Role of sodium hydroxide for hydrogen gas production and storage

Sushant Kumar, Surendra K. Saxena
Center for the Study of Matter at Extreme Conditions, College of Engineering and Computing, Florida International University, Miami, Florida 33199, USA

The rapid depletion of fossil fuel, increase in pollution and related environmental hazards require us to discover new energy sources. H₂ is an efficient energy carrier with a very high specific energy content (~120MJ/kg) and energy density (10Wh/kg). It has been technically shown that hydrogen can be used for transportation, heating and power generation, and could replace current fuels in all the present applications. Hydrogen can be produced using a variety of starting materials, derived from both renewable and non-renewable sources, through different process routes. Although sodium hydroxide is corrosive in nature, it has a vast growing application as a starting ingredient in the field of hydrogen production and storage.

Various current technologies include sodium hydroxide to lower the operating temperature, accelerate hydrogen generation rate as well as sequester carbon dioxide during hydrogen production. Sodium hydroxide finds applications in all the major H₂ production methods such as steam methane reforming, coal gasification, biomass gasification, electrolysis, photochemical and thermochemical. Sodium hydroxide, being alkaline, acts as a catalyst, promoter or even a precursor. Different combinations of binary and complex hydrides when assisted with sodium hydroxide can efficiently absorb/desorb hydrogen at relatively mild conditions. Here, we discuss the technical and scientific role of sodium hydroxide for hydrogen gas production and storage.

Keywords sequester; steam methane reforming; coal/biomass gasification; electrolysis; photochemical/thermochemical; hydrides

1. Introduction

Hydrogen is the lightest and most abundant element on the earth. However, unlike oxygen, hydrogen is not found as free in the nature at any significant concentration. Hydrogen is produced using both renewable and non-renewable resources, through various process routes. The available technologies for hydrogen production are reforming of natural gas; gasification of coal and biomass; and the splitting of water by water-electrolysis, photo-electrolysis, photo-biological production, water splitting thermochemical cycle and high temperature decomposition. The principal methods for the production of hydrogen involve water-electrolysis and natural gas reforming processes [1]. However, photo-electrolysis, photo-biological production and high temperature decomposition all are still in their early stage of development. Thus, an extensive R&D is needed to mature these technologies for any future commercial applications.

In recent times, various researchers either proposed a modified version of the existing H₂ production technologies or suggested some innovative routes. Interestingly, a large number of the methods included sodium hydroxide as an essential ingredient. The use of sodium hydroxide for production of hydrogen is not new and was in application even during 19th century. In the following sections the significance of sodium hydroxide for the hydrogen production and storage process will be discussed in details.

1.1 Overview of Sodium hydroxide (NaOH)

Previous technology for sodium hydroxide production included mixing of calcium hydroxide with sodium carbonate. This process was named as “causticizing”.

\[
\text{Ca (OH)}_2 (aq) + \text{Na}_2\text{CO}_3 (s) = \text{CaCO}_3 \downarrow + 2 \text{NaOH} (aq) \quad (1)
\]

Currently, sodium hydroxide is produced by the electrolysis of brine (NaCl):

\[
2\text{NaCl} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{Cl}_2 \uparrow + \text{H}_2 \uparrow \quad (2)
\]

Besides H₂ evolution, reaction (2) produces chlorine (a toxic gas) and sodium hydroxide. Moreover, the electrolysis of brine is also a high energy consuming process. Thus, the combined effect of high energy requirement and emission of chlorine gas makes the production of sodium hydroxide using electrolysis of brine, an environmentally unsafe process.

Table 1 compares the three commercially available production methods for sodium hydroxide. It can be observed that diaphragm cell process produces the lowest quality electrochemical caustic soda solutions (only 12wt. %). Therefore, evaporation is required to raise the concentration up to 50 wt. % solution as in mercury-cell process. Hence, the amount of steam consumption varies according to the strength of the produced electrochemical caustic soda solutions.
### Table 1
Comparison of the commercially available production methods for NaOH

<table>
<thead>
<tr>
<th>Factors</th>
<th>Diaphragm</th>
<th>Mercury</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use of mercury</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Chlorine as a byproduct</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Operating current density (kA/m²)</td>
<td>0.9-2.6</td>
<td>8-13</td>
<td>3-5</td>
</tr>
<tr>
<td>Cell voltage (V)</td>
<td>2.9-3.5</td>
<td>3.9-4.2</td>
<td>3.0-3.6</td>
</tr>
<tr>
<td>NaOH strength (wt. %)</td>
<td>12</td>
<td>50</td>
<td>33-35</td>
</tr>
<tr>
<td>Energy consumption (kWh/MT Cl₂) at a current density (kA/m²)</td>
<td>2720(1.7)</td>
<td>3360(10)</td>
<td>2650(5)</td>
</tr>
<tr>
<td>Steam consumption (kWh/MT Cl₂) for concentration to 50% NaOH</td>
<td>610</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>% NaOH produced in USA</td>
<td>62</td>
<td>10</td>
<td>24</td>
</tr>
</tbody>
</table>

Figure 1 illustrates the membrane cell used for the electrolysis of brine.

![Membrane cell process schematic for production of sodium hydroxide](image)

**Fig. 1** Membrane cell process schematic for production of sodium hydroxide.

### 2. Hydrogen Production and storage process

#### 2.1 Modified Industrial Hydrogen Production

Currently, steam methane reformation (SMR) is the most common and the least expensive industrial technology to produce hydrogen [1]. Methane reacts at a high temperature 700-1100 °C with steam to form syn gas (CO+ H₂).

\[
\text{CH}_4 (g) + H_2O (g) = CO (g) + 3H_2 (g) \Delta H= 397 \text{kJ/mol (1227°C)} \tag{3}
\]

Syn gas can further react to form additional H₂ at a lower temperature.

\[
\text{CO} (g) + H_2O (g) = CO_2 (g) + H_2 (g) \Delta H= -242 \text{ kJ/mol (327°C)} \tag{4}
\]

The combined reaction is

\[
\text{CH}_4 (g) + 2H_2O (g) = CO_2 (g) + 4H_2 (g) \Delta H= 431 \text{ kJ/mol (927°C)} \tag{5}
\]

The enthalpy change (ΔH) is given for the temperatures at which the reaction is generating maximum H₂ levels. A simple calculation can show that while producing 1 gram of H₂ via SMR technique, about 10.5 grams of CO₂ is emitted. Such an undesired vast emission of CO₂ endangers the prolong use of conventional SMR technique to produce H₂. Thus, any method which can produce H₂ without or with reduced CO₂ emission is required. In this regard, several methods have been proposed but most of them are either expensive compared to those using fossil fuels or are in the very early stages of development [2-7].
Reaction between NaOH and CO yielding sodium formate (HCOONa) was described by Berthelot in 1856. When heated above 250°C, HCOONa transforms into oxalate with release of H₂:

$$\text{NaOH} (s) + \text{CO} (g) = \text{HCOONa} (s)$$  \hspace{1cm} (6)

$$2\text{HCOONa}(s) = \text{Na}_2\text{C}_2\text{O}_4(s) + \text{H}_2(g)$$  \hspace{1cm} (7)

In 1918 Boswell and Dickson demonstrated that when carbon monoxide is heated with excess of sodium hydroxide at temperatures at which formate is transformed into oxalate, oxidation almost quantitatively to CO₂ occurs with the evolution of an equivalent amount of H₂ [8]:

$$2 \text{NaOH} (s) + \text{CO} (g) = \text{Na}_2\text{CO}_3(s) + \text{H}_2(g)$$  \hspace{1cm} (8)

Similarly, Saxena proposed the inclusion of sodium hydroxide as an additional reactant to the conventional SMR system. The addition of sodium hydroxide serves the dual purpose of carbon sequestration and H₂ production [9].

$$2\text{NaOH} (s) + \text{CH}_4(g) + \text{H}_2\text{O} (g) = \text{Na}_2\text{CO}_3(s) + 4\text{H}_2(g) \Delta H= 244 \text{ kJ/mol (427°C)}$$  \hspace{1cm} (9)

Figure 2 compares the standard SMR (5) and modified SMR (9). It can be observed from the phase equilibrium diagram that the unlike modified SMR method, standard SMR technique produces a more complex composition of gas (CO, CO₂, H₂O,H₂) and also requires comparatively more energy (431kJ/mol at 927°C vs 244 kJ/mol at 427°C). However, the modified SMR reaction cannot be considered as a global solution. As sodium hydroxide is produced using electrolysis of brine which itself is a very energy intensive process.

Other methods such as coal-gasification and water-gas shift (WGS) reaction also produce H₂ at a large scale. Coal-gasification needs coal as a reactant and is a very energy consuming process. However, the WGS method is an exothermic reaction and operates at a low temperature. WGS reaction is an integral step for SMR technique as it produces additional H₂. Therefore, any modifications to these conventional techniques that can significantly reduce CO₂ emission are highly welcome.

Thermodynamic calculation shows that the addition of sodium hydroxide to CH₄, C and CO lowers the operating temperature and can also significantly reduce the CO₂ emission. Moreover, the amount of coal needed to run the processes is also lowered. Table 2 summarizes the inclusion of sodium hydroxide to CH₄, C and CO. Sodium hydroxide captures CO₂ and forms sodium carbonate (Na₂CO₃), which finds huge application in different chemical sectors. A series of experimental work which establishes the optimum operation condition and illustrated the use of suitable catalysts for these systems can be found elsewhere [10-12].
A similar concept of sodium hydroxide inclusion for enhanced H₂ production is already in use at industrial scale. For instance, the black liquor gasification process utilizes alkali hydroxide to serve the dual purpose of H₂ production and carbon sequestration. In a typical pulping process for paper production, approximately one-half of the raw materials are converted to pulp and other half is dissolved in the black liquor. The black liquor solution consists of well-dispersed carbonaceous material, steam and alkali metal which are burned to provide part of energy for the plant. Due to the presence of carbonaceous material and water in the liquor, following carbon-water reaction predominates:

\[
C(s) + H_2O(g) = CO(g) + H_2(g)
\]  

(10)

\[
CO(g) + H_2O(g) = CO_2(g) + H_2(g)
\]  

(11)

However, due to the thermodynamic limitations, reaction (11) never proceeds towards completion; therefore H₂ concentration does not exceed a certain limit. However, in the presence of NaOH, CO₂ capture medium, the equilibrium can be shifted to drive reaction (11) towards completion and therefore maximize H₂ concentration. Consequently, CO and CO₂ concentration reduces significantly in the product gases.

Table 2 Thermodynamic properties for different hydrogen production methods after inclusion of NaOH

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>CH₄ + H₂O</th>
<th>NaOH+ CH₄ + H₂O</th>
<th>C + H₂O</th>
<th>NaOH + C + H₂O</th>
<th>CO + H₂O</th>
<th>NaOH+ CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>700-1100</td>
<td>600-800</td>
<td>800-1200</td>
<td>500-700</td>
<td>130</td>
<td>300-400</td>
<td></td>
</tr>
<tr>
<td>Enthalpy (ΔH, kJ/mol)</td>
<td>431(327°C)</td>
<td>244 (427°C)</td>
<td>95.73(327°C)</td>
<td>64.58(327°C)</td>
<td>-242(327°C)</td>
<td>-119(327°C)</td>
</tr>
</tbody>
</table>

Mixture of product gases

<table>
<thead>
<tr>
<th></th>
<th>CO₂,CO₂,H₂</th>
<th>H₂</th>
<th>CO,CO₂,H₂</th>
<th>H₂</th>
<th>CO₂, H₂</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal / H₂(g/g)</td>
<td>1.64</td>
<td>0.93</td>
<td>3.73</td>
<td>3.49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO₂,H₂(g/g)</td>
<td>10.5</td>
<td>3.41</td>
<td>13.67</td>
<td>1.80</td>
<td>22(No H.R.)</td>
<td>- (No H.R.)</td>
</tr>
</tbody>
</table>

H.R.: Heat Recovery

2.2 Biomass

Biomass is a renewable energy resource obtained from solar energy, carbon dioxide and water. Biomass does not increase CO₂ level in the atmosphere as it uptakes the same amount of carbon while growing as releases when burnt as a fuel.

\[
\text{Biomass + heat + steam} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{Light/ Heavy hydrocarbons + Char}
\]

(12)

One of the major issues other than high carbon emission in biomass gasification is to deal with tar formation that occurs during the gasification process. The undesirable tar may cause the formation of tar aerosol and a more complex polymer structure, which are unfavorable for H₂ production through steam reforming. The existing methods to minimize tar formation are: (a) proper designing of gasifier (b) proper control and operation and (c) use of additives or catalysts. Sodium hydroxide-promoted biomass gasification to generate H₂ without CO or CO₂ formation generates H₂ and capture carbon [13]. Cellulose [C₆H₁₂O₆], D-glucose [C₆H₁₂O₆] and sucrose [C₁₂H₂₂O₁₁] react with water vapor in the presence of sodium hydroxide to form sodium carbonate and hydrogen. However, the product consists of hydrocarbons such as CH₄ and thus lowers the % hydrogen yield. Nickel catalysts supported on alumina can reduce the formation of CH₄ and increase the hydrogen yield to roughly 100% [14-17]. The mechanism of alkali promoted steam gasification of biomass indicates that the dehydrogenation of cellulose in presence of Na⁺ and OH⁻ ions yields hydrogen. The concentration of Na⁺ and OH⁻ ions strongly influences the dehydrogenation of cellulose [18-19].

Despite that the sodium hydroxide-promoted reaction provides many advantages; the alkali metal costs and their recycling are major concerns [3,20]. Su et al used a new catalyst derived from sodium aluminum oxide (Al₂O₃,Na₂O), Al₂O₃,Na₂O,xH₂O/NaOH/Al(OH)₃, to increase the hydrogen content in the product after steam gasification of cellulose. The gasification temperature was kept below 500°C to prevent any tar formation [21-22]. Moreover, sodium hydroxide can also significantly decrease the pyrolysis temperature of biomass species [23]. Sodium ion, being small, can penetrate into the biomass texture and break the hydrogen bridges. Consequently, devolatilization occurs rapidly. Thus, it can be seen that sodium hydroxide does play a significant role in biomass gasification.

2.3 Metals

Metals can react in the presence or absence of water and sodium hydroxide to produce hydrogen. Transition metals form metal oxides and hydrogen during the reaction with sodium hydroxide [24]. Moreover, ferrosilicon when reacts with sodium hydroxide produces sodium silicate and hydrogen [25]. Here, we focus on the Al-NaOH-H₂O system.
Hydrogen gas is generated from the chemical reaction between Al and water (3.7 wt% H₂, theoretical yield) [26]. Al/H₂O system is indeed a safe method to generate H₂. But the system has kinetic limitations as the metal surface passivation in neutral water occurs more easily and the metal activity with water is extremely low. Thus, improving the aluminum activity in water is an important task. To solve the problem of surface passivation of Al, various solutions have been suggested so far. The solutions either include the addition of hydroxides [27-28] metal oxides [29-30] selected salts [31-32] or alloying Al with low melting point metal [33-36]. Alkali-promoted Al/H₂O system is favored over other metal systems because of high H₂ generation rate. When the reaction between Al and water is assisted by alkali, OH⁻ ions are able to destroy the protective oxide layer on the aluminum surface forming AlO₂⁻.

The reaction between Al and H₂O with sodium hydroxide solution produces H₂, which can be expressed as follows [6, 12]

\[ 2\text{Al} + 6\text{H}_2\text{O} + \text{NaOH} \rightarrow 2\text{NaAl(OH)}_4 + 3\text{H}_2 \uparrow \quad (13) \]
\[ \text{NaAl(OH)}_4 \rightarrow \text{NaOH} + \text{Al(OH)}_3 \downarrow \quad (14) \]

Sodium hydroxide consumed for the H₂ generation in exothermic reaction (13) will be regenerated through the decomposition of NaAl(OH)₄ via reaction (14). Reaction (14) also produces a crystalline precipitate of aluminum hydroxide. The combination of above two reactions completes the cycle and shows that only water will be consumed in the whole process if the process is properly monitored. Previous works reported kinetics of the reaction between Al and H₂O with sodium hydroxide solution and calculated the activation energy in the range of 42.5-68.4 kJ/mol [37-38].

Several researchers examined the effects of other crucial parameters which control the H₂ generation behavior for alkali assisted Al/H₂O system. The parameters include temperature, alkali concentration, morphology, initial amount of Al, and concentration of aluminate ions [4, 39-40]. Moreover, Soler et al. compared the H₂ generation performance of three different hydroxides: NaOH, KOH and Ca(OH)₂ and found that NaOH solution consumes Al faster compared with other two hydroxides [40]. Interestingly, S.S. Martinez et al. treated Al-can wastes with NaOH solution at room temperature to generate highly pure hydrogen. The byproduct (NaAl(OH)₃) was used to prepare a gel of Al(OH)₃ to treat drinking water contaminated with arsenic [41]. On the basis of the above mentioned reactions, several patents have been filed in last decade [42-49].

### 2.4 Water Splitting Thermochemical Cycle

Solar energy is used to produce H₂ via 2 or 3 steps water splitting process. It should be noted that water is not directly split in H₂ and O₂ using this technology solution. But there is a series of chemical reactions which utilizes oxides and thermal energy from renewable sources (such as solar energy) that can convert water into stoichiometric amounts of H₂ and O₂ [50-52]. The water splitting thermochemical cycle is demonstrated in Figure 3. The figure demonstrates a 3 step water splitting process – (1) reduction of oxides (energy intensive process, 800-1000°C) (2) reaction of reduced oxide with sodium hydroxide (hydrogen generation step) and (3) hydrolysis reaction (sodium hydroxide recovery step).

Any thermodynamically favorable oxide can be selected and use to generate hydrogen. Thus, so far, a large number of oxides have been considered. The water splitting thermochemical cycle reactions can be mainly classified as (1) 2- step water splitting [53-57] (2) iodine-sulfur process [58-60] and (3) calcium-bromine process [61-63].

![Fig. 3 Schematic for Water Splitting Thermochemical Cycle (MO= metal oxide)](image)

Here, we focus only on the alkali metal assisted water splitting thermochemical cycles and table 3 summarizes them. The presence of alkali hydroxide (sodium hydroxide) is able to reduce the H₂ generation reaction temperature. Recently, Miyoka et al considered sodium redox reaction and conducted several experiments in a non-equilibrium condition but could not achieve a 100% conversion [64]. It was attributed to the slow kinetics of both the hydrogen generation
reaction and sodium recovery. Moreover, sodium hydroxide facilitates oxidation in the water splitting step. But the volatility of sodium hydroxide at temperature higher than 800°C and incomplete Na⁺ extraction by water to recover sodium hydroxide limits its application. Several research groups concluded that even though sodium or sodium hydroxide assisted reaction has major advantages; their recovery could be a big challenge. Interestingly, Weimer et al. recommends membrane separation to recover sodium hydroxide [65]. Few researcher groups also pointed out the possibility of using sodium carbonate rather than sodium hydroxide [66-68].

Table 3 Alkali metal assisted water splitting thermochemical cycle

<table>
<thead>
<tr>
<th>System</th>
<th>Reactions</th>
<th>Conditions</th>
<th>H₂ Yield</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>Mn₂O₃ = 2MnO + 0.5O₂ (&lt;1600°C) 2MnO + 2NaOH = H₂ + 2Na₂NaMnO₄ (&lt;700°C) H₂O = H₂ + 0.5O₂</td>
<td>H₂ generation at 750°C</td>
<td>100% conversion under vacuum (0.5h) and under N₂ purge (3h)</td>
<td>NaOH recovery improved from 10% to 35% in (MnO + Fe) mixture Difficult Mn₂O₃ - NaOH separation</td>
<td>[69]</td>
</tr>
<tr>
<td>Ce₂Ti₂O₇</td>
<td>MO(ox) = MO(red) + 0.5 O₂ 2MO + 2NaOH = 2Na₂MO + H₂</td>
<td>Mixed oxide synthesis around 1500°C</td>
<td>(1.5-1.94) mmol/g oxide</td>
<td>At 530°C, Ce₂Si₂O₇ (highest reaction efficiency) H₂ generation infeasible up to 1000°C</td>
<td>[70]</td>
</tr>
<tr>
<td>Ce₆Si₂O₇, CeFe₂O₇, CeVO₄, CeNbO₄</td>
<td>Zn₁₀,₆₅Mn₁₉₂O₄₋₀.₃₃ = 2Zn₁₀,₆₅Mn₁₉₂O₄₋₀.₃₃ + 0.5O₂ (&lt;1600°C) 2Zn₁₀,₆₅Mn₁₉₂O₄₋₀.₃₃ + 2NaOH = H₂ + Na₂Zn₁₀,₆₅Mn₁₉₂O₄₋₀.₃₃ (&lt;650°C) Na₂Zn₁₀,₆₅Mn₁₉₂O₄₋₀.₃₃ + H₂O = Zn₁₀,₆₅Mn₁₉₂O₄₋₀.₃₃ + 2NaOH (&lt;100°C)</td>
<td>H₂ generation above 650°C</td>
<td>80-90% conversion rate under low pressure and residence time of 0.5h</td>
<td>NaOH may be recovered using membrane process</td>
<td>[65]</td>
</tr>
<tr>
<td>Zn-Mn-O</td>
<td>2NaOH + Na = Na₂O + H₂ (T = 32°C) 2NaO + Na₂O = 2Na₂ + 2Na (T = 1870°C) Na₂O + H₂O = 2NaOH + 0.5O₂ (100°C)</td>
<td>H₂ production, below 400°C</td>
<td>&gt;80% at 350°C</td>
<td>Yield of H₂ generation and Na separation &lt;100% , kinetic limitation, suitable catalysts needs to be investigated</td>
<td>[64]</td>
</tr>
</tbody>
</table>

Besides sodium hydroxide recovery, there are other limitations too. For instance, the reduction of oxides requires a very high temperature. If such a high temperature will be provided by the solar energy, a large scale solar heat plants is needed. Thus at present, the construction of thermochemical hydrogen production plants is restricted by the location, cost and safety issues. Therefore, the major challenge is to lower the operating temperature of water splitting process. A low temperature water splitting process will allow the utilization of small-scale solar heat systems or even exhaust heat from industries. As sodium hydroxide can significantly reduce the operating temperature of the water splitting process, hence sodium hydroxide has a major role to play.

2.5 Organic Compounds

2.5.1 Formic acid (HCOOH)

Formic acid and its solution are industrial hazards. Any use of such chemical waste will be of a great advantage. Formic acid is considered for both H₂ production and storage. Basically, formic acid can produce hydrogen using two methods: (1) Thermo catalytic decomposition and (2) Electrolysis in presence of sodium hydroxide.

Formic acid thermally decomposes to produce H₂ and CO₂ (ΔG° = -32.9 kJ/mol, ΔH° = 31.2 kJ/mol), which is actually the reversible reaction of CO₂ hydrogenation [71-79]. Electrolysis of formic acid solutions in the presence of sodium hydroxide requires theoretically much lower energy than water [80]. Hence, use of formic acid solution to generate hydrogen will have double benefits of tackling pollution and generating clean energy. The electrochemical reaction for the electrolysis of formic acid solutions is as follows [81]:

Anode: HCOOH + OH⁻ → CO₂ + H₂O + 2e⁻
Cathode: 2H₂O + 2e⁻ → H₂ + 2OH⁻
Overall reaction: HCOOH → H₂ + CO₂ (15)
Figure 4 demonstrates the scheme of electricity generation via the combined use of alkaline hydroxide (sodium hydroxide) for the electrolysis of formic acid (HCOOH) and fuel cell. The separation of H₂ and CO₂ is desired prior to injection in the fuel cell.

2.5.2 Formaldehyde (HCHO)
An aqueous solution of formaldehyde when mixed with sodium hydroxide produces very small amount of hydrogen [82]. Thus, it is obvious that H₂ evolution competes with the disproportionation of formaldehyde to corresponding alcohol and acid [83-84]. Further, Ashby et al proposed a mechanistic explanation of hydrogen evolution from formaldehyde in the presence of sodium hydroxide [85]. The mechanism indicates that one hydrogen atom originates from the water and the other from the organic moiety. The experimental study exhibits that when a dilute solution of formaldehyde (4x10^{-4}M) reacts with concentrated sodium hydroxide (19M) at room temperature, hydrogen is produced in a significant amount. However, concentrated solution of formaldehyde when interacts with dilute sodium hydroxide solution produces only a trace amount of hydrogen.

When solution of hydrogen peroxide is mixed with formaldehyde in presence of sodium hydroxide, hydrogen is generated [86]. Hydrogen peroxide oxidizes formaldehyde to formic acid and sodium hydroxide further neutralizes the acid.

\[
\text{H}_2\text{O}_2 + 2\text{HCHO} + 2\text{NaOH} = 2\text{HCOONa} + \text{H}_2 + 2\text{H}_2\text{O} \tag{16}
\]

However, no trace of hydrogen is observed in the absence of sodium hydroxide [87-88]. The reaction (16) is limited by slow kinetics and requires a large excess of alkali hydroxide. When hydrogen peroxide is replaced by cuprous oxide, H₂ is generated in a quantitative amount.

2.6 Hydrides
Hydride rapidly reacts with water to produce hydrogen. For instance, the binary hydride (LiH) reacts spontaneously with water while the complex hydride (NaBH₄) reacts slowly unless catalyzed [89-92]. However, for both hydrides, it is difficult to achieve the stoichiometric amount of hydrogen.

2.6.1 Binary Hydrides
(a) NaH/ LiH- NaOH
Reaction of LiH with water produces LiOH. LiOH is hygroscopic in the nature and therefore binds excess water [93]. A large amount of water requires extra heat to regenerate anhydrous LiOH. To avoid such situation, LiH is mechanically mixed with NaOH in a molar ratio of 1:1 and 2:1 to generate H₂ [94].

\[
\text{NaOH} + 2\text{LiH} \rightarrow \text{Li}_2\text{O} + \text{NaH} + \text{H}_2 \quad \Delta H^\circ = -48.1 \text{ kJ/mol-H}_2 \tag{17}
\]

\[
\text{NaOH} + \text{LiH} \rightarrow 0.5\text{Li}_2\text{O} + 0.5\text{NaH} + \text{H}_2 \quad \Delta H^\circ = 8.1 \text{ kJ/mol-H}_2 \tag{18}
\]

It can be observed that as the molar ratio of LiH increases, the reaction between NaOH and LiH tends to be an exothermic reaction and thus expected to occur at a lower temperature. The following mixtures with the molar ratio of 1:1 and 2:1 for LiH and NaOH, heated at 250°C, produces 1.92 and 3.20 wt. % H₂ respectively. These yields are about 50% and 66% of the total hydrogen content present in the mixtures. After heating the mixtures at 250°C, besides H₂, product also contains Li₂O, NaH and NaOH. There was no sign of Na₂O and LiOH formation. The reabsorption of H₂ by the product mixture was not reported so far, thus the reversibility of the presented scheme still needs to be investigated.
When LiH is replaced by NaH, only H₂ and Na₂O are the products. The combination of NaH and NaOH can release/uptake ~ 3 wt. % H₂ reversibly at temperature below 300°C [95]. It should be noted that the reaction between NaH and NaOH has a large endothermic enthalpy (ΔH = 64.3 kJ/mol-H₂) and ΔG° is negative only above 400°C. Na₂O is unstable in H₂ atmosphere at temperatures below 400°C.

\[ \text{NaH} + \text{NaOH} \leftrightarrow \text{Na}_2\text{O} + \text{H}_2 \]  

Q. Xu et al. reported complete conversion of Na₂O to NaH and NaOH under H₂ atmosphere (100 bars) at 150°C. The addition of NaOH to NaH can also significantly decrease the dehydrogenation temperature of NaH. However, neither LiH-NaOH nor NaH-NaOH release/uptake H₂ in a significant amount and therefore lags behind the target set up by US Department of Energy. Moreover, the operating temperature of absorption and desorption does not meet the goal. The current price of Li or Na hydride is too much and hence is unfit to deliver economical H₂.

### 2.6.2 Complex Hydrides

**(a) Mg (NH₂)₂-2LiH-NaOH**

Mg (NH₂)₂ -LiH system undergoes reaction as shown below to produce H₂ reversibly. The desorption enthalpy change for the first step is 38.9kJ/mol-H₂ [96] which is much lower than LiNH₂-LiH mixture (66kJ/mol-H₂). The reduced enthalpy change permits the H₂ to be absorbed/desorbed at moderate temperature and pressure.

\[ \text{Mg} (\text{NH}_2)_2 + 2\text{LiH} \leftrightarrow \frac{1}{2} \text{Li}_2\text{Mg}_2\text{N}_3\text{H}_3 + \frac{1}{2} \text{LiNH}_2 + \frac{1}{2} \text{LiH} + 3/2 \text{H}_2 \leftrightarrow \text{Li}_2\text{Mg} (\text{NH})_2 + 2\text{H}_2 \]  

Several efforts have been devoted to lower the operating temperatures (<200°C) and enhancing the hydrogenation/dehydrogenation rate of Mg (NH₂)₂-2LiH system [97-101]. Liang et al introduced NaOH to the Mg (NH₂)₂-2LiH system as a catalyst precursor and investigated its effect on the operating temperatures for hydrogenation/dehydrogenation rate [102]. They achieved ~36°C reduction in the dehydrogenation peak temperature for Mg (NH₂)₂-2LiH-0.5NaOH. During ball milling, NaOH reacts with Mg (NH₂)₂ and LiH to convert to NaH, LiNH₂ and MgO. The hydrogen desorption temperature may be reduced by the addition of NaOH to the system. However, the use of NaOH has an adverse effect on the hydrogen capacity of the hydride sample. The total hydrogen capacity decreased from 5.28 wt. % [pristine sample] to ~3.61 wt. % [Mg (NH₂)₂-2LiH-0.5NaOH sample] due to the dilution of NaOH.

**(b) NaBH₄-NaOH**

A NaBH₄ solution with alkaline stabilizer, sodium hydroxide, reacts with water in the presence of catalysts to produce H₂ and sodium metaborate (NaBO₂) [103-109]. The catalytic reaction for NaBH₄-NaOH system is heterogeneous, irreversible and exothermic in nature. Hung et al has tabulated the kinetic models for different catalysts, concentration of NaBH₄, temperature, time and activation energy for NaBH₄-NaOH system [110]. The reaction is generally performed in the temperature range of 10-60°C for various times and the activation energy varies from 40-55 kJ/mol. Based on these conditions and various catalysts behavior, different reaction kinetic models such as zero- order, first-order and Langmuir- Hinshelwood have been suggested for NaBH₄-NaOH system.

\[ \text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{NaBO}_2 \quad \Delta H^\circ = -210 \text{ kJ/mol} \]  

A study for hydrolysis kinetics of NaBH₄-NaOH system over Ru/G (Ruthenium -Graphite) catalysts is recently reported. The result shows that H₂ generates at a rate of 32.3 L min⁻¹ g⁻¹ Ru in a 10 wt. % NaBH₄ + 5 wt. % NaOH solution [111]. The Ru/G catalyst with high activity and durability demonstrates a potential for the portable fuel generators.

### 3. Conclusion

The use of sodium hydroxide for hydrogen production and storage is justified by the high reaction rate, lower operating temperature and overall reduction in CO₂ emission. Depending on the reaction and its conditions, sodium can produce or store hydrogen. Moreover, several situations illustrate how sodium hydroxide binds with CO₂ and forms valuable chemical compound, Na₂CO₃.

However, a major limitation for the inclusion of sodium hydroxide as one of the primary ingredients for obtaining the hydrogen is the production route of sodium hydroxide itself. At present, high energy intensive process (electrolysis of brine) is the prime method to produce sodium hydroxide. It will be of a great interest to invent or modify a method in which sodium hydroxide can be produced using the renewable resources such as solar, water and wind. Any such method would certainly mitigate the CO₂ emission by a huge amount and eventually increase the role of sodium hydroxide for hydrogen production and storage purpose.
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