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## COMMUNICATION

# Biomass Conversion to H<sub>2</sub> with Substantially Suppressed CO<sub>2</sub> Formation in the Presence of Group I & Group II Hydroxides and a Ni/ZrO<sub>2</sub> Catalyst

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**The production of H<sub>2</sub> with substantially suppressed CO<sub>2</sub> formation is achieved using Group I and II hydroxides in the Alkaline Thermal Treatment of cellulose. Although strong hydroxides (i.e., NaOH) have shown greater conversion to H<sub>2</sub> with minimal gaseous byproducts, similar performance is also achieved with Ca(OH)<sub>2</sub>, using a Ni/ZrO<sub>2</sub> catalyst.**

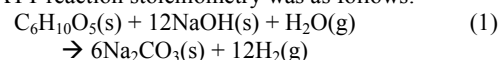
Fossil fuels are essential to modern society and have driven the economic growth of developed and developing countries alike, with an expectation that energy demand will increase by 56% by 2040.<sup>1</sup> The issues of climate change and ocean acidification have raised concerns over anthropogenic CO<sub>2</sub> emissions from the use of fossil fuels, therefore, alternatives have been sought to satisfy the energy demand as well as protect the environment.

The use of H<sub>2</sub> derived from sources other than fossil fuels leads to a new approach of energy generation involving distributed renewable energy sources, and opens up the possibility of integrating with small-scale fuel cells for localized energy conversion. The current demand for H<sub>2</sub> is 44.5 million tons per year, however, it is hoped that by 2040 H<sub>2</sub> will replace the use of 18.3 million barrels of oil and thus increase demand to 150 million tons of H<sub>2</sub>.<sup>2</sup> Approximately 96% of all H<sub>2</sub> was derived directly from fossil fuels<sup>3</sup> with CO<sub>2</sub> as a by-product. In order to mitigate issues related to CO<sub>2</sub> emissions and satisfy increasing demand, H<sub>2</sub> will need to be produced using more renewable methods.

Biomass presents itself as a possible renewable fuel source to generate H<sub>2</sub>, although its conversion is often challenged by its low energy density and high moisture content.<sup>4</sup> Yet, several technologies have been developed that can convert biomass to H<sub>2</sub>, such as gasification, pyrolysis and super/subcritical hydrothermal treatment,<sup>5,6</sup> with H<sub>2</sub> production via gasification showing an exergetic efficiency similar to other renewables.<sup>7</sup> However, as argued in the latest IPCC report<sup>8</sup>, bioenergy with carbon capture and storage (BECCS) is an important technology for the future of sustainable energy and the environment. Thus, a new reaction called the Alkaline Thermal Treatment (ATT) has been suggested to produce H<sub>2</sub> while fixing the CO<sub>2</sub> into a solid carbonate matrix.<sup>9,10</sup>

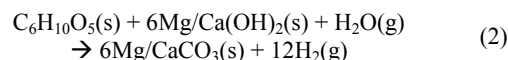
Literature has demonstrated that NaOH can be used as a successful additive, in both the gasification<sup>11</sup> of glucose and the supercritical water (SCW) reaction of cellulose<sup>12,13</sup>, to enhance H<sub>2</sub> production. Specifically, SCW has shown to be a very effective method of producing H<sub>2</sub>, likely due to its unique properties of dissociated water and ability to solubilize cellulose. The presence of the OH<sup>-</sup> ion from dissociated water in SCW may be analogous to the

use of a base in the ATT reaction scheme.<sup>9,10</sup> Ishida et al demonstrated that the addition of NaOH could significantly improve the H<sub>2</sub> yield from cellulose at a relatively low temperature of 573 K. Their suggested ATT reaction stoichiometry was as follows:



The efficacy of NaOH in producing H<sub>2</sub> lies in its ability not only to fragment cellulose<sup>14-16</sup>, but also to increase cellulose dissolution.<sup>17</sup> Furthermore CO<sub>2</sub> produced during this reaction is captured as a solid carbonate, thus generating H<sub>2</sub> with little or no CO<sub>2</sub>. Comparison of literature regarding the SCW reaction with NaOH and ATT reaction suggests that the hydroxyl group may allow for H<sub>2</sub> generation from cellulose at lower temperatures and pressures.<sup>9,10,18</sup>

Despite the desirable properties of NaOH as a reactant, it is far too expensive at \$921 per ton for a large-scale commercial process.<sup>19</sup> On the other hand, group II hydroxides such as Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> are less expensive at \$74/ton and \$250/ton, respectively.<sup>19</sup> In fact, CaO, the precursor to Ca(OH)<sub>2</sub>, has already demonstrated itself as a useful additive when attempting to promote the WGS in favour of H<sub>2</sub> formation.<sup>20</sup> Furthermore, these hydroxides can be derived from industrial wastes (e.g., steel slags, waste cements, etc.) or natural silicate minerals (e.g., wollastonite, serpentine, etc.) that are currently being considered as carbon storage media.<sup>21,22</sup> Therefore, in this study, Group II hydroxides are investigated as replacements to NaOH, with Equation 2 showing the stoichiometry of H<sub>2</sub> formation from cellulose:



While Group II hydroxides and their complementary oxides are interesting choices due to their lower cost and potential for carbon capture, the main challenge is that they are weak bases with poor solubility and will decompose at elevated temperatures. These differences are expected to reduce their chemical reactivity and create mass transfer issues during the ATT reaction. To the authors' knowledge, no study exists which compares the activity of both types of hydroxides in the ATT reaction.

Although the exact role of catalysts and hydroxides in the ATT reaction is not fully understood, there appears to be some general consensus regarding parameters that are important in affecting the catalysis of cellulose to H<sub>2</sub>. Alkali salts have been suggested as suitable additives to promote H<sub>2</sub> production.<sup>23-26</sup> Certain zeolites and catalytic supports are also effective in catalysing the conversion of cellulose.<sup>27,28</sup> Many types of metal catalysts have

also been investigated with Ruthenium (Ru), Nickel (Ni), and Iron (Fe) being identified as metals of interest.<sup>13,29,30</sup> Ni presents itself as the most interesting catalyst due to its relatively low cost, and its ability to improve the H<sub>2</sub> yield in various reaction schemes.<sup>18,30-34</sup> Given the large body of literature regarding the catalytic properties of Ni and the relatively small amount of work done on alternative hydroxides in the ATT reaction, this study focuses on determining whether the activities of Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> can be catalysed to the level of NaOH using a 10% Ni/ZrO<sub>2</sub> catalyst.

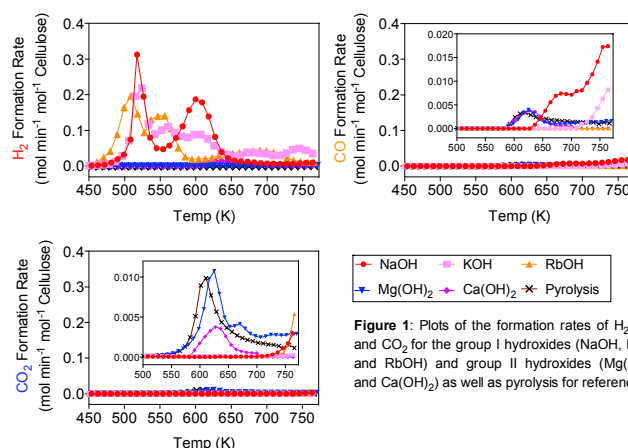
In the current study, Group II samples were prepared by mixing cellulose (Acros, micro-crystalline 50 μm particle size) powder with Mg(OH)<sub>2</sub> or Ca(OH)<sub>2</sub> powder (both from Acros) at a 1:6 molar ratio according to Equation 2. Group I samples were prepared by mixing cellulose with 50wt% NaOH or 45wt% KOH solutions (Sigma-Aldrich) or a RbOH powder (Sigma-Aldrich) at a 1:12 molar ratio as per Equation 1. The mixture was then combined with the Ni/ZrO<sub>2</sub> catalyst particles to create an overall mixture of which 20% of the sample mass was catalyst. The sample was then loaded into a 1.05 cm I.D. quartz tube and held in place between two pieces of quartz wool. The mass of sample was always kept between 600 and 800 mg and all the results were normalized to the moles of cellulose used in order to enable accurate comparisons. The Ni-catalyst was prepared by dissolving 550.5 mg of Nickel (II) Nitrate Hexahydrate in 30 mL of D.I. water upon which one gram of finely ground ZrO<sub>2</sub> (Alfa-Aesar) was added to the stirred solution. The mixture was then heated and left to evaporate thus gradually concentrating the solution and impregnating the metal salt into the support. The catalyst was then dried at 363 K overnight and calcined in air while heating at a rate of 0.4 K/min to 563 K and holding for 2 hours. The oxidized metals were then reduced in a tube furnace in a pure H<sub>2</sub> atmosphere for 1 hour at 773 K.

In case of Group II hydroxides, their solubilities are low, and are therefore mixed in as solid powders. The average particle sizes of Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> are 9 and 19 μm, respectively, while cellulose is about 50 μm. The surface areas of cellulose and Group II hydroxides are relatively low ranging from 2.5 m<sup>2</sup>/g (cellulose), 5.7 m<sup>2</sup>/g (Mg(OH)<sub>2</sub>) to 15 m<sup>2</sup>/g (Ca(OH)<sub>2</sub>). The average particle sizes of the ZrO<sub>2</sub> support and 10% Ni/ZrO<sub>2</sub> catalyst are 14 and 16 μm, respectively, similar to cellulose and the Group II hydroxides, while their surface areas are relatively high (ZrO<sub>2</sub> support (88 m<sup>2</sup>/g) and 10% Ni/ZrO<sub>2</sub> (71 m<sup>2</sup>/g)). The CO chemisorption value for the 10% Ni/ZrO<sub>2</sub> catalyst is 34.5 μmol/g, which is used to calculate the dispersion (~2%) and the average size of the Ni crystals in the catalyst, 56 nm. The number of active Ni sites is low, likely due to the synthesis procedure and high loading of metal.

The ATT reactions were carried out in a reactor system designed by Micromeritics. The quartz tube containing the sample was placed inside the reactor, sealed, and purged of O<sub>2</sub> under a constant N<sub>2</sub> flow of 20 mL/min. After the purging step, the reactor and the surrounding hotbox were pre-heated at a heating rate of 4 K/min to 373 K. Samples prepared using NaOH and KOH solutions required an isothermal heating treatment at 373 K for 20 minutes in order to remove the excess water. Once the loaded sample was preheated, water was injected into the hotbox via a high-pressure liquid pump at a rate of 0.007 mL/min, where it was preheated and mixed with N<sub>2</sub> to prepare steam at a given flow rate for the ATT reaction. The ATT reaction was then initiated by heating the reactor at a rate of 4 K/min to 773 K while introducing steam. The gas stream exiting the reactor was fed into a Peltier condenser to separate condensable compounds from light gases. The product gases were then quantified online via an Inficon Micro-GC 3000 with a sampling rate of 2.3 minutes. The detection limits of the instrument were 20 ppm for H<sub>2</sub>, and in the ppm ranges for O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub>. The overall H<sub>2</sub> yields were determined by

analysing the gaseous products, which were collected in a tedlar bag.

Figure 1 presents the online gaseous product formation rates as a function of temperature up to 773 K for the non-catalytic conversion of cellulose with different Group I and Group II metal hydroxides and compares it to cellulose pyrolysis. It can be seen that the Group I metal hydroxides have distinct gaseous product formation behaviours, in agreement with literature.<sup>9,10</sup> With respect to H<sub>2</sub> formation, two distinct peaks are seen for the Group I hydroxides with the first peak of H<sub>2</sub> formation occurring between 500 K and 525 K. A secondary H<sub>2</sub> peak is also observed with the peak shifting to lower temperatures with increasing OH<sup>-</sup> strength: 600 K for NaOH, 561 K for KOH and 546 K for RbOH. The shift in the secondary peaks indicates that the presence of more OH<sup>-</sup> may favour the reaction pathways occurring at higher temperature. Yet, despite the difference in the H<sub>2</sub> formation curves, the conversion of cellulose for all Group I hydroxides is similar at approximately 31% to 33%.



**Figure 1:** Plots of the formation rates of H<sub>2</sub>, CO and CO<sub>2</sub> for the group I hydroxides (NaOH, KOH, and RbOH) and group II hydroxides (Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>) as well as pyrolysis for reference.

In contrast, group II metal hydroxides show little or no activity. Pyrolysis and Mg(OH)<sub>2</sub> show small H<sub>2</sub> formation peaks at 773 K and 761, with their actual conversions being ~0% and ~0.4%, respectively. Conversely, Ca(OH)<sub>2</sub> shows some improvement with a peak of H<sub>2</sub> formation occurring at 636 K and an overall conversion of ~1.2%. The clear difference between the activity of the Group I and Group II hydroxides brings up the important distinction between pyrolysis and ATT driven gas formation. Gas formation through pyrolysis does not begin until elevated temperatures, generally above 670 K<sup>35</sup>, whereas the ATT of cellulose produces gases with a high selectivity for H<sub>2</sub> at much lower temperatures.<sup>9,10</sup>

CO<sub>2</sub> is also significantly suppressed for the Group I hydroxides except at temperatures above 700 K where it is possible that small amounts of cellulose are undergoing pyrolysis to produce some CO<sub>2</sub>. The decomposition of any formed carbonates can be ruled out since the thermal decomposition temperatures of Na<sup>36</sup>, K<sup>37</sup> and Rb-carbonate<sup>38</sup> species are higher than the temperature range studied. In comparison, the Group II hydroxides do not form carbonates easily, with literature indicating that it is infeasible to carbonate Mg(OH)<sub>2</sub> at ambient pressure<sup>39</sup> and that Ca(OH)<sub>2</sub> only shows significant carbonation above 613 K.<sup>40</sup> Conversely, NaOH is known to form carbonate spontaneously in the presence of room air (500ppm).<sup>41</sup> This explains why a small amount of CO<sub>2</sub> formation is observed above 550 K for the Group II hydroxides but not for the Group I hydroxides. However, keeping consistent with the trend of increasing hydroxide strength, Ca(OH)<sub>2</sub> shows less CO<sub>2</sub> formation than Mg(OH)<sub>2</sub> or pyrolysis.

With respect to CO, its formation for the Group II hydroxides is similar with the peak occurring at around 625 K. The similarity between the Group II hydroxides and pyrolysis would imply that the Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> behave more similarly to pyrolysis and do not follow the ATT stoichiometry. For group I

hydroxides, CO formation begins at higher temperatures with increasing hydroxide strength; 627 K for NaOH, 708 K for KOH and RbOH, which does not produce CO in the temperature range of the current study. This observation is supported by literature which shows that CO can react mildly with NaOH to produce  $H_2$ .<sup>42</sup>

Overall, the results in Figure 1 show that Group I hydroxides show advantages in converting cellulose to  $H_2$ , which include higher conversion to  $H_2$ , lower  $H_2$  formation temperatures and suppressed  $CO_x$ . However, for large-scale applications, the production of Group I hydroxides consumes too much energy and is expensive. Group I hydroxides are produced via the electrolysis of brine<sup>43</sup>, thus reducing the net energy output of the cellulose conversion reaction. Group II hydroxides, in particular  $Ca(OH)_2$ , can be derived from CaO, which could potentially be sourced from waste materials such as stainless steel slag, of which 40% of the output is stockpiled and can contain CaO contents of up to 12%.<sup>44</sup> However, due to the low activity of  $Ca(OH)_2$  and  $Mg(OH)_2$ , it is necessary to develop a metal catalyst that can catalyse their respective reactions.

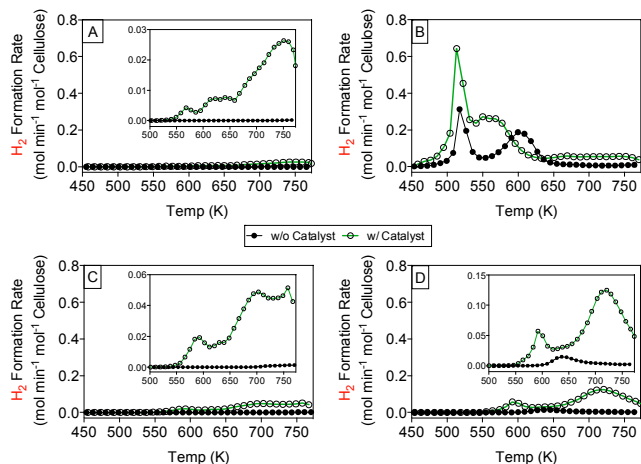
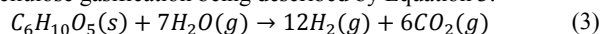


Figure 2: Plots of the formation rates of  $H_2$  for the non-catalytic and catalytic cases of (A) Pyrolysis, (B) NaOH, (C)  $Mg(OH)_2$  and (D)  $Ca(OH)_2$

Figure 2 illustrates the effect of the inclusion of the 10% Ni/ZrO<sub>2</sub> catalyst on the formation rate of  $H_2$  for the cases of pyrolysis, NaOH,  $Mg(OH)_2$  and  $Ca(OH)_2$ . For pyrolysis, the conversion to  $H_2$  increases from 0% to 5.8%. Ni is known to aid in the cracking of tar to gaseous products,<sup>45,46</sup> as evidenced by the increase in the  $H_2$  formation rate as observed in the cases of pyrolysis,  $Mg(OH)_2$  and  $Ca(OH)_2$  at elevated temperatures. For NaOH the inclusion of the catalyst causes an increase in conversion from 33% to 66%. It is clear that the mechanisms of this reaction are quite different from that of pyrolysis and Group II hydroxides. For both the catalytic and non-catalytic cases, NaOH have two distinct  $H_2$  peaks, with the first peak appearing at ~515 K for the non-catalytic case. The addition of the catalyst results in an increase in the magnitude of the first peak and a shift in the second peak from 600K to 559K.

It is interesting to note that for the catalytic case, NaOH shows a significant increase in  $CO_2$  production (Figure 3) while eliminating the production of CO (Figure 4). However,  $Mg(OH)_2$  and pyrolysis show an enhancement in both CO and  $CO_2$ , with a significant correlation between the  $CO_2$  and  $H_2$  formation curves. It seems that in these cases the production of  $H_2$  is linked with the production of  $CO_2$ . The ratio of formation rates ( $H_2/CO_2$ ) during  $H_2$  formation for  $Mg(OH)_2$  and pyrolysis is ~2. Several papers have reported the various reactions of cellulose to  $H_2$  with cellulose gasification being described by Equation 3.<sup>29,47,48</sup>



This result indicates that the addition of catalyst causes the reaction

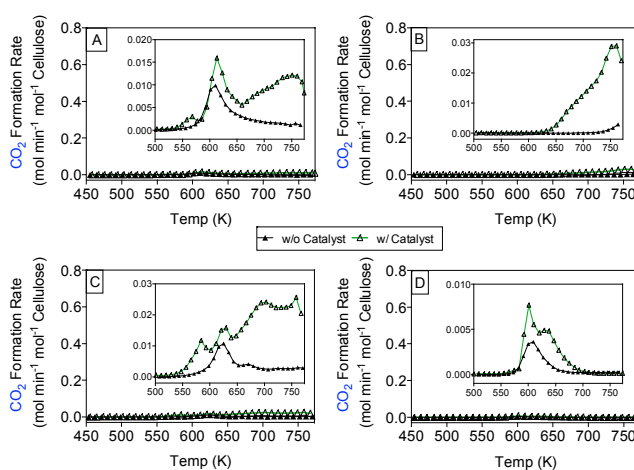


Figure 3: Plots of the formation rates of  $CO_2$  for the non-catalytic and catalytic cases of (A) Pyrolysis, (B) NaOH, (C)  $Mg(OH)_2$  and (D)  $Ca(OH)_2$

to favour this particular stoichiometry. This illustrates that at lower temperatures (<600 K) NaOH is capable of generating  $H_2$  while suppressing  $CO_2$  formation due to its strong carbon absorption capability, whereas  $Mg(OH)_2$  and pyrolysis will always form  $CO_2$  due to the lack of a strong carbon sorbent. The addition of the catalyst to  $Ca(OH)_2$ , on the other hand, has different characteristics, with no clear correlation between  $H_2$  and  $CO_2$  formation. This does not imply that  $CO_2$  is not produced, but rather that the  $CO_2$  absorption ability of  $Ca(OH)_2$  is greater than  $Mg(OH)_2$ .

With respect to catalysing the activity of the Group II hydroxides, the addition of the catalyst to  $Mg(OH)_2$  significantly increases the  $H_2$  yield from 0.4% and 16.1%. Overall, the effect of  $Mg(OH)_2$  for the non-catalytic case does very little to improve the pyrolysis of cellulose, however, the combination of  $Mg(OH)_2$  and the 10% Ni/ZrO<sub>2</sub> catalyst shows a near tripling in  $H_2$  production when compared to pyrolysis of cellulose (5.8%). Similarly, the reaction of  $Ca(OH)_2$  with cellulose shows that the inclusion of the catalyst results in a significant increase in the yield of  $H_2$  from 1.2% to 31.4%. This conversion is comparable to the conversion of cellulose with NaOH without the 10% Ni/ZrO<sub>2</sub> catalyst (~33%). By dividing the amounts of excess  $H_2$  produced by the CO chemisorption value, the turnover numbers for the 10% Ni/ZrO<sub>2</sub> catalyst in the presence of  $Mg(OH)_2$ ,  $Ca(OH)_2$  and NaOH are found to be 426, 696 and 704, respectively, thus indicating that these reactions are catalytic. Integration of the  $H_2$  and  $CO_2$  formation rate curves given in Figures 1 and 3 indicates that the  $H_2/CO_2$  ratios of

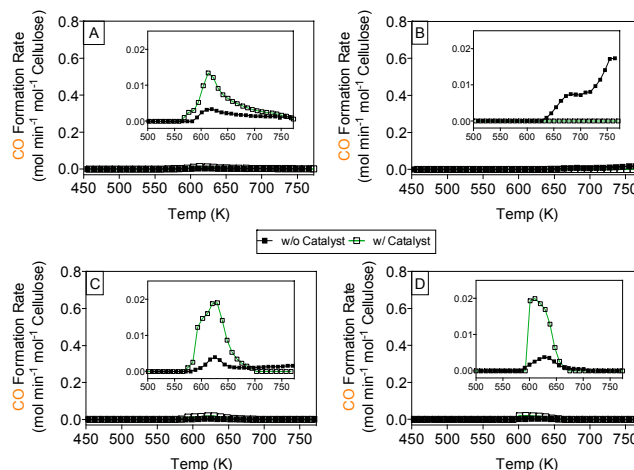


Figure 4: Plots of the formation rates of CO for the non-catalytic and catalytic cases of (A) Pyrolysis, (B) NaOH, (C)  $Mg(OH)_2$  and (D)  $Ca(OH)_2$



the final gas products for NaOH and Ca(OH)<sub>2</sub>+10% Ni/ZrO<sub>2</sub> is 38 and 35, respectively. This result demonstrates that not only can NaOH greatly outperform cellulose gasification in relation to the CO<sub>2</sub> released (H<sub>2</sub>/CO<sub>2</sub>=2), but Ca(OH)<sub>2</sub> with a 10% Ni/ZrO<sub>2</sub> catalyst can also achieve similar results. Furthermore it is apparent that the addition of 10% Ni/ZrO<sub>2</sub> to Ca(OH)<sub>2</sub> bears some resemblance to the H<sub>2</sub> formation curves of NaOH, except the peaks are slightly broader and are shifted to higher temperatures appearing at 592 K and 721 K.

## Conclusions

These results demonstrate that when attempting to convert cellulose to H<sub>2</sub>, there are two main types of hydroxides that can be used. Group I hydroxides achieve higher conversion, have lower gaseous side-product yield and require a lower operating temperature. Their costs and energy-intensive manufacture, however, make them impractical for large-scale use. A 10% Ni/ZrO<sub>2</sub> catalyst is used to catalyse weak hydroxides such as Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> to the effectiveness of NaOH. It is found that Mg(OH)<sub>2</sub> without catalyst (0.4%) behaves very similarly to pyrolysis (0%) and has a similar distribution of gaseous side-products. However, Mg(OH)<sub>2</sub> with catalyst sees a near tripling (16.1%) in the H<sub>2</sub> yield compared to pyrolysis with catalyst (5.8%). Similarly, the addition of 10% Ni/ZrO<sub>2</sub> to Ca(OH)<sub>2</sub> (1.2%) showed an even larger increase in H<sub>2</sub> yield (31.4%). These results demonstrate the feasibility of using the combination of 10% Ni/ZrO<sub>2</sub> and Ca(OH)<sub>2</sub> to achieve performance similar to NaOH for the production of H<sub>2</sub> with substantially suppressed CO<sub>2</sub> formation.

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## Notes and References

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