

## Chapter 2

# Sodium Hydroxide for Clean Hydrogen Production

**Abstract** Hydrogen can be generated in several ways utilizing either renewable or non-renewable sources. However, the lack of a clean hydrogen generation methods at a large scale is considered to be one of the obstacles to implement hydrogen economy. The role of sodium hydroxide is increasing as a valuable ingredient to produce hydrogen. However, the vast use of sodium hydroxide is limited due to its (i) corrosive nature and (ii) high-energy-intensive production method. 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 hydrogen production methods such as steam methane reforming (SMR), coal gasification, biomass gasification, electrolysis, photochemical and thermochemical. Sodium hydroxide, being alkaline, acts as a catalyst, promoter or even a precursor.

**Keywords** Hydrogen economy • Energy-intensive • Sequester • Steam methane reforming • Coal/biomass gasification • Electrolysis • Photochemical/thermochemical

## 2.1 Introduction

Hydrogen has a potential to become an environmentally benign energy carrier for the future. However, clean production methods for hydrogen are yet to be identified. Hydrogen's source is either hydrocarbons or water. The primary methods for the generation of hydrogen involve reactions of coal, char, or hydrocarbons with steam at high temperatures. Hydrocarbons are preferred because of their inherent advantages such as their availability, comparable cost, ease of storage and distribution, and relatively high H/C ratio [1]. As stated earlier, water can also produce  $H_2$  (electrolysis process). However, the electrolysis of water is a very energy-intensive process. As burning of fossil fuel is the main energy source for

water electrolysis, splitting of water into its chemical constituents ( $H_2$  and  $O_2$ ) indirectly leads to vast carbon dioxide emissions. Because of the aforementioned reasons, it seems certain that hydrocarbons are likely to play a significant role in hydrogen production in the near- to medium-term future.

The methods for hydrogen production using hydrocarbon feedstock can be categorized either as follows:

- (a) Oxidative (uses oxidants or their combination— $O_2$ ,  $H_2O$ ,  $CO_2$ ) or
- (b) Non-oxidative (splitting of the C–H bond using energy input).

Most of the industrial hydrogen production processes (e.g., steam methane reformation (SMR), partial oxidation, auto-thermal reforming) belong to the oxidative category. The use of oxidants is always accompanied by the vast release of carbon dioxide. A typical oxidant-based hydrogen plant with a capacity of 2.5 million  $m^3$  hydrogen per day vents 1 million  $m^3$  of  $CO_2$  into the atmosphere [1]. Fortunately, the non-oxidative method does not require any oxidant, and therefore, no carbon dioxide is directly emitted via this process. However, the non-oxidative method (e.g., water electrolysis) produces carbon dioxide indirectly through the consumption of fossil-derived electricity.

Of course, the aim is to mitigate carbon emission during hydrogen production. The possible ways are as follows:

- (a) use of carbon dioxide absorption unit at a hydrogen plant,
- (b) use of nuclear reactors, and/or
- (c) thermal dissociation of hydrocarbons into hydrogen and carbon.

However, none of these technologies can completely curb  $CO_2$  emissions and they tend to emit greenhouse gases directly or indirectly. Thus, at present, all these suggested methods have their own limitations. For instance, the integration of carbon dioxide capture unit with hydrogen production process would increase the cost of hydrogen production by about 25–30 % [2]. In the same line, the use of nuclear reactors for hydrogen production gained substantial attention in the last decade because nuclear reactors already produce enough heat for changing water into steam and the electricity for splitting the steam down into hydrogen and oxygen. However, these nuclear reactors are very expensive and cannot be economically feasible to serve world energy demand. As mentioned earlier, another possible way is to thermally dissociate hydrocarbons to produce hydrogen and solid carbon. The thermal dissociation process produces solid carbon, which is far easier to separate compared to gaseous carbon dioxide. It is noteworthy that such method is free of  $CO_2$  separation step, which is highly energy-intensive process. However, at present, the thermal dissociation process itself is fossil-derived and thus cannot eliminate the emission of  $CO_2$ .

Currently, there are no other known methods of hydrogen production that do not involve carbon emission, other than those using non-fossil energy. Having this in mind, fossil fuel-based processes that can mitigate carbon dioxide will be worth

investigating. Recently, many researchers have proposed the inclusion of sodium hydroxide to the existing hydrogen production technologies. For instance, Reichman et al. [3] suggested a process called Ovonic Renewable Hydrogen (ORH). This method involves sodium hydroxide for the reformation of organic matter to produce hydrogen gas. Moreover, Onwudili and William [4] used sodium hydroxide as a promoter to produce hydrogen gas via hydrothermal gasification of glucose and other biomass samples. Similarly, Kamo et al. [5] pyrolyzed dehydrochlorinated polyvinyl chloride (PVC) and activated carbon with sodium hydroxide and steam to generate hydrogen gas and sodium carbonate with methane, ethane, and carbon dioxide as by-products.

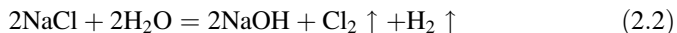
The use of sodium hydroxide for the production of hydrogen has been in application since the nineteenth century. Sodium hydroxide has been proposed as an essential ingredient for most of the present hydrogen producing technologies. Below, sodium hydroxide-based modifications for the methods using fossil fuels, biomass, metal, organic compounds, and water are reviewed. The related concepts and their results are discussed in the following sections.

### 2.1.1 Overview of Sodium Hydroxide (NaOH)

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

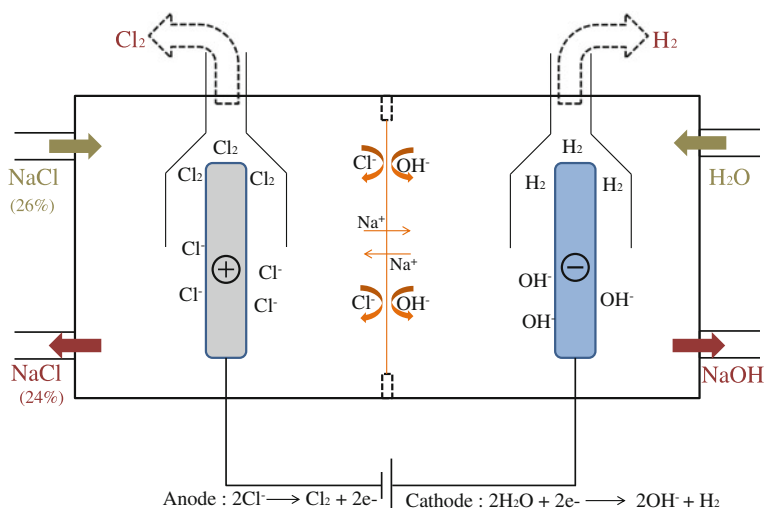


Currently, sodium hydroxide is produced by the electrolysis of brine (NaCl):



Reaction (2.2) is an energy-intensive process and thus has significant carbon footprint. Besides sodium hydroxide, reaction (2.2) also produces toxic chlorine and hydrogen as by-products. It is necessary to modify reaction (2.2) in such a way that can significantly reduce the emission of  $\text{CO}_2$  and toxic chlorine to the atmosphere.

Figure 2.1 illustrates the membrane cell used for the electrolysis of brine [6]. The three commercially available production methods for sodium hydroxide are compared here (Table 2.1). The strength of soda solutions and amount of required steam varies for different production methods. As a diaphragm cell produces the least concentrated soda solutions, evaporation is required to raise the concentration up to 50 wt% solution as in mercury cell process.



**Fig. 2.1** Membrane cell process schematic for the production of sodium hydroxide previously published in [6], with permission from Formatex Research Center © 2013

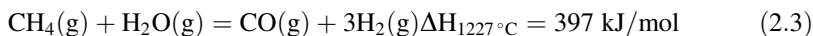
**Table 2.1** Comparison of the commercially available production methods for NaOH [81]

Factors	Diaphragm	Mercury	Membrane
Use of mercury	No	Yes	No
Chlorine as a by-product	Yes	No	Yes
Operating current density ( $\text{kA}/\text{m}^2$ )	0.9–2.6	8–13	3–5
Cell voltage (V)	2.9–3.5	3.9–4.2	3.0–3.6
NaOH strength (wt%)	12	50	33–35
Energy consumption ( $\text{kWh}/\text{Mt Cl}_2$ ) at a current density ( $\text{kA}/\text{m}^2$ )	2,720 (1.7)	3,360 (10)	2,650 (5)
Steam consumption ( $\text{kWh}/\text{MT Cl}_2$ ) for concentration to 50 % NaOH	610	0	180
% NaOH produced in USA	62	10	24

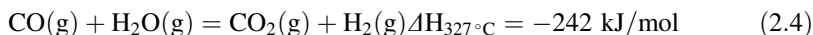
## 2.2 Hydrogen Production

### 2.2.1 Fossil Fuels

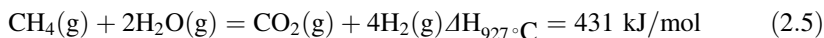
Currently, SMR is the most common and the least expensive industrial technology to produce hydrogen [7]. Methane reacts at a high temperature (700–1,100) °C with steam to form syngas ( $\text{CO} + \text{H}_2$ ).



Syngas can further react with steam to form additional hydrogen at a lower temperature.



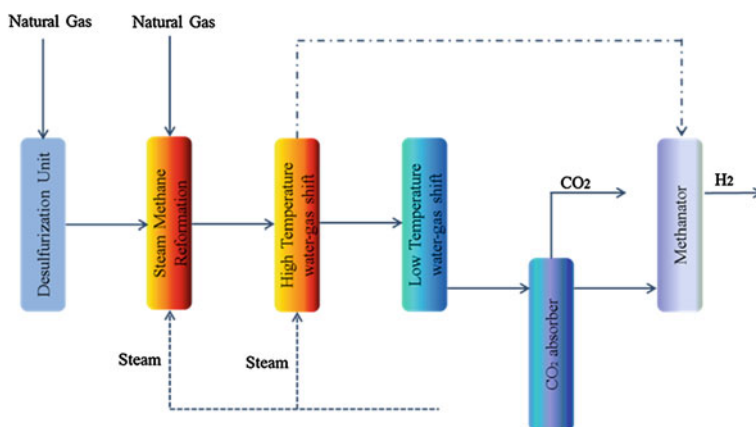
Thus, the combined reaction is



The enthalpy change ( $\Delta H$ ) is provided for temperatures at which the reaction is producing the maximum hydrogen and calculated using FACTSAGE<sup>TM</sup> software. It should be noted that the equilibrium values of the gases are different from what is given by stoichiometric proportions of species on the product side of the equations.

Figure 2.2 depicts the simplified block diagram of SMR technique equipped with carbon dioxide absorption unit and a methanation reactor. The main operating units include natural gas feedstock desulfurization, catalytic reforming, water–gas shift reactor, and  $\text{CO}_2$  gas separation and hydrogen purification [8].

In the desulfurization unit, sulfur-based organic compounds (such as thiols) are first converted into  $\text{H}_2\text{S}$  by catalytic hydrogenation reaction ( $\text{Co-Mo}$  catalysts,  $290\text{--}370^\circ\text{C}$ ) [9]. Further,  $\text{H}_2\text{S}$  reacts with  $\text{ZnO}$  to form  $\text{ZnS}$ . ( $\text{H}_2\text{S} + \text{ZnO} \rightarrow \text{ZnS} + \text{H}_2\text{O}$ ,  $340\text{--}390^\circ\text{C}$ ). Natural gas feedstock must be pretreated before mixing with steam (2.6 MPa). And then, the mixture should be heated to  $500^\circ\text{C}$  prior to sending the SMR unit. SMR is favored by low pressure and performed in the reactor at usually 2.0–2.6 MPa. The gaseous mixture ( $\text{H}_2$ ,  $\text{CO}$  and steam) leaves the reformer at  $800\text{--}900^\circ\text{C}$ . It is cooled rapidly to  $350^\circ\text{C}$  and fed to the water–gas shift

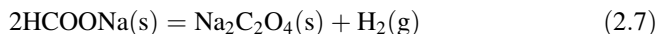


**Fig. 2.2** A schematic of hydrogen production by SMR—with solvent removal of  $\text{CO}_2$  and a methanation unit [8]

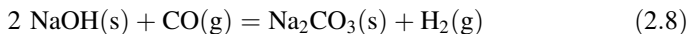
reactor, where reaction (2.4) is operated. Reaction (2.4) produces hydrogen and carbon dioxide. Carbon dioxide is captured using amine-based solvent—monoethanolamine (MEA). And the remaining residuals,  $\text{CO}_2$  and  $\text{CO}$ , are fed to methanation reactor, where the mixture is converted to  $\text{CH}_4$  in the presence of hydrogen (320 °C, Ni or Ru on oxide support as catalyst) [8].

Interestingly, a simple calculation shows that about 10.5 g of  $\text{CO}_2$  is emitted per gram of  $\text{H}_2$  production via SMR technique. Such an undesired vast emission of  $\text{CO}_2$  endangers the prolonged use of conventional SMR technique to produce hydrogen. However, as mentioned earlier, the integration of an amine-based  $\text{CO}_2$  capture unit to hydrogen production process would significantly increase the cost of hydrogen per ton. Therefore, at present, most of the SMR sites are not equipped with  $\text{CO}_2$  absorber unit.

In this regard, several new methods are proposed that could solve the existing problems [10–15]. Berthelot described the reaction between  $\text{NaOH}$  and  $\text{CO}$  which yields sodium formate ( $\text{HCOONa}$ ). When heated above 250 °C,  $\text{HCOONa}$  transforms into oxalate with the release of hydrogen:



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 convert to carbon dioxide occurs with the evolution of an equivalent amount of hydrogen [16]:



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  $\text{H}_2$  production [17].

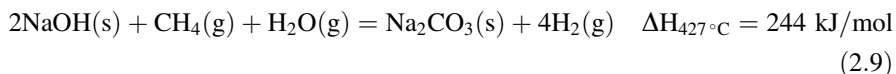
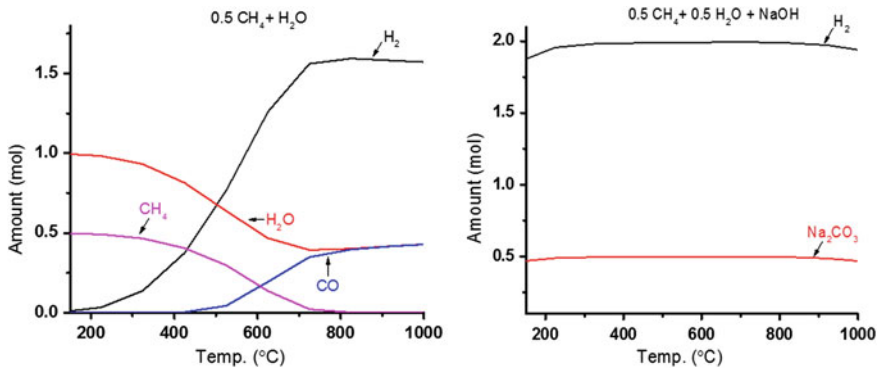


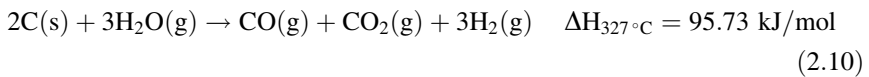
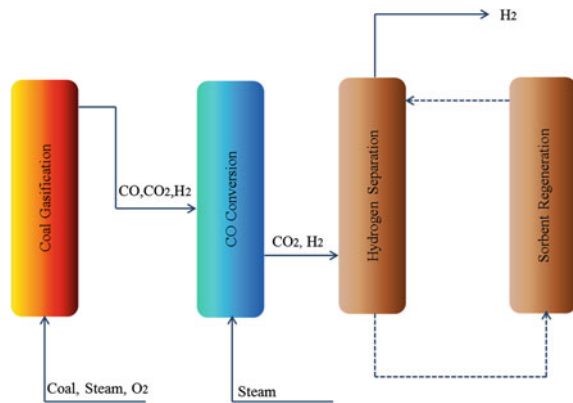
Figure 2.3 compares the standard SMR (5) and modified SMR (9). It can be observed from the phase equilibrium diagram that unlike modified SMR method, conventional SMR technique produces a more complex composition of gas ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ) and also requires comparatively more energy (431 kJ/mol at 927 °C versus 244 kJ/mol at 427 °C).

Coal gasification is another well-established technology to produce hydrogen. However, it is also an energy-intensive process. Here, oxygen or steam is passed over coal to produce a gaseous mixture of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  from which  $\text{H}_2$  is separated (Fig. 2.4).



**Fig. 2.3** Calculated equilibrium in the system **a** conventional SMR and **b** modified SMR reactions

**Fig. 2.4** Production of hydrogen from coal gasification [1]



Coal-made hydrogen has applications in the production of ammonia, methanol, methane, and Fischer–Tropsch products. However, coal gasification suffers critical limitations [1], and it is given as follows:

- (a) not as cost-effective as producing hydrogen from oil or natural gas;
- (b) an endothermic reaction; and
- (c) with vast emission of  $\text{CO}_2$ .

Figure 2.5 illustrates the thermodynamic calculation on  $[\text{NaOH(s)} + \text{C(s)} + \text{H}_2\text{O(g)}]$  using Factsage<sup>TM</sup> software. The inclusion of sodium hydroxide to the coal–steam system can significantly reduce the energy input (95.73 kJ/mol reduced to 64.58 kJ/mol at 327 °C) [18]. The system not only captures  $\text{CO}_2$  in the form of soda ash but also produces hydrogen. Moreover, the system does not produce complex mixture of gases.

**Fig. 2.5** Calculated equilibrium in the system  $2\text{NaOH(s)} + \text{C(s)} + \text{H}_2\text{O(g)}$

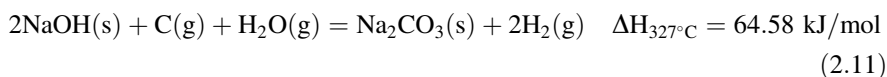
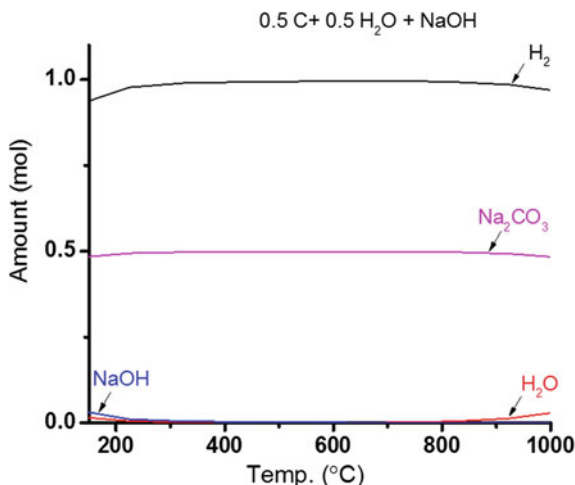


Table 2.2 summarizes the thermodynamic calculation and the effect for the addition of sodium hydroxide to methane and coal. It can be observed that the inclusion of alkali reduces both the operating temperature and carbon dioxide emission. As a consequence, the amount of coal required to run these processes is also reduced. Table 2.2 summarizes the inclusion of sodium hydroxide to  $\text{CH}_4$  and C in the presence of steam. Sodium hydroxide captures  $\text{CO}_2$  and forms sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), which has huge application in different chemical sectors such as glass manufacturing, electrolyte, textiles, and domestic use.

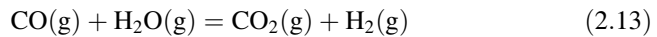
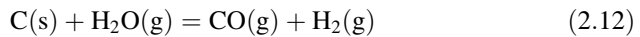
Sodium hydroxide is already in use for hydrogen production at industrial scale. For instance, the black liquor gasification process utilizes alkali hydroxide to serve the dual purpose of hydrogen production and carbon sequestration. In a typical pulping process for paper production, approximately one-half of the raw materials are converted to pulp and other half are dissolved in the black liquor. The black liquor solution consists of well-dispersed carbonaceous material, steam, and alkali

**Table 2.2** Thermodynamic properties for different hydrogen production methods after inclusion of NaOH [82]

	$\text{CH}_4 + \text{H}_2\text{O}$	$\text{NaOH} + \text{CH}_4 + \text{H}_2\text{O}$	$\text{C} + \text{H}_2\text{O}$	$\text{NaOH} + \text{C} + \text{H}_2\text{O}$
Temperature ( $^\circ\text{C}$ )	700–1,100	600–800	800–1,200	500–700
Enthalpy ( $\Delta H$ , kJ/mol)	431 (927 $^\circ\text{C}$ )	244 (427 $^\circ\text{C}$ )	95.73 (327 $^\circ\text{C}$ )	64.58 (327 $^\circ\text{C}$ )
Mixture of product gases	$\text{CO}$ , $\text{CO}_2$ , $\text{H}_2$	$\text{H}_2$	$\text{CO}$ , $\text{CO}_2$ , $\text{H}_2$	$\text{H}_2$
Coal/ $\text{H}_2$ (g/g)	1.64	0.93	3.73	3.49
$\text{CO}_2/\text{H}_2$ (g/g)	10.5	3.41	13.67	1.80



metal which are burned to provide part of energy for the plant. Due to the presence of carbonaceous material and water in the liquor, the following carbon–water reaction dominates:



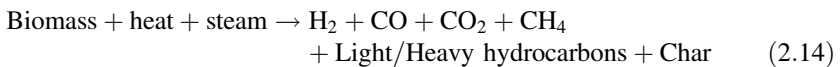
However, due to the thermodynamic limitations, reaction (2.13) never proceeds toward completion; therefore, hydrogen concentration does not exceed a certain limit. Interestingly, in the presence of NaOH, CO<sub>2</sub> capture medium, the equilibrium can be shifted to drive reaction (2.13) toward completion and therefore maximize hydrogen concentration. Consequently, the concentration of CO and CO<sub>2</sub> is reduced significantly in the product gases.

It is noteworthy that the modifications based on the use of sodium hydroxide cannot be considered as a solution on the global scale. Sodium hydroxide itself is produced using electrolysis of brine which is a highly energy-intensive process.

### 2.2.2 Biomass

Biomass is a renewable energy source and is regarded as a carbon-neutral fuel. It consumes the same amount of carbon while growing as much it releases when burnt as a fuel.

Biomass gasification means incomplete combustion of biomass resulting in the production of combustible gases consisting of CO, H<sub>2</sub>, and traces of CH<sub>4</sub>.



The major challenges that the gasification process mainly faces are as follows: (1) undesirable tar formation and (2) huge carbon emission. The tar may cause the formation of tar aerosol and a more complex polymer structure, which are not favorable for hydrogen production through steam reformation. The suggested solutions to minimize tar formation are as follows:

- (a) proper designing of gasifier;
- (b) proper control and operation; and
- (c) use of additives or catalysts.

The addition of sodium hydroxide to biomass gasification can solve some of the existing problems [19]. Firstly, inclusion of sodium hydroxide can reduce the carbon emission. Cellulose [C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>], D-glucose [C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>], and sucrose [C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>] react with water vapor in the presence of sodium hydroxide to form sodium carbonate and hydrogen. The mechanism of the alkali-promoted reaction

suggests that the dehydrogenation of cellulose in presence of  $\text{Na}^+$  and  $\text{OH}^-$  ions yields hydrogen. The concentration of  $\text{Na}^+$  and  $\text{OH}^-$  ions strongly influences the dehydrogenation of cellulose [20, 21]. However, the product also consists of hydrocarbons such as  $\text{CH}_4$  and lowers the percentage of hydrogen yield. But nickel catalysts supported on alumina can reduce the formation of  $\text{CH}_4$  and maximize the hydrogen yield [4, 20–22].

Secondly, sodium hydroxide can also reduce the pyrolysis temperature of biomass species [23]. Sodium ions, being small, can penetrate into the biomass texture and break the hydrogen bridges. Consequently, devolatilization occurs rapidly. Su et al. used a new catalyst derived from sodium aluminum oxide ( $\text{Al}_2\text{O}_3\cdot\text{Na}_2\text{O}$ ),  $\text{Al}_2\text{O}_3\cdot\text{Na}_2\text{O}\cdot x\text{H}_2\text{O}/\text{NaOH}/\text{Al}(\text{OH})_3$ , to increase the hydrogen yield for steam gasification of cellulose. The gasification temperature was kept below  $500^\circ\text{C}$  to prevent any tar formation [24, 25].

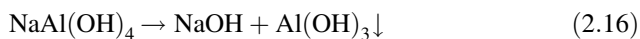
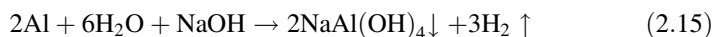
Sodium hydroxide acts as a promoter of hydrogen gas during the hydrothermal gasification of glucose and other biomass samples. However, the cost of alkali metal and its proper recycling are major concerns for the use of sodium hydroxide in the biomass gasification.

### 2.2.3 Metals

Metals can react with sodium hydroxide in the presence or absence of water to produce hydrogen. Transition metal reacts with sodium hydroxide to form metal oxides and hydrogen [26]. Ferrosilicon too generates hydrogen on reacting with sodium hydroxide [27].

Here, the reaction of aluminum (the most abundant metal in Earth's crust) is considered with sodium hydroxide in the presence of water vapor. As can be expected, hydrogen gas is generated from the chemical reaction between Al and water (3.7 wt%  $\text{H}_2$ , theoretical yield) [28]. Al/ $\text{H}_2\text{O}$  system is indeed a safe method to generate hydrogen. 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, aluminum activity in water needs to be improved. To solve the problem of surface passivation of Al, various solutions have been suggested so far. The solutions either include the addition of hydroxides [29, 30], metal oxides [31, 32], selected salts [33, 34], or alloying Al with low melting point metal [35–38]. The alkali-promoted Al/ $\text{H}_2\text{O}$  system is favored over other metal systems because of the high hydrogen generation rate.

The reaction between Al and  $\text{H}_2\text{O}$  with sodium hydroxide solution produces hydrogen, which can be expressed as follows:



Sodium hydroxide consumed for the hydrogen generation in exothermic reaction (2.15) will be regenerated through the decomposition of  $\text{NaAl(OH)}_4$  via reaction (2.16). Reaction (2.16) also produces a crystalline precipitate of aluminum hydroxide. The combination of above two reactions completes the cycle and demonstrates that only water will be consumed in the whole process if the process is properly monitored. Some of the previous work conducted in this sphere reported kinetics of the reaction between Al and  $\text{H}_2\text{O}$  with sodium hydroxide solution and calculated the activation energy in the range of 42.5–68.4 kJ/mol [39, 40].

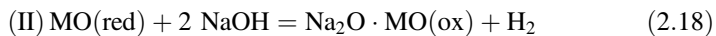
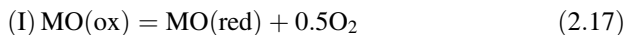
Many researchers examined the effects of other crucial parameters that control the hydrogen generation properties for alkali-assisted Al/ $\text{H}_2\text{O}$  system. The parameters include temperature, alkali concentration, morphology, initial amount of Al, and concentration of aluminate ions [41, 42]. Moreover, Soler et al. compared the hydrogen generation performance for three different hydroxides: NaOH, KOH, and  $\text{Ca(OH)}_2$ . They observed that sodium hydroxide solution consumes Al faster compared with other two hydroxides [42]. Similarly, S.S. Martinez et al. treated Al-can wastes with NaOH solution at room temperature to generate pure hydrogen. The by-product ( $\text{NaAl(OH)}_4$ ) was used to prepare a gel of  $\text{Al(OH)}_3$  to treat drinking water contaminated with arsenic [43].

### 2.2.4 Water-Splitting Thermochemical Cycle

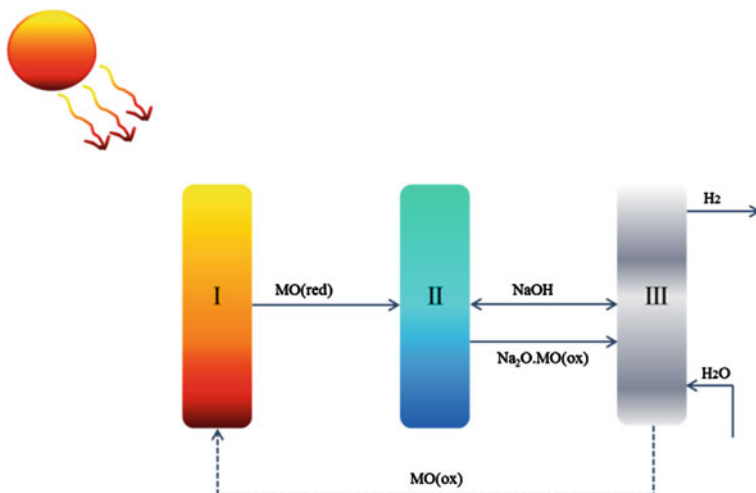
Water is a basic source of hydrogen. However, direct splitting of water in hydrogen and oxygen requires huge amount of energy. Therefore, researchers are exploring innovative methods to resolve such issue. One interesting concept is the utilization of renewable sources (such as solar energy) to split water in the presence of metal oxides [44–46]. Figure 2.6 illustrates this concept, which commonly known as water-splitting thermochemical cycles.

The figure conveys a three-step water-splitting process:

1. reduction of oxides (energy-intensive process, 800–1,000 °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 to generate hydrogen. Thus, so far, a large number of oxides have been considered. The water-splitting



**Fig. 2.6** Schematic for water-splitting thermochemical cycle *MO* metal oxide

thermochemical cycle reactions can be mainly classified as (1) two-step water-splitting process [47–51] (2) iodine–sulfur process [52–54] and (3) calcium–bromine process [55–57].

Table 2.3 summarizes the findings for various alkali metals used for water-splitting thermochemical cycles. Sodium hydroxide is able to generate hydrogen at a reduced temperature. Recently, Miyoka et al. [58] considered sodium redox reaction and conducted several experiments in a non-equilibrium condition but could not achieve a 100 % conversion. 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 temperatures higher than 800 °C and incomplete  $\text{Na}^+$  extraction by water to recover sodium hydroxide limit 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. In the same line, Weimer et al. recommend membrane separation to recover sodium hydroxide [59]. In recent times, few researchers also investigated the use of  $\text{Na}_2\text{CO}_3$  as an alternative to NaOH [60–62].

Besides sodium hydroxide recovery, there are other limitations too. For instance, the reduction of oxides requires very high temperature. To attain such high temperature, a large-scale solar heat plant will be required. At present, the construction of a large thermochemical hydrogen plants is limited by the location, cost, and safety issues. Therefore, techniques to lower the operation temperature of water-splitting process should be investigated. 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 operation temperature of the water-splitting process, it could be considered for such use.

**Table 2.3** Alkali metal-assisted water-splitting thermochemical cycle

System	Reactions	Conditions	Hydrogen yield	Remarks	Ref.
MnO	$\text{Mn}_2\text{O}_3 = 2\text{MnO} + 0.5\text{O}_2$ ( $<1,600^\circ\text{C}$ ) $2\text{MnO} + 2\text{NaOH} = \text{H}_2 + 2\alpha\text{-NaMnO}_2$ ( $\sim 700^\circ\text{C}$ ) $2\alpha\text{-NaMnO}_2 + \text{H}_2\text{O} = \text{Mn}_2\text{O}_3 + 2\text{NaOH}$ ( $<100^\circ\text{C}$ ) $\text{H}_2\text{O} = \text{H}_2 + 0.5\text{O}_2$	Hydrogen generation at $750^\circ\text{C}$	100 % conversion under vacuum (0.5 h) and under $\text{N}_2$ purge (3 h)	NaOH recovery improved from 10 to 35 % in (MnO + Fe) mixture. Difficult $\text{Mn}_2\text{O}_3$ -NaOH separation	[83]
$\text{Ce}_2\text{Ti}_2\text{O}_7$ , $\text{Ce}_2\text{Si}_2\text{O}_7$ , $\text{CeFeO}_3$ , $\text{CeVO}_4$ , $\text{CeNbO}_4$	$\text{MO(ox)} = \text{MO(red)} + 0.5\text{O}_2$ $\text{MO(red)} + 2\text{M'OH} = \text{M'}_2\text{O.MO(ox)} + \text{H}_2$ $\text{M'}_2\text{O.MO(ox)} + \text{H}_2\text{O} = \text{MO(ox)} + 2\text{M'OH}$	Mixed oxide synthesis around $1,500^\circ\text{C}$ Hydrogen generation T range $500\text{--}800^\circ\text{C}$	$(1.5\text{--}1.94)$ mmol/g oxide  80–90 % conversion rate under low pressure and residence time of 0.5 h	At $530^\circ\text{C}$ , $\text{Ce}_2\text{Si}_2\text{O}_7$ (highest reaction efficiency) Hydrogen generation infeasible up to $1,000^\circ\text{C}$	[84]
Zn–Mn–O	$\text{Zn}_{0.66}\text{Mn}_{2.0}\text{O}_{3.66} = 2\text{Zn}_{0.33}\text{MnO}_{1.33} + 0.5\text{O}_2$ ( $\sim 1,600^\circ\text{C}$ ) $2\text{Zn}_{0.33}\text{MnO}_{1.33} + 2\text{NaOH} = \text{H}_2 + \text{Na}_2\text{Zn}_{0.66}\text{Mn}_{2.0}\text{O}_{4.66}$ ( $>650^\circ\text{C}$ ) $\text{Na}_2\text{Zn}_{0.66}\text{Mn}_{2.0}\text{O}_{4.66} + \text{H}_2\text{O} = \text{Zn}_{0.66}\text{Mn}_{2.0}\text{O}_{3.66} + 2\text{NaOH}$ ( $<100^\circ\text{C}$ )	Hydrogen generation above $650^\circ\text{C}$		NaOH may be recovered using membrane process	[59]
NaOH	$2\text{NaOH} + \text{Na} = \text{Na}_2\text{O} + \text{H}_2$ ( $T_{\text{eq}} = 32^\circ\text{C}$ ) $2\text{Na}_2\text{O} = \text{Na}_2\text{O}_2 + 2\text{Na}$ ( $T_{\text{eq}} = 1,870^\circ\text{C}$ ) $\text{Na}_2\text{O}_2 + \text{H}_2\text{O} = 2\text{NaOH} + 0.5\text{O}_2$ ( $100^\circ\text{C}$ )	Non-equilibrium technique for hydrogen production, below $400^\circ\text{C}$	$>80\%$ at $350^\circ\text{C}$	Yield of $\text{H}_2$ generation and Na separation $<100\%$ , kinetic limitation, suitable catalysts need to be investigated	[58]

## 2.2.5 Organic Compounds

### 2.2.5.1 Formic Acid (HCOOH)

Formic acid and its solution are industrial hazards. Any use of such chemical waste will be of a great advantage for environment. Formic acid can produce hydrogen using two methods: (1) thermo catalytic decomposition and (2) electrolysis in the presence of sodium hydroxide.

Formic acid thermally decomposes to produce  $H_2$  and  $CO_2$  [ $HCOOH(l) \rightarrow H_2(g) + CO_2(g)$ ,  $\Delta G^\circ = -32.9 \text{ kJ/mol}$ ,  $\Delta H^\circ = 31.2 \text{ kJ/mol}$ ], the reversible reaction of  $CO_2$  hydrogenation [63–71]. Electrolysis of formic acid solutions in the presence of sodium hydroxide requires theoretically much lower energy than water [72]. The electrochemical reaction for the electrolysis of formic acid solutions is as follows [73]:

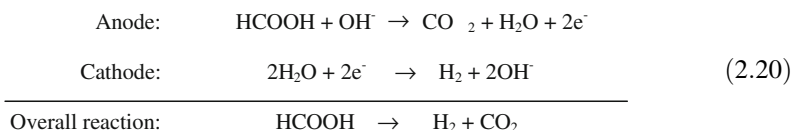
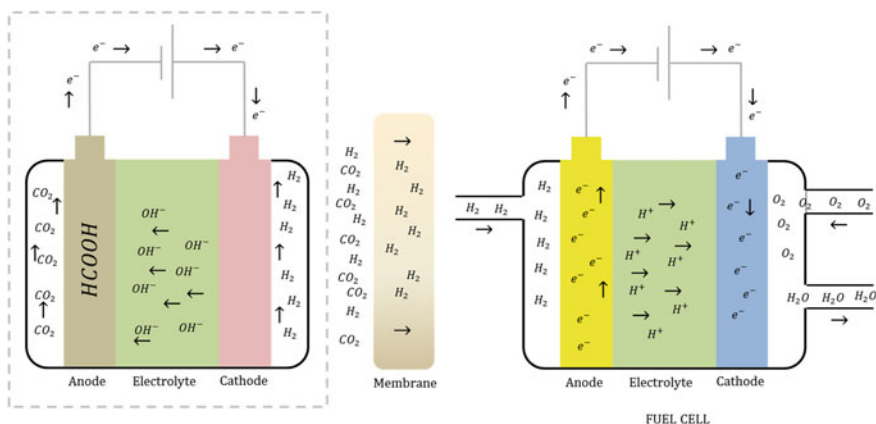


Figure 2.7 demonstrates the scheme of electricity generation via the combined use of alkaline hydroxide (sodium hydroxide) for the electrolysis of formic acid (HCOOH) and fuel cell. The separation of  $H_2$  and  $CO_2$  is desired prior to injection in the fuel cell.



**Fig. 2.7** Electricity generation using alkaline hydroxide (NaOH) for the electrolysis of HCOOH

### 2.2.5.2 Formaldehyde (HCHO)

An aqueous solution of formaldehyde reacts with sodium hydroxide to produce small amounts of hydrogen [74]. The generation of hydrogen competes with the disproportionation of formaldehyde to form corresponding alcohol and acid [75, 76]. Further, Ashby et al. [77] proposed a mechanistic explanation of this process. The mechanism indicates that one hydrogen atom originates from the water and the other from the organic moiety. According to an experimental study, when a dilute solution of formaldehyde ( $4 \times 10^{-4}$  m) reacts with concentrated sodium hydroxide (19 m) at room temperature, hydrogen is produced in a significant amount [77]. However, when concentrated solution of formaldehyde interacts with dilute sodium hydroxide solution, only a trace amount of hydrogen is produced.

Moreover, when a solution of hydrogen peroxide mixes with formaldehyde and sodium hydroxide, hydrogen is generated again [78]. Hydrogen peroxide oxidizes formaldehyde to formic acid and sodium hydroxide further neutralizes the acid.



However, no trace of hydrogen is observed in the absence of sodium hydroxide [79, 80]. The reaction (2.21) is limited by slow kinetics and requires a large excess of alkali hydroxide. When hydrogen peroxide is replaced by cuprous oxide, hydrogen is generated in a quantitative amount.

## 2.3 Conclusion

Sodium hydroxide locks  $\text{CO}_2$  in the form of valuable chemical compound,  $\text{Na}_2\text{CO}_3$ . The use of sodium hydroxide for the production of hydrogen results in high hydrogen generation rates, lower operation temperatures, and overall reduction in carbon emission. Apparently, sodium hydroxide has significant role to play for the methods using either renewable or non-renewable energy sources. But the energy-intensive production method of sodium hydroxide (electrolysis of brine) limits its application at a large scale. Thus, it will be of a great interest to invent or modify a method that can produce sodium hydroxide using renewable resources such as solar energy, water, and wind. Moreover, new hydrogen generation concepts that can replace sodium hydroxide with industrial hazards or waste should also be explored. In the following chapter, a detail for the role of sodium hydroxide to the industrial hydrogen production technologies such as SMR and coal gasification is provided. The chapter also presents the effect of different catalysts over the kinetics of these modified reactions.

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