A Mechanochemical Approach to Generate Hydrogen from Cellulose

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ABSTRACT

Cellulose [$C_6(H_2O)_5$] was co–ground with calcium ($Ca(OH)_2$) and nickel ($Ni(OH)_2$) hydroxides, followed by heating the ground samples up to 1000 °C for determination of temperature range at which hydrogen (H_2) gas can be generated. The results showed that the main gaseous products were; H_2, CH_4, H_2O, CO, and CO_2 with H_2 as the dominant gas generated between 350 and 550 °C. Analyses of the gaseous products by TG–MS and gas–chromatography, and solid products by TG–DTA and XRD showed that CO_2 gas was fixed as $CaCO_3$ at temperatures between 350 to 600 °C allowing generation of H_2 gas with concentrations ranging from 90 to 99% with carbon oxide (CO, CO_2) concentrations less than 1%. A plausible reaction mechanism is attributed to the interaction between cellulose and $Ca(OH)_2$ to transform the carbon in cellulose into $CaCO_3$, to which nickel works as catalyst. Accompanying the carbonate formation reaction, H_2 emission occurs correspondingly. This process offers a new approach to produce H_2 gas from the renewable biomass sources.

Keywords: hydrogen; cellulose; biomass; carbonation; mechanochemical

1. INTRODUCTION

The current production of hydrogen from non–renewable natural gas and petroleum does not meet the expectation for the development of hydrogen society resulting from the concern over the exhaustion of fossil fuel reserves and the environmental pollution. Hydrogen from water splitting by using renewable source such as solar energy remains as a challenge /1-2/, so does the biomass transformation. In case of cellulose, for example, yields of the derived gases for steam reforming are quite low particularly at a low heating rate with tar and char as main products /3-6/. Some progresses have been reported to produce hydrogen from renewable sources with less molecular weight than cellulose by means of catalyst use, supercritical process, CO_2 gas fixation or the combinations of several methods /7-12/.

Cellulose and other biomass are generally solids. The well known steam reforming process for natural gas can not be applied to these solid samples efficiently considering the low yield of gasification of cellulose. A solid state operation based on mechanochemical treatment particularly with other additives may offer a different approach. Triggered by mechanical force /13-14/, different pathway for gas emission may be expected. During our previous studies on the mechanochemical decompositions of chlorinated polymers, carbonation has been observed when CaO was used as

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dechlorination additive /15-16/, indicating the possible conversion of carbon from the dechlorinated hydrocarbons into carbonate. Referring to the effect of water in the steam reforming of natural gas, hydroxide of calcium is used as additive for the treatment. Therefore, as a new effort for converting solid plastic wastes, we have reported hydrogen emission by heating the ground samples of polymers with hydroxides at low temperatures /17-20/.

This work presents the application of the same concept to produce hydrogen from renewable source of cellulose based on mechanochemical treatment with hydroxide addition. Although many publications are available about the promoted effect of CO_2 capture for hydrogen generation during biomass gasification /21-23/, this process exhibits clearly different advantages, particularly with the catalysis promotion of nickel hydroxide as catalyst.

2. EXPERIMENTAL

2.1. Sample preparation

Cellulose [$C_6(H_2O)_5$] sample used was microcrystalline powder (~20 µm) obtained from Sigma–Aldrich, and other chemical reagents used; $Ca(OH)_2$, $Ni(OH)_2$, NiO and Ni powder (~3 µm) were supplied by Wako Pure Chemicals Osaka, Japan. Cellulose was mixed with $Ca(OH)_2$ at the same ratio of C to Ca (6 moles C in cellulose) and nickel compounds were added at 0.5 to 1 mole Ni for every mole cellulose. A 3.0 g sample mixture was ground in a planetary ball mill (Pulverisette – 7, Fritsch, Germany), which has two mill pots (45 cm^3 inner volume each) made of ZrO_2 with 7x15 mm diameter ZrO_2 balls. Grinding speed in this work was fixed at 700 rpm and grinding time ranged between 0 and 240 min, where hand–mixed sample is defined as the one ground for 0 min.

2.2. Gasification

TG/MS analysis of the ground samples to observe temperature range at which H_2 gas generation occurs was performed using a thermobalance connected to a quadrupole mass spectrometer (Rigaku Thermo–Mass: Thermo plus TG–8120 with M–201QA). The measurements were carried out with helium gas at a flow rate of 300 ml/min. About 5 mg of the milled samples were heated from 20 to 1000 °C at a heating rate of 20 °C/min through a transfer line heated to 200 °C.

For evaluating the concentration of component gaseous products upon heating, two methods were used to prepare gaseous samples and in both cases, 2.0 g of the ground samples was put on a sample holder and placed in a glass tube inserted in a furnace connected to line with argon gas flow. In the first method, the sample in the furnace was heated to 525 °C at a heating rate of 9 °C/min and maintained for 30 min. The product gases were collected in aluminium packs through the discharge line for three different temperature ranges during the heating process at 350–450 °C, 450–525 °C and 525 °C for gas concentration analysis. In the second method, the each 2.0 g sample was heated to an appointed temperature (350, 450, 550, 650 °C) and all the gases were collected in a cylinder as a single sample to evaluate both concentration and amount for the determination of hydrogen yield.

The gaseous products collected were quantitatively analyzed for component gas concentrations with a TCD micro–gas chromatograph with an MS–5A column and a Pora Plot Q column (Agilent Micro GC 3000A) under helium carrier gas using Cerity QA/QC program.

2.3. Characterization of solids

X–ray powder diffraction (XRD) analysis was carried out using Rigaku, RINT–2200/PC system with a CuKα irradiation source (λ = 1.5405 Å) at 40 kV and 50 mA for samples after grinding and the ground samples after heating.

3. RESULTS AND DISCUSSION

3.1. Analysis of gaseous product

TG–DTA and TG/MS patterns taken for the Cellulose–$Ca(OH)_2$–$Ni(OH)_2$ (C:Ca:Ni = 6:6:1) sample mixture ground for 2 h are shown in **Figure 1**. The first broad endothermic peak ranging from 100 to 300 °C is due to loss of H_2O and the main endothermic peak at

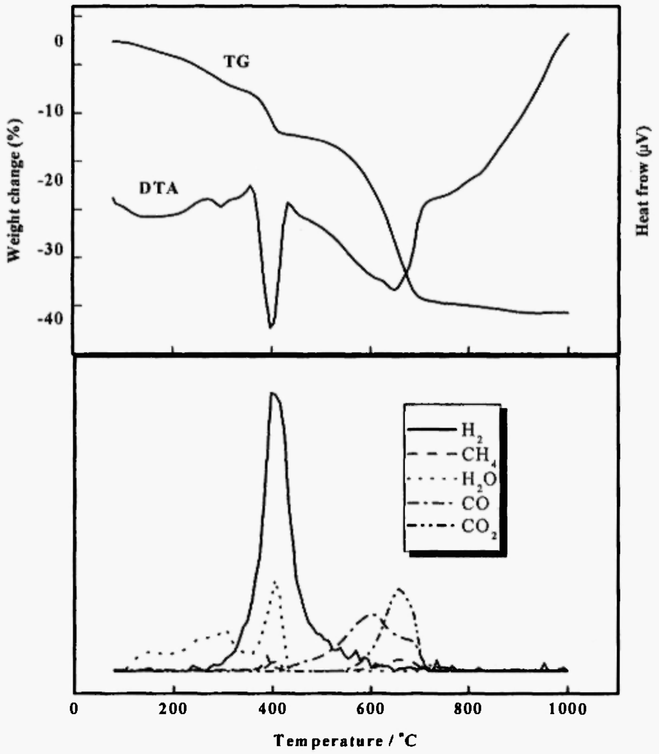

Fig. 1: TG-DTA and TG/MS spectra of cellulose/$Ca(OH)_2$/$Ni(OH)_2$ [C:Ca:Ni = 6:6:1 molar ratio] sample mixture ground for 2 h.

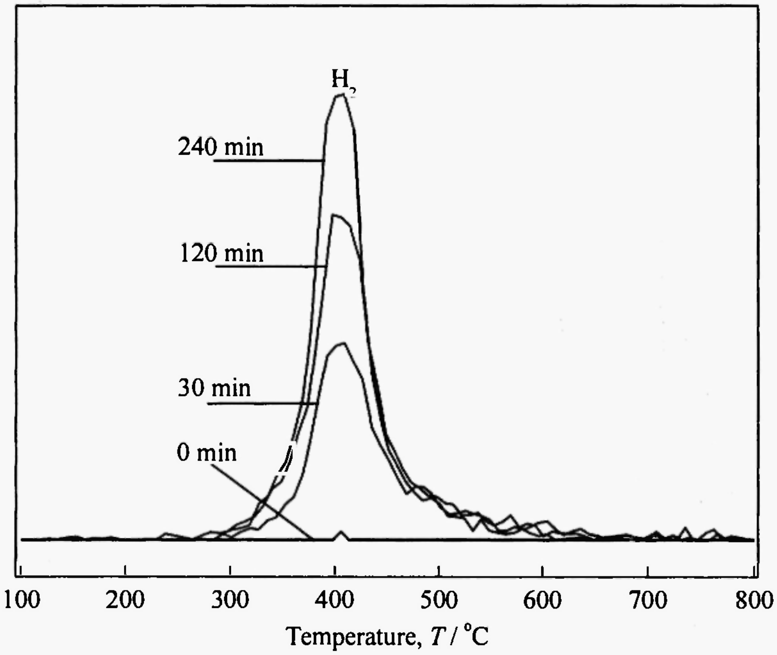

Fig. 2: spectrum of hydrogen (H_2) from the cellulose/$Ca(OH)_2$/$Ni(OH)_2$ [C:Ca:Ni = 6:6:1 molar ratio] sample mixture ground for different times.

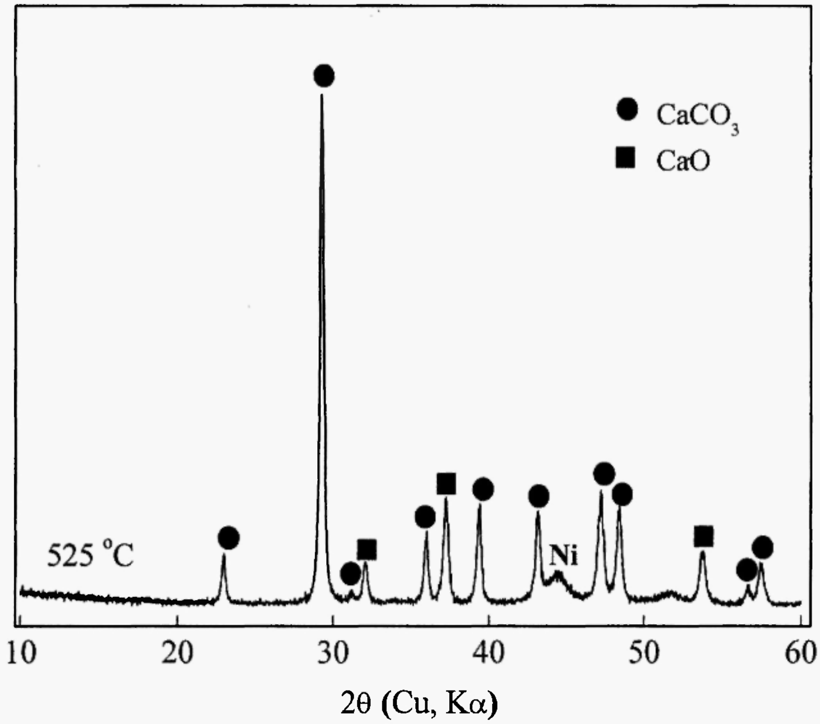

Fig. 3: X-ray diffraction pattern of the ground mixture [cellulose/$Ca(OH)_2$/$Ni(OH)_2$ (C:Ca:Ni = 6:6:1)] after heating at 525 °C for 30 min.

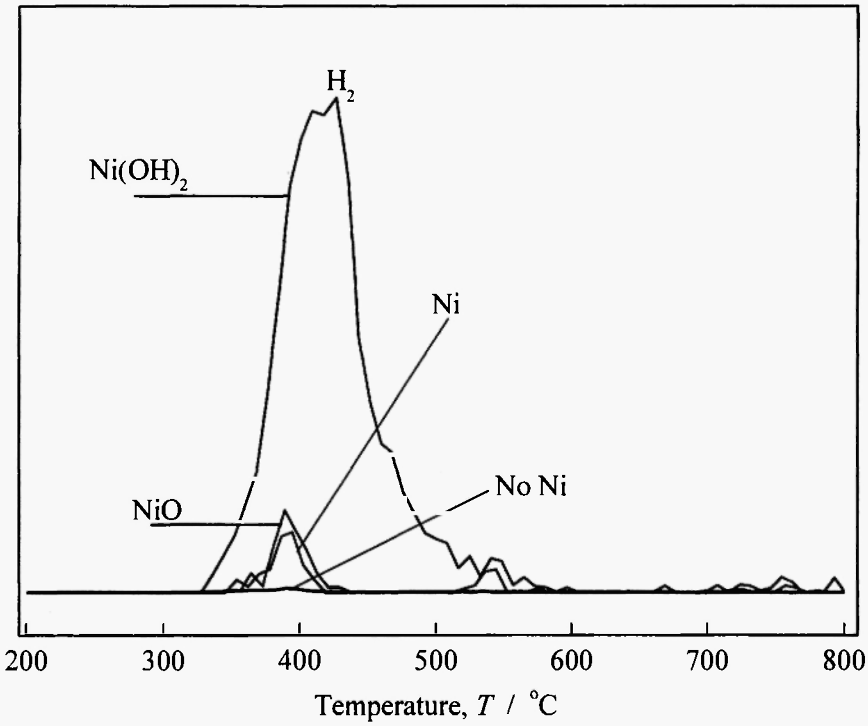

Fig. 4: MS spectrum of hydrogen (H_2) from cellulose ground with $Ca(OH)_2$ and different nickel samples [cellulose:$Ca(OH)_2$:$Ni(OH)_2$/NiO/Ni (6:6:1)] for 120 min.

400 °C is mainly due to release of H_2 gas and also H_2O and the other endothermic peak at 650 °C is due to the release of CO_2/CO gases. The TG–DTA profile can be related to characteristic peaks of each gas on TG/MS profile on the same figure. Gas emissions are observed with these temperature ranges with H_2 as dominant gas around 400 °C and CO/CO_2 gases around 650 °C. Small peak of CH_4 was also detected around 400 °C. The fact that H_2 emission occurs at different temperature from that of carbon oxides indicates the possibility to obtain high purity H_2 in a single step with no additional gas separation process.

In other preliminary experiments, hydroxides of aluminium and magnesium were ground separately with cellulose. Analyses of the ground samples by TG/MS showed no observable H_2 emission, although H_2O release remained as dominant composition.

Figure 2 shows the MS spectrum of only H_2 emission from the cellulose/$Ca(OH)_2$/$Ni(OH)_2$ [C:Ca:Ni = 6:6:1] sample mixture ground for different times. For the sample mixed by hand (0 min) no observable peak of H_2 appeared around 400 °C, however, clear peaks of H2 were observed for sample mixtures milled for different times at 700 rpm. The peak intensity of H2 increases as milling time is increased from 30 min to 240 min. The result indicates that the grinding operation was necessary to achieve high H_2 emission.

3.2. Characterization of solid samples

Figure 3 shows the XRD pattern of cellulose/Ca(OH)2/Ni(OH)2 [C:Ca:Ni = 6:6:1] sample mixture ground and heated at 525 °C for 1 h. No direct reaction was observed to occur during grinding operation. In the pattern of the heated sample, CaCO3 as the main phase, together with CaO and Ni metal were detected. If the mixtures of the three starting compounds decompose by heating without any reaction, apart from the gaseous composition and tar from cellulose, CaO and NiO should be observed in the solid residues with some char from cellulose. The formations of metal Ni and CaCO3 as well as the H2 emission (**Figure 1**) suggest that a different reaction pathway occurred when the ground sample was heated.

A simple discussion on the reaction mechanism is performed for hydrogen occurrence. Gasification of cellulose sample and subsequent reactions of the gases with hydroxides represented as following equations may be one explanation.

$$C_6(H_2O)_5 \rightarrow 2CH_4 + 4CO + H_2O \qquad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ (under Ni catalyst)} \qquad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (4)$$

Because there are no direct evidence to support such two step reaction mechanism and it is not easy to understand why the reactions may occur at such a low temperature, we discuss it in another route. Together with gas emission data from MS analysis and XRD pattern, the following formula can be used to represent the overall reaction mechanism. Further investigation is needed to understand such a solid state reaction.

$$C_6(H_2O)_5 + 6Ca(OH)_2 + 0.5Ni(OH)_2 = 11.5H_2 + 0.5Ni + 6CaCO_3 \qquad (5)$$

It is known that $Ni(OH)_2$ can be reduced to Ni metal by hydrogen, here from the reaction between cellulose and $Ca(OH)_2$ which has been confirmed in the preliminary test. The *in situ* formed nickel powders functions as catalyst to facilitate the reaction between cellulose and $Ca(OH)_2$ to form $CaCO_3$ and emit H_2. The addition of $Ni(OH)_2$ has been ranged from 0.5 to 2 moles for every mole of cellulose (C:Ni = 6:0.5–2.0 mole ratio), but the intensity of the H_2 emission from MS spectra remained consistently the same, indicating that $Ni(OH)_2$ addition at 0.5 mole for every mole cellulose can work well as catalyst when fully dispersed from milling operation. For easy detection of the Ni metal peak in the XRD patterns, 1 mole of $Ni(OH)_2$ was used instead of 0.5 moles.

We have also noticed that when hydroxides of magnesium and aluminium were used, the solid residues after heating were their corresponding oxides without formations of any carbonates. Although water was

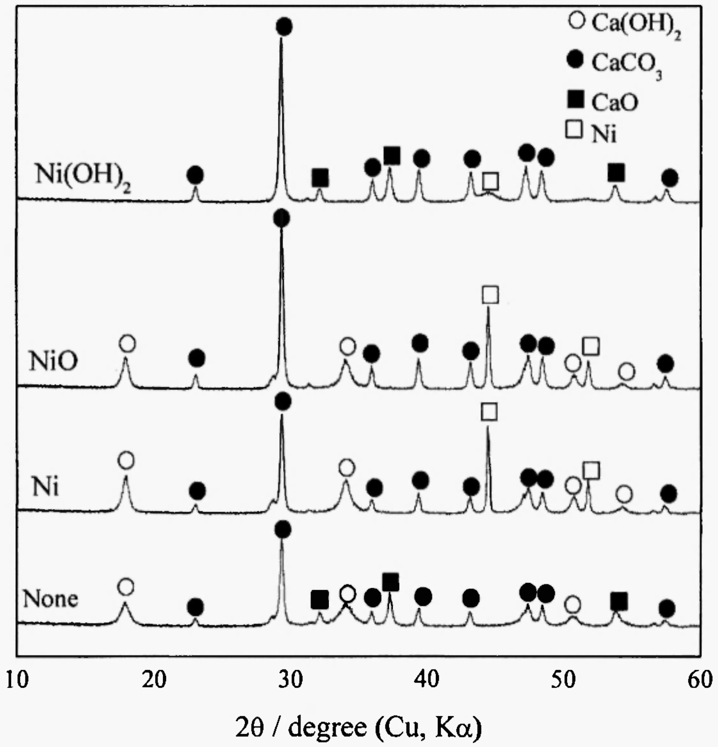

Fig. 5: X-ray diffraction patterns of [cellulose:$Ca(OH)_2$:$Ni(OH)_2$/NiO/Ni (6:6:1)] ground samples heated at 525 °C for 30 min.

released in the same way from the decomposition $Ca(OH)_2$, H_2 emission was not observed. Such a difference in H_2 emission between $Mg(OH)_2$ and $Ca(OH)_2$ indicates clearly that hydrogen emission does not depend on the water supply, but it depends on the formation of carbonate. The use of $Ca(OH)_2$ allows the conversion of carbon from cellulose into $CaCO_3$ resulting in H_2 generation. Such a reaction mechanism from the ground mixture works at a low temperature around 400 °C, different from the well known steam reforming process of which a higher temperature is usually required.

A yellow liquid of tar formation clearly observed during heating of cellulose without $Ca(OH)_2$ and $Ni(OH)_2$, continued to appear when cellulose was milled with $Ca(OH)_2$ and heated, although not as much as when cellulose was heated alone. However, when the cellulose sample was milled with both $Ca(OH)_2$ and $Ni(OH)_2$ and heated for hydrogen generation, a high carbon conversion was achieved and tar formation was not seen, indicating the mechanochemical treatment of cellulose with the hydroxides has successfully prevented tar formation. The black colour due to the formation of char composition in the solid sample implies also the incomplete carbonation of carbon in cellulose.

3.3. Effect of NiO and Ni

In industrially applied steam reforming process, Ni is widely chosen among other catalysts such as Rh, Ru, Pd, Pt, Cu, Co mostly due to its low cost and high activity [24–28]. In other studies we have successfully used $Ni(OH)_2$ to provide Ni as catalyst for C–C bond rupture and allow carbonization reaction to proceed resulting in H_2 gas generation, which again proved successful in the current study with cellulose.

The effect of Ni metal and NiO and compared against $Ni(OH)_2$ when milled and heated with cellulose and $Ca(OH)_2$ at (C:Ca:Ni = 6:6:1) molar ratio for H_2 generation was investigated. The MS spectra of different nickel compounds used is shown in **Figure 4** clearly indicating that $Ni(OH)_2$ addition provides the most significant impact on H_2 emission. Low peaks of

H_2 are observed for NiO and Ni which is clearly absent from sample mixtures with no nickel addition.

In order to understand the differences in H_2 emission observed for the three types of nickel compounds, the solid residues of the respective mixtures ground and heated at 525 °C for 1 h were examined by XRD (**Figure 5**). It was interesting to note that the peaks of Ni metal appeared in the sample mixtures containing $Ni(OH)_2$, NiO and Ni metal, which indicated that both the $Ni(OH)_2$ and NiO have been reduced to Ni metal during heating by the *in situ* formed H_2 gas. A notable difference in the peak intensity of Ni metal for the three samples were clearly observed, indicating that there exists a large difference in the crystal size and was calculated by the Scherrer's equation from the width at half its maximum intensity. The crystal size of the Ni resulting from the use of $Ni(OH)_2$ was found to be in the range of several nanometers. Since initial amount of nickel added was same for the three types, the existence of much finer particles could imply that more efficient dispersion of nickel to the cellulose or carbon surface during milling resulting in higher catalytic capacity. This fine nano particles of nickel formed *in situ* function as an excellent catalyst to facilitate C–C bond rupture in cellulose and allow reaction with Ca offered by $Ca(OH)_2$ to form $CaCO_3$ resulting in H_2 gas.

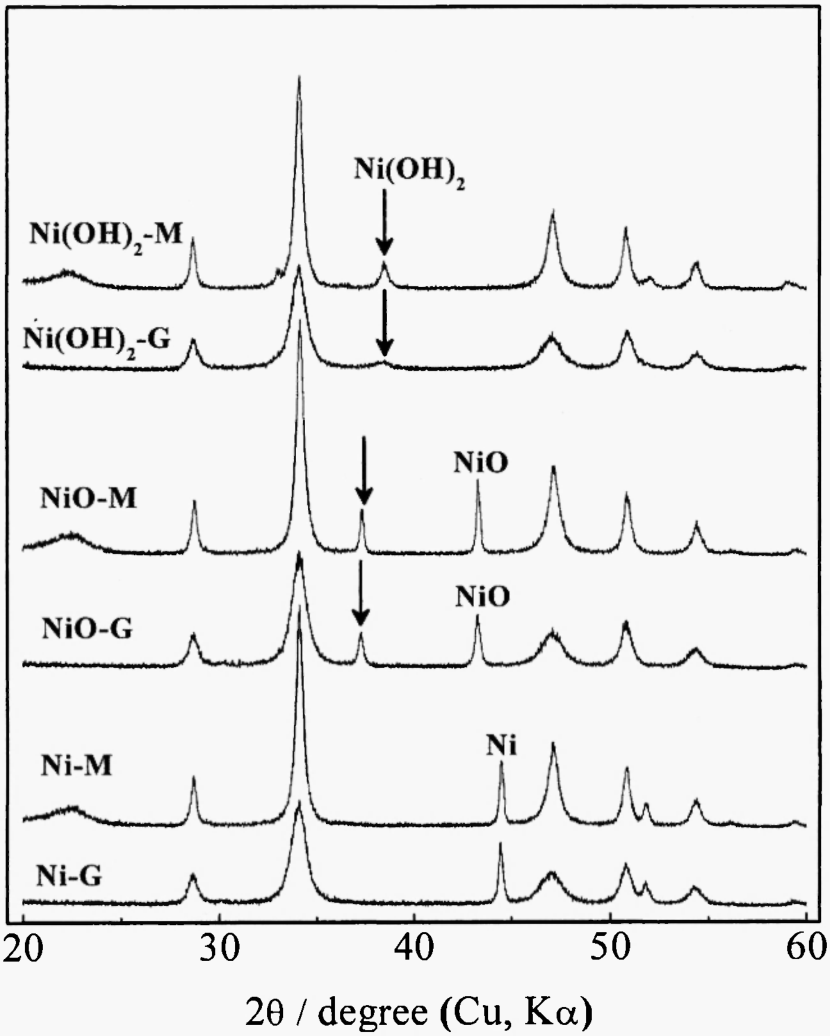

Fig. 6: X-ray diffraction patterns of [cellulose:$Ca(OH)_2$:$Ni(OH)_2$/NiO/Ni (6:6:1)] sample mixtures obtained both before and after grinding.

To understand why nickel particles of similar size in several microns differ after the heating operation, XRD patterns of cellulose and $Ca(OH)_2$ samples mixed with $Ni(OH)_2$, NiO and Ni were taken both before and after grinding for 2 h as shown in **Figure 6**. Characteristic peaks of the starting samples continued to appear in the milled products and no new peaks, indicating that no direct solid state reactions occurred during the grinding operation. The milling action facilitated mixing in which the homogeneous degrees of mixing seem to vary. In the case of samples containing NiO and Ni metal, only a slight decrease in their peak intensities was observed from grinding which indicated that under the current milling conditions NiO and Ni metal were not easily decomposed. However, for the sample system with $Ni(OH)_2$, the milling operation resulted in near complete amorphization and its peak intensity decreased to nearly unobservable level, implying that the crystal sizes was broken down to nanoscale. This result showed that the three nickel samples exhibited evidently different stabilities against grinding operation. It is generally known that $Ni(OH)_2$ is relatively easy to cause destruction of its crystal structure by mechanical force, compared with metal nickel (high malleability) and NiO (stable cubic structure). Another reason is that the hydrogen bonding between OH base among the mixed samples allows the well dispersion of the broken fine particles of $Ni(OH)_2$ among the counterparts.

The grinding operation breaks the $Ni(OH)_2$ particles and assists dispersion of the Ni particles onto surfaces of cellulose and $Ca(OH)_2$ and when heated, the nano–particles of Ni remain well dispersed among the ground heated sample. Such nickel nano–particles work as excellent catalysts to facilitate the conversion reaction of cellulose. If readily available or prepared nickel nano–particles are well dispersed among the mixture of cellulose and $Ca(OH)_2$, high conversion of cellulose could be achieved, however, it is usually difficult. The success of the present process is the grinding operation that allows the use of cheap commercially available $Ni(OH)_2$ which is reduced to amorphous phase, at the same time is well dispersed onto surfaces of the cellulose compound.

Table 1

Gas compositions (in mole %) from cellulose ground either with or without addition of $Ca(OH)_2$ and $Ni(OH)_2$ at different temperature ranges.

(a) Cellulose ground without $Ca(OH)_2$ and $Ni(OH)_2$

Temperature (°C)	Tot. gas (%) (H_2, CH_4, CO, CO_2	Gas conc. (%)			
		H_2	CH_4	CO	CO_2
350–450	4.22	0.00	1.60	3.62	94.81
450–525	12.70	0.00	9.02	36.10	54.89
525	12.31	0.00	20.6	36.31	43.22

(b) Cellulose ground with $Ca(OH)_2$ [C:Ca = 1:1 molar ratio]

Temperature (°C)	Tot. gas (%) (H_2, CH_4, CO, CO_2	Gas conc. (%)			
		H_2	CH_4	CO	CO_2
350–450	8.35	99.30	0.12	0.55	0.02
450–525	8.67	93.91	5.18	0.92	0.01
525	9.10	89.12	9.97	0.89	0.06

(c) Cellulose ground with $Ca(OH)_2$ and $Ni(OH)_2$ [6:6:1 molar ratio]

Temperature (°C)	Tot. gas (%) (H_2, CH_4, CO, CO_2	Gas conc. (%)			
		H_2	CH_4	CO	CO_2
350–450	26.30	97.30	2.33	0.42	0.00
450–525	49.52	93.50	6.39	0.07	0.01
525	17.21	94.11	5.55	0.25	0.16

3.4. Quantitative analyses of gaseous product

Analysis of the gas compositions obtained from cellulose sample both with and without $Ca(OH)_2$ and $Ni(OH)_2$ milled and heated at three different temperature ranges (350–450°C, 450–525°C, 525°C) is shown in **Table 1**. Helium gas was used as carrier gas during heating for collection of gaseous product for analysis, and it was observed that H_2, CH_4, CO and CO_2 were the main compositions in the gaseous products. The results in **Table 1(A)** shows product gas analysis for cellulose sample milled and heated without $Ca(OH)_2$ and $Ni(OH)_2$. It was clearly observed that no H_2 gas emission occurred at all temperature ranges and total gas generation remained very low at around 12%. Carbon oxides (CO_2 and CO) were dominant constituents lower CH_4 gas was also emitted.

For the cellulose sample milled and heated with $Ca(OH)_2$ (**Table 1(B)**), again total gas generation at all three temperature ranges remained very low at less than 10%. However, H_2 gas generation was observed with purity over 90%. Concentration of CO and CO_2 were significantly reduced to less than 1% due to the existence of $Ca(OH)_2$ where the carbon oxides are fixed as $CaCO_3$.

When the cellulose sample was milled with both $Ca(OH)_2$ and $Ni(OH)_2$ (6:6:1 = C:Ca:Ni) followed by heating, a much higher product gaseous generation exceeding 20% and reaching a high of 49.52% at 450–525°C temperature range was achieved (Table 1(C)). H_2 gas concentrations consistently above 93% were achieved with CO/CO_2 concentrations below 1%. CO concentration was in a low level around 500 ppm so such gaseous product with high purity H_2 gas and low CO concentration can be directly used in phosphoric acid fuel cells, but could require further purification for use in polymer electrolyte fuel cell.

To evaluate the yield of H_2 generation (grams per kg cellulose), the cellulose sample milled with both $Ca(OH)_2$ and $Ni(OH)_2$ (6:6:1 = C:Ca:Ni) were heated under helium gas flow at 250, 150, 550, 650 °C and analysis of the product gases collected is shown in **Table 2**. H_2 gas yield increases with increase in heating temperature and reaches a maximum of 85.9 g/kg cellulose at 550 °C. When temperature was further increased to 650°C, H_2 yield was found to decrease, at the same time, CO concentration increases to over 3% resulting from partial decomposition of $CaCO_3$, which is consistent with MS and XRD data that H_2 can be generated at temperatures below 600 °C, different from the normally reported steam reforming processes. A report on the energy analysis of biomass by other researchers [29] indicated that H_2 yield may reach as high as 80–130 g H_2/kg biomass from the steam reforming process. Although further improvement to the H_2 yield by our research group is under investigation, the present mechanochemical process simply enables the H_2 yield to reach over 80 g/kg biomass with the aid of solid state reaction to form $CaCO_3$.

We have also applied the same process to investigate other practical samples containing cellulose and other compositions encountered in our daily lifes such as paper, tree leaves, solid residue of coffee beans, etc., and obtained similar results with H_2 gas as dominant

Table 2

Changes in the yield of H_2 gas and the concentration CO with heating temperature.
Samples used were obtained from grinding; cellulose,
$Ca(OH)_2$ and $Ni(OH)_2$ [6:6:1 molar ratio] for 2 h.

Temperature (°C)	H_2 yield (g)/ per kg cellulose	CO concentration (%)
350	46.8	0.41
450	74.9	0.37
550	85.9	0.56
650	68.6	3.15

composition. Examination on the influence of impurities on this process was performed and was found that addition of kaolin as the model composition of soil did not cause much change with H_2 generation. Only the existence of sulphur decreased largely the H_2 generation due to catalyst deactivation.

The present findings confirm that a simple milling operation of cellulose with two hydroxides show excellent selectivity for the production of H_2 at high conversion rate of cellulose. We understand that formations of CH_4 and CO gases may mainly result from the separate decomposition of the samples at the surface layers rather than the reaction at the core of the samples put in the furnace. When sample amount is increased from grams to kilograms or tons, the percentage of the surface layer will become much less. The formation yield of CH_4 and CO may go down further. Further improvement is expected with detailed investigations particularly on scaled up tests.

4. CONCLUSIONS

Selective H_2 emission from cellulose has been realized by heating the co–ground samples with both $Ca(OH)_2$ and $Ni(OH)_2$ at a low temperature of 500 °C. The H_2 emission was accompanied by the conversion reaction of carbon in cellulose into $CaCO_3$. A high conversion rate was obtained without observable tar occurrence. The success of selective H_2 emission is attributed to the grinding operation which enables the breakdown and well dispersion of $Ni(OH)_2$ particles so that the well dispersed nickel nano–partilces can be prepared *in situ* during heating operation. This process is also applicable to other hydrocarbons and real samples with complicated compositions as well as cellulose.

REFERENCES

1. Zou ZG, Ye JH, Sayama K and Arakawa H.: Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature*, **414**:,625–27 (2001).
2. Khan SUM, Al-Shahry M and Ingler WB.: Efficient photochemical water splitting by a chemically modified n–TiO_2. *Science*, **297**, 2243–45(2002).
3. Huber GW, Iborra S and Corma A.: Synthesis of transportation fuels from biomass: Chemistry, *catalysts, and engineering. Chemical Reviews*, **106**, 4044–98(2006).
4. Abu El-Rub Z, Bramer E.A and Brem G.: Review of catalysts for tar elimination in Biomass gasification processes. *Industrial & Engineering Chemistry Reseasrch*, **43**, 6911–19(2004).
5. Fushimi C, Araki K,Yamaguchi Y and Tsutsumi A.: Effect of heating rate on steam gasification of biomass 2: *Thermogravimetric-mass spectrometric (TG–MS) analysis of gas evolution. Industrial & Engineering Chemistry Research*, **42**, 3929–36(2003).
6. Jakab E, Liu K and Meuzelaar HLC.: Thermal decomposition of wood and cellulose in the presence of solvent vapours. *Industrial & Engineering Chemistry Research*, **36**, 2087–95(1997).
7. Cortright RD, Davda RR and Dumesic JA.: Hydrogen from catalytic reforming of biomass–derived hydrocarbons in liquid water. *Nature*, **418**, 964–67(2002).
8. Deluga GA, Salge JR, Schmidt LD and Verykios XE.: Renewable hydrogen from ethanol by autothermal reforming. *Science*, **303**, 993–97(2004).
9. Huber GW, Shabaker JW and Dumesic JA.: Raney Ni–Sn catalyst for H_2 production from biomass–derived hydrocarbons. *Science*, **300**, 2075–77(2003).
10. Furusawa T, Sato T, Sugito H, Miura Y, Ishiyama Y, Sato M, Itoh N and Suzuki N.: Hydrogen production from the gasification of lignin with nickel catalysts in supercritical water. *International Journal of Hydrogen Energy*, **32**, 699–704(2007).
11. Xu GW, Murakami T, Suda T, Kusama S and Fujimori T.: Distinctive effects of CaO additive on atmospheric gasification of biomass at different temperatures. *Industrial & Engineering Chemistry Research*, **44**, 5864–68(2005).
12. Lin SY, Harada M, Suzuki Y and Hatano H.: Gasification of organic material/CaO pellets with high-pressure steam. *Energy & Fuels*, **18**, 1014–20(2004).

13. Hickenboth CR, Moore JS, White SR, Sottos NR, Baudry J and Wilson SR.: Biasing reaction pathways with mechanical force. *Nature*, 2007, **446**, 423–27(2007).
14. Beyer MK, Clausen–Schaumann and H. Mechanochemistry: The mechanical activation of covalent bonds. *Chemical Reviews*, 105, 2921–48(2005).
15. Tanaka Y, Zhang QW and Saito F.: Mechanochemical dechlorination of trichlorobenzene on oxide surfaces. *Journal of Physical Chemistry B*, **107**, 1109–17(2003).
16. Zhang QW, Matsumoto H and Saito F.: Baron M. Debromination of hexabromobenzene by its co-grinding with CaO. *Chemosphere*, **48**, 787–93(2002).
17. Tongamp W, Zhang Q and Saito F.: Hydrogen generation from polyethylene by milling and heating with $Ca(OH)_2$ and $Ni(OH)_2$. *International Journal of Hydrogen Energy*, **33**, 4097–4103(2008).
18. Tongamp W, Zhang Q and Saito F.: Generation of hydrogen gas from polyethylene mechanically milled with Ni–doped layered double hydroxide. *Fuel Processing Technology*, **90**, 909–13(2009).
19. Tongamp W, Zhang Q, Miyagi S and Saito F.: Generation of hydrogen from polyvinyl chloride by milling and heating with CaO and $Ni(OH)_2$. *Journal of Hazardous Materials*, **167**, 1002–06(2009).
20. Tongamp W, Zhang Q and Saito F. Generation of hydrogen from PS and PVA by milling and heating with CaO and $Ni(OH)_2$. *Fuel Processing Technology*, **91**, 272–76(2010).
21. Florin NH and Harris AT.: Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chemical Engineering Science*, **63**, 287–316(2008).
22. Florin NH and Harris AT.: Mechanistic study of enhanced H_2 synthesis in biomass gasifiers with in–situ CO_2 capture using CaO. *AICHE Journal*, **54**, 1096–1109(2008).
23. Hu GX, Huang H and Li YH.: The gasification of wet biomass using $Ca(OH)_2$ as CO_2 absorbent: The microstructure of char and absorbent. *International Journal of Hydrogen Energy*, 33, 5422–29(2008).
24. A.J. Vizcaíno, A. Carrero and J.A. Calles: Hydrogen production by ethanol steam reforming over Cu–Ni supported catalysis, *Int. J. Hydrogen Energy*, **32**, 1450–1461 (2007).
25. F. Mariño, M. Boveri, G. Baronetti and M. Laborde: Hydrogen production via catalytic gasification of ethanol. A mechanism proposal over copper–nickel catalysis, *Int. J. Hydrogen Energy*, **29**, 67–71(2004).
26. J.W.C. Liberatori, R.U. Ribeiro, D. Zanchet, F.B. Noronha, J.M.C. Bueno, Steam reforming of ethanol on supported nickel catalysts, Applied Catalysis A: General 327 (2007) 197–204.
27. A. Tanksale, Y. Wong, J.N. Beltramini, G.Q. Lu, Hydrogen generation from liquid phase catalytic reforming of sugar solutions using metal–supported catalysts, Int. J. Hydrogen Energy 32 (2007) 717–724.
28. R.M. de Almeida, H.V. Fajardo, D.Z. Mezalira, G.B. Nuernberg, L.K. Noda, L.F.D. Probst, N.L.V. Carreño, Preparation and evaluation of porous nickel–alumina spheres as catalyst in the production of hydrogen from decomposition of methane, Journal of Molecular Catalysis A: Chemical 259 (2006) 328–335.
29. Abuadala A, Dincer 1, Naterer GF. Energy analysis of hydrogen production from biomass gasification. . International Journal of Hydrogen Energy *inpress*.