CaO to provide Ca for CO<sub>2</sub> or CO adsorption. In the second stage, the milled products were heated in He/Ar gas environments and product gases generated between 400–700 °C were evaluated for optimum conditions of hydrogen generation.

Results for all samples investigated showed that the addition of Ni and Ca to the samples and sufficient milling allowed high gas generation mainly composed of H<sub>2</sub> and CH<sub>4</sub>, CO, CO<sub>2</sub> during heating at temperatures from 400–600 °C. Carbon oxides (CO<sub>2</sub>, CO) were fixed as CaCO<sub>3</sub> and hydrogen gas with purity >95% and CO/CO<sub>2</sub> concentrations <0.5% were achieved. The process offers a novel approach to treat solid waste hydrocarbon based polymer by transforming it into hydrogen.

### 1. Introduction

Production of hydrogen which is a valuable raw material for chemical and petrochemical industry and as a clean energy for combustion has received greater attention in recent. It is usually achieved by the steam reforming of hydrocarbons with the assistance of catalyst and adsorbents. Generation of hydrogen from hydrocarbon based compounds and derivatives is well known and can be achieved by the steam reforming process with water Eq. (1) or by oxygen in the partial oxidation process Eq. (2), and product CO further participating in water–gas shift reaction for hydrogen Eq. (3) [1–4].



Steam reforming is most efficient and industrially applied process for hydrogen production. Among many catalysts (Rh, Ru, Pd, Pt, Cu, Co) offered in steam reforming reactions for C–C bond rupture in hydrocarbons, Ni is the most often used due to its low cost and high activity [2–4]. CaO and LDHs as CO<sub>2</sub> adsorbents is discussed in literature [5–8].

Although the steam reforming process has been successfully applied for industrial production of hydrogen from natural gas, there exists difficulty for direct application of this process for solid samples, particularly hydrocarbon–contained solid wastes or biomass samples. Gasification of the solid wastes may be one effort to produce gases which are used again for steam reforming to replace natural gas. Direct pyrolysis of the solid wastes to emit hydrogen will become possible if catalyst can be fully dispersed among the solid wastes. Recently we reported such a process to convert PE, PVC, PS, cellulose into hydrogen [9–12] by milling with Ca(OH)<sub>2</sub> or CaO and Ni(OH)<sub>2</sub> or Ni–doped LDH and heating the milled sample at temperatures in the range of 400–600 °C. Ni is fully dispersed among the samples and reduced into Ni–metal during heating operation, which works as catalyst to facilitate release of hydrogen and Ca to fix carbon oxides allowing production of hydrogen gas.

## 2. Experimental

PE, PVC, PS, PVA, cellulose, CaO, Ca(OH)<sub>2</sub> and Ni(OH)<sub>2</sub> chemical reagents used as starting materials were supplied by Wako Chemicals–Japan and the Ni–doped LDH was prepared by a mechanochemical route [12–14]. A 3.0 g sample mixture was milled by a planetary ball mill (Pulverisette – 7, Fritsch, Germany), which has two mill pots (45 cm<sup>3</sup> inner volume each) made of ZrO<sub>2</sub> with 7x15 mm diameter ZrO<sub>2</sub> balls. Milling time in this work was ranged from 30–120 min and mill speed from 300–700 rpm. Each polymer was mixed with Ca at equal molar ratio to fix carbon content and catalyst at varying amounts. Characterization by a set of analytical methods of X–ray diffraction (XRD), infrared spectroscopy (FT–IR), thermogravimetry–mass spectroscopy (TG–MS) and gas chromatography (GC) were performed on the milled and heated samples to monitor the process.

## 3. Results and discussion

### 3.1 PE[–CH<sub>2</sub>–]<sub>n</sub>–Ca(OH)<sub>2</sub>–Ni(OH)<sub>2</sub>/Ni–doped LDH sample systems

TG/MS analysis of gaseous products up to 700 °C showed H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O with H<sub>2</sub> patterns dominant between 400–500 °C, reaching maximum at 430 °C. H<sub>2</sub> concentration >95% was obtained for a mixture (6:14:1 = C:H<sub>2</sub>O:Ni) sample and the concentration of CO and CO<sub>2</sub> was kept below 0.5%. H<sub>2</sub> concentration dropped to between 60–90% when mole H<sub>2</sub>O was reduced to 12, 10, 7 moles resulting in an increase in CH<sub>4</sub> concentration to over 25%,

## PART II GASIFICATION

however, concentration of CO and CO<sub>2</sub> was consistently below 0.5% of gases collected. The intensity and concentration of H<sub>2</sub> gas generated increased as milling progressed from 10–60 min, mill speed from 300–700 rpm. Analysis of solid product after heating at 500 °C by XRD and TG–DTA showed that over 80% of the heated sample was CaCO<sub>3</sub> indicating that over 80% H<sub>2</sub> gas has been generated from PE sample. Water molecules in both hydroxides assist in water–gas shift reaction for H<sub>2</sub> gas generation with CaO as adsorbent for fixing CO<sub>2</sub> and Ni as catalyst assisting C–C bond rupture.

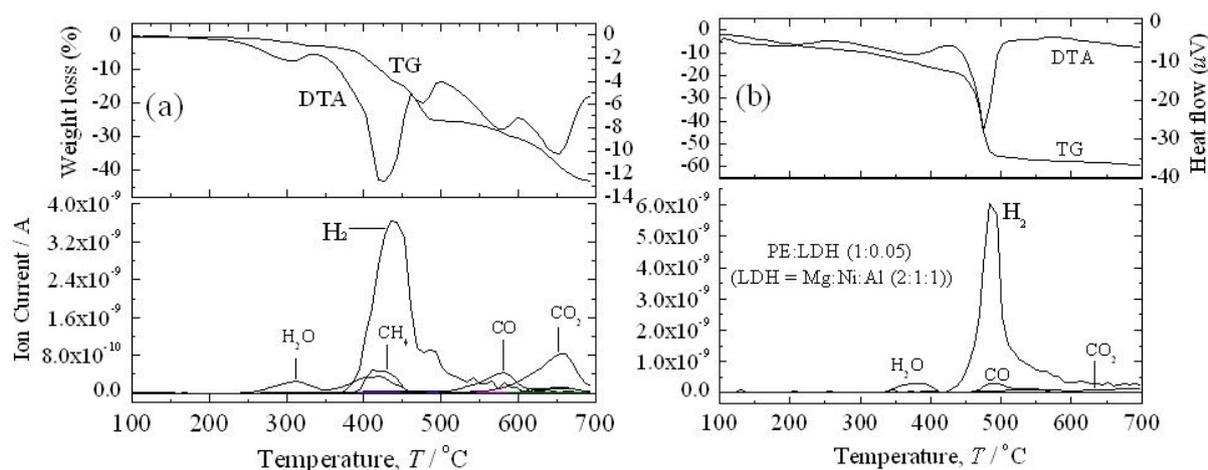


Fig 1 TG–DTA and TG–MS profiles of (a) PE/Ca(OH)<sub>2</sub>/Ni(OH)<sub>2</sub> (6:6:1) and (b) PE/LDH (1:0.05) mixtures prepared by milling for 60 min at 700 rpm and heated under helium flow of 300 ml.min<sup>-1</sup>.

A mixture of PE and Ni–doped LDH milled for 1 h followed by heating produced gaseous products mainly consisted of H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> with H<sub>2</sub> concentration over 80% between 450–550 °C, showing almost similar results for PE milled/mixed with Ni(OH)<sub>2</sub> is indicated in Fig. 1 [12].

Tab. 1 Total gaseous product generation and composition analysis of gas constituents for different sample systems at 400–550 °C.

Sample system	Tot. gas (%) (H <sub>2</sub> , CH <sub>4</sub> , CO, CO <sub>2</sub> )	Gas conc. (%)			
		H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>
PE–Ca(OH) <sub>2</sub> –Ni(OH) <sub>2</sub>	59.4	94.6	5.3	0.2	0.0
PE–Ca(OH) <sub>2</sub> –(Ni–LDH)	49.4	80.6	15.2	2.9	1.3
PVC–CaO–Ni(OH) <sub>2</sub>	28.4	95.4	3.9	0.5	0.2
PS–Ca(OH) <sub>2</sub> –Ni(OH) <sub>2</sub>	11.7	95.8	3.1	1.0	0.3
PVA–Ca(OH) <sub>2</sub> –Ni(OH) <sub>2</sub>	31.3	98.8	1.1	0.1	0.1
Cellulose–LiOH–Ni(OH) <sub>2</sub>	52.9	>97	<4.0	<0.5	<0.5

### 3.2 PVC–Ca(OH)<sub>2</sub>–Ni(OH)<sub>2</sub> sample system

Analyses by thermogravimetry–mass spectroscopy (TG–MS) and gas chromatography (GC) showed H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub> as main constituents. The results clearly show that addition of Ni(OH)<sub>2</sub> to provide nickel as catalyst and CaO as adsorbent to fix CO<sub>2</sub> and HCl gases generated during heating, assisted in clean H<sub>2</sub> generation with concentration near 90% at temperatures between 450–550 °C. Analyses of solids after heating by X–ray diffraction and TG–DTA techniques showed both CaOHCl and CaCO<sub>3</sub> as main phases in the product [10].

### 3.3 PS / PVA–Ca(OH)<sub>2</sub>–Ni(OH)<sub>2</sub> sample system

Analysis of the gaseous products by TG–MS, Gas–chromatography, and solid products by TG–DTA and XRD show that CO<sub>2</sub> gas was fixed as CaCO<sub>3</sub> at temperatures between 350–600 °C allowing generation of H<sub>2</sub> gas with concentrations >95% for PS and >98% for PVA . The results in this study show that milling of solid based hydrocarbon compounds with nickel and calcium hydroxides allows dispersion of nickel to hydrocarbon surfaces and facilitates C–C bond rupture in polymer(s) during heating at temperatures below 500 °C, at the same time calcium adsorbs CO<sub>2</sub>.

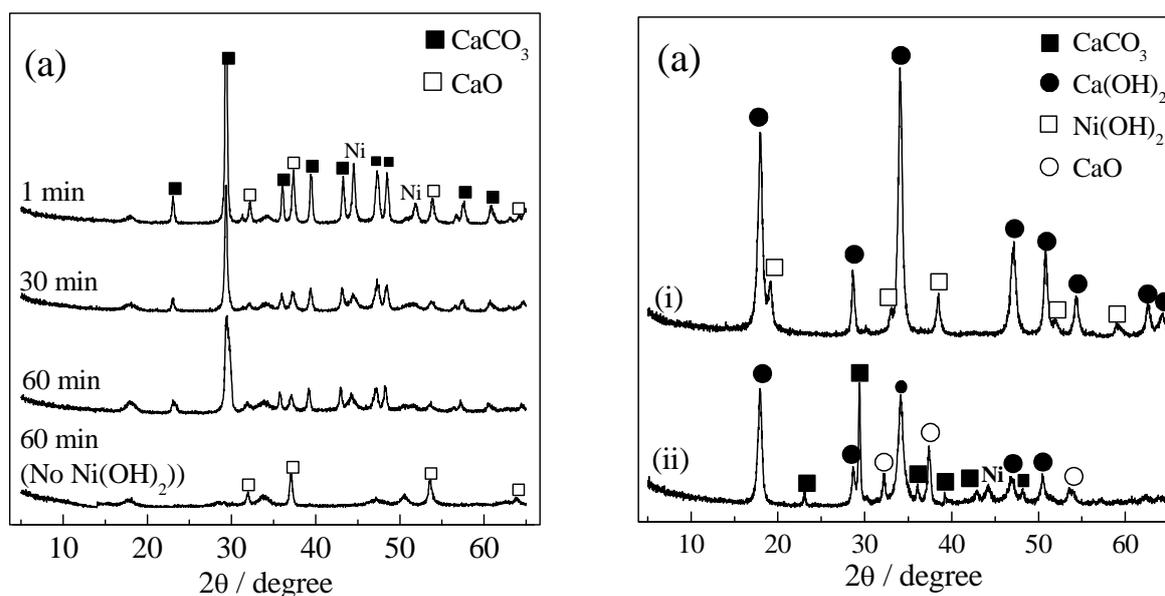


Fig. 2. XRD patterns of (a) PE/Ca(OH)<sub>2</sub>/Ni(OH)<sub>2</sub> (6:6:1) mixture prepared by milling for different times and heated at 500 °C for 120 min under helium gas; (b) PS/Ca(OH)<sub>2</sub>/Ni(OH)<sub>2</sub> (1:8:1) mixture; (i) product after milling for 60 min and, (ii) milled product heated at 500 °C under argon gas atmosphere.

Representative results in Fig. 2 show that carbon oxides (CO<sub>2</sub> and CO) released from decomposition of the polymers and / or solid hydrocarbon based compounds during heating is fixed as CaCO<sub>3</sub> allowing generation of high purity hydrogen gas.

### 3.4 Cellulose–LiOH–Ni(OH)<sub>2</sub> sample system

For this system, LiOH was used in place of Ca but for the same purpose to adsorb CO<sub>2</sub> released allowing generation of clean hydrogen gas. Use of Ni(OH)<sub>2</sub> and Ni(COOH)<sub>2</sub> were observed as to give higher hydrogen yield as compared to Ni–metal [11].

## 4. Conclusion

The results in the study investigating milling of solid based hydrocarbon compounds or polymers such as PE, PVC, PS, PVA, cellulose with Ca compounds (CaO, Ca(OH)<sub>2</sub>) and Ni compounds (Ni(OH)<sub>2</sub>, Ni–doped LDH) followed by heating at temperatures below 550 °C can allow generation of high purity hydrogen gas.

This shows both Ca and Ni offered as adsorbent/catalyst and water moles offered by hydroxides and LDH could allow water–gas shift reactions to proceed. Carbon oxides were clearly fixed by Ca and Li suggesting a separate gas separation process could be avoided in this process. More work is in progress to evaluate this process for further development by considering regeneration of adsorbents and catalysts and evaluation of costs in milling and heating operations.

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