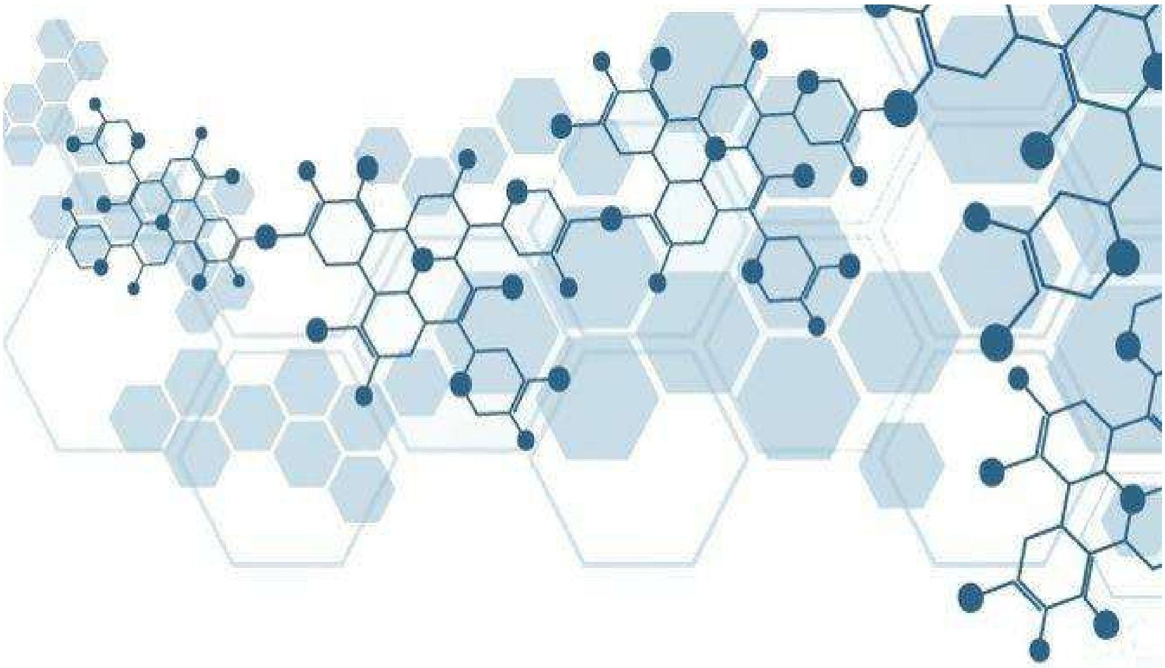
Chapter: 2

Literature Review & Objective of the Research Work



2.0. Metal-organic frameworks (MOF): Introduction

Heterogeneous catalysts are used extensively in mainly chemical, pharmaceutical and refinery processes. Among heterogeneous catalysts, pure metallic (e.g., Ni) and metal oxides (e.g., CoO, NiO, CuO) type catalysts have remained at the center of focus for a variety of industrial applications due to their chemical and thermal stability[1]. The catalytic properties of metallic catalysts are significantly improved by combining different metals. These properties are also strongly affected by the preparation method, production conditions and source material. Therefore, it is proven that combining different metals using suitable methods leads to exciting opportunities for the development of well-defined morphology and size catalysts [2].

Similarly, it is increasingly possible to develop well-defined porous matrices, which can act as catalytic supports from a wide variety of inorganic materials. These capabilities contribute to the production of single-site catalysts, in which all active sites are identical to each other. Nano-sized porous structures provide high surface area and significantly improve product yields [2]. The porosity of material normally depends on the method by which it is produced[3]. Catalysts with highly ordered structures composed of building blocks containing multiple channels have higher porosity than catalysts with less ordered structures. These unique porous structures of the polymetallic catalysts are important for many industrial applications [4].

In this respect, metal-organic frameworks (MOFs) have shown outstanding potential because of their controllable structure, unique electrochemical properties and large surface areas[5]. The use of MOFs for clean energy production has been widely considered. Several researchers have prepared heterogeneous catalysts via MOFs. These methods have significantly improved the efficiency, stability and reusability of catalysts. However, these methods can produce specific catalysts and cannot produce a wide range of heterometallic catalysts. Therefore, there is a high demand for a suitable method to formulate a wide range of the required heterometallic catalysts for industrial processes. Besides this, the process must be environmentally friendly and cost-effective.

MOFs are usually synthesized through the coordination of the metals with ligands. A large number of metals particularly, transition metals, are used to synthesize the MOFs. In the organic ligand, rigid molecules are normally used since they result in highly crystalline, stable and porous structures [6, 7]. In addition, 2,2′-bipyridine is the most widely used ligand because of its ease of functionalization and robust redox stability. MOFs are usually synthesized in the liquid phase using a single solvent or a blend of solvents.

In most cases, MOFs are synthesized by mixing two solutions containing the organic ligand and metal component, either at ambient conditions or under solvothermal environment. Sometimes, the addition of a second molecule is also required. A variety of metal atoms with their stable oxidation states have been utilized to synthesize MOFs. These metals include alkaline, alkaline earth, transition metals and even rare earth group. In an organic ligand, rigid molecules are normally used since they result in highly crystalline, stable and porous MOFs [6, 7].

Metal-organic frameworks (MOFs) are a rapidly growing class of adsorbent material with the remarkable characteristics of well-defined channels and cavities of regular size and shape easily tunable on the nanometer scale [1–3]. These fascinating properties of MOFs make them ideal candidates for gas molecule storage, for example, hydrogen or the entrapment of large amounts of greenhouse gases [4–6]. In addition, a unique aspect of MOFs that form highly flexible frameworks that undergo structural and mechanical changes in response to specific stimuli has inspired various other potential applications, including gas separation, catalysis, chiral separation, sensing, and gas chromatography [7,8]. Strategies for utilizing MOFs have focused on maximizing their porous characteristics.

2.1. Hydrogen: The Global perspective

Hydrogen is one of the most abundant elements in the earth's elemental mass[8], and due to its simplicity, it is recognized as the most promising alternative potential future energy carrier. It is not an independently existing primary energy in nature. Hydrogen is a secondary form of energy that can produce electricity, transportation, and domestic use. Recent development in fuel cell technology indicated that hydrogen would be used to a large extent as a secondary energy carrier to produce electricity. Fuel cell eliminates toxic emissions and has a higher efficiency than internal combustion engines for converting chemical energies of the fuel to electrical energies. Most experts agree that hydrogen has a significant role as an important energy carrier in the future energy sector [9, 10]. Hydrogen is an energy carrier and serves as an important raw material for fertilizers, oil refineries, methanol production, and metallurgical industries [11]. Hydrogen is mainly used in ammonia production, which is the primary raw material for the fertilizer industry. In the petroleum industry, in the hydrodesulfurization process of petroleum, large amounts of hydrogen were used. Hydrogen is used in the food industry for the hydrogenation of vegetable oils of coconut, soya beans, fish and peanut. Hydrogen gas is being explored in the cosmetic industry to manufacture soap via hydrogenation of inedible oils and grease. Hydrogen is also employed in the glass industry to make a float and to cut glass in oxyhydrogen. Hydrogen plays a major part in the production and processing of silicon in the electronics industry. In the metallurgical industry, hydrogen performs as an outstanding purification agent [12]. Hydrogen possesses a very high energy density of ~122MJ/Kg, approximately 2.75 times more than any other hydrocarbon fuel [13]. Compared to other fuels, its combustion values are shown in Table 2.1, making it a most promising non-fossil energy carrier.

Table 2.1: Combustion values of hydrogen and fossil fuels

Energy source	Combustion value (MJ/Kg)
Hydrogen	140
Biogas (CH_4)	50
Natural gas	49
Liquefied petroleum gas	46
Gasoline	45
Coal	29

Further, hydrogen does not emit any harmful by-products except water when combusted; therefore, hydrogen is preferred, safe and clean fuel compared to other fuels. Hydrogen can be used as a gas or a liquid, depending on the application, making it a versatile fuel. Nowadays, hydrogen as a transportation and stationary application finds great attention at a technical and policy level [14]. Hydrogen is being investigated for use in combustion engines and fuel cell electric vehicles. However, gas at normal temperature and pressure conditions is the main barrier for transportation and storage application than the existing conventional liquid fuels [13]. Hydrogen can be stored chemically or physio-chemically in various solid and liquid compounds (metal hydrides, carbon nanostructures, alienates, borohydrides, methane, methanol, light hydrocarbons) [15]. However, these ways of storing hydrogen are problematic.

Moreover, safety aspects are involved in the use of compressed hydrogen. Additionally, there is no appropriate infrastructure for H_2 transportation and distribution. Availability of hydrogen in a free state from nature is not possible; therefore, the utilization of the eco-friendly characteristics of hydrogen as a fuel mainly depends on the process design, the raw material involved and the source of energy employed for its production.

2.1.1 Current status of Hydrogen

Hydrogen can be produced from various primary energy sources and various production technologies (discussed in the next section). Fig.2.1 shows the different commercial routes of hydrogen production. It is mainly produced by steam reforming or partial oxidation of natural gas (49%), from naphtha (29%), via coal gasification (18%) and from other renewable resources (4%). However, all these processes generate environmental pollutions for nature. Hydrogen production from biomass can be an alternative source for a green and sustainable energy generation method because biomass is a natural solar-energy storage medium, and it is renewable, abundant and more stable to use than wind and solar energy [16] [17]. In recent years, the technologies investigated for hydrogen production are steam gasification of biomass[18] and subsequent biomass conversion to bio-oil via fast pyrolysis followed by steam reforming of bio-oil [19]. The latter process is a well-proven and widely accepted promising technique for producing hydrogen-rich gas [20]. Therefore, biomass is the only carbon-neutral renewable source used as a primary source for hydrogen production.

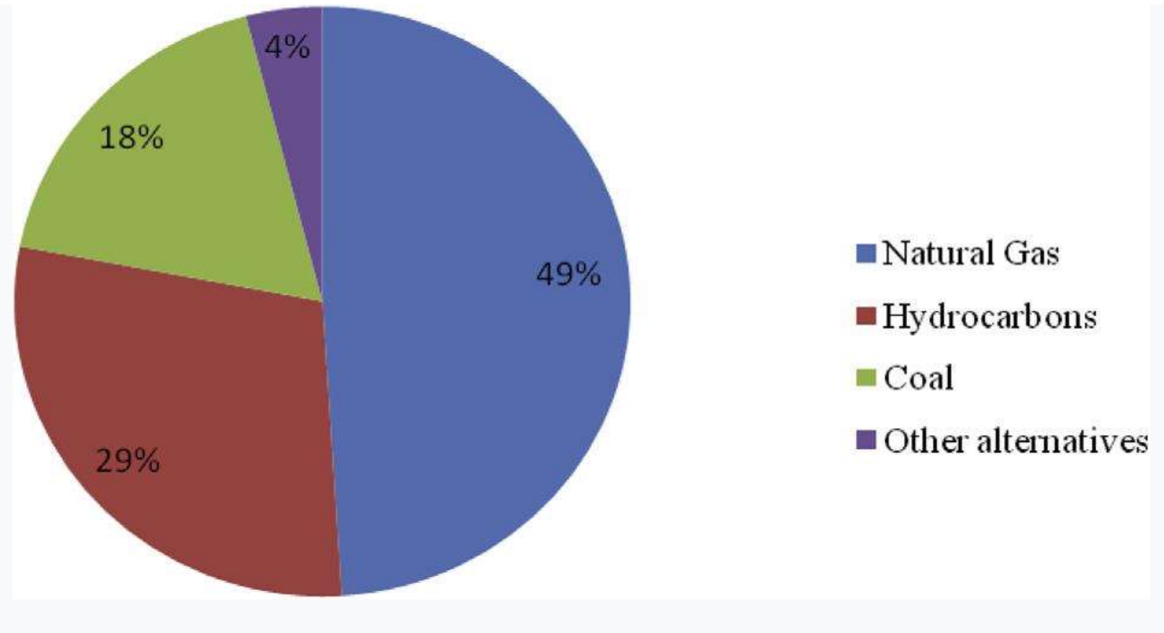


Fig. 2.1 Different sources of hydrogen generation adapted from Parthasarathy et al. [12]

2.2 Biomass

Maximum of the world's energy resources are non-renewable and fulfilling through fossil fuel sectors. Those are depleting day by day due to their extensive uses, and there is a rising concern for greenhouse gas emissions[21]. In this respect, biomass can be used as the most important renewable source for alternative energy. Biomass as a renewable resource has recently been described as a material of biological origin. The term biomass contains common crops and their by-products, forestry wastes, or even municipal solid wastes. Some examples of lignocellulosic biomass are wastes from woods, agricultural wastes, and various residue of crops, urban wastes, forest products (wood, logging residues, trees, shrubs), energy crops starch crops such as corn, wheat, barley; sugar crops; grasses; woody crops; vegetable oils; hydrocarbon plants, or aquatic biomass (algae, waterweed, water hyacinth) [22]. In the current scenario, change from present conventional energy system to renewable non-conventional system, plant-based materials explicitly known as lignocellulosic biomass plays an emerging role in obtaining hydrogen because of its sustainable nature, universal availability, and net-zero emissions of CO_2 [23]. Biomass is the only renewable, carbon-containing and carbon-neutral fuel resource globally, and its derived fuels have ever been considered promising alternatives to fossil fuels [22, 24, 25]. The major components in biomass are lignin (18-35%), cellulose (40-50%), hemicelluloses (20-40%), ash and water content. There are two main pathways for the conversion of biomass: biochemical or thermochemical. The thermochemical pathway involves heat and catalysts. The biochemical pathways use enzymes or microorganisms. Biomass can produce chemicals similar to those currently obtained from fossil resources and other products like bio-based polymers, levoglucosan, and different fuels. Thermal conversion of biomass is one of the effective methods to produce hydrogen. Nevertheless, these thermal conversions typically generate a lot of bio-oil, which has higher energy density than biomass but it has lower heating

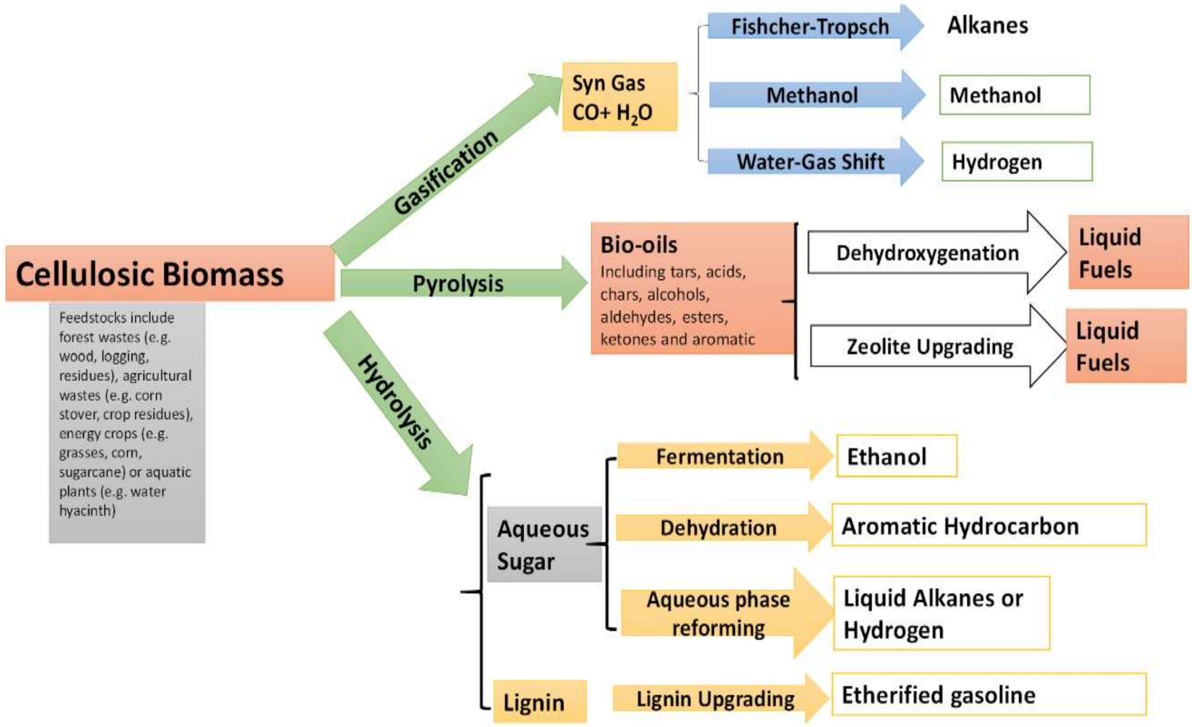


Fig. 2.2. Strategies for production of fuels from lignocellulosic biomass

values than petroleum-derived fuels and hardly can be used directly. For this reason, the production of biofuels needs to be optimized to sustain the present energy economy. Fig. 2.2 illustrates the strategies for the production of fuels from lignocellulosic biomass. This figure clearly shows how cellulosic biomass can be converted into potential products. The gasification, coupled with the water-gas shift and the fast pyrolysis and bio-oil steam reforming, represent candidates for renewable routes to H_2.

2.3 Bio-oil

Bio-oil, also known as pyrolysis oil/pyrolytic liquid, is a complex oxygenated compound and its composition significantly depends on the pyrolytic conditions and type of biomass [26]. It is obtained from the thermal decomposition of biomass and is usually dark brown color and smoky odor liquid obtained from the degradation of three main biomass components, namely cellulose, hemicelluloses and lignin[27]. Bio-oil can be readily stored and transported more efficiently than biomass; it is also used as a raw material for producing many economic value-added chemicals after purification [28, 29]. Bio-oil possesses nearly zero sulfur than crude oil, which makes it advantageous over the existing transportation fuels. The conversion of biomass to biofuels concentrates most of the chemical energy contained in bulky biomass into a denser liquid form. Major advantages of bio-oil are associated with the ease and economics of transportation, handling and storage. A much-cited application is to transport bio-oil from distributed pyrolysis units to a centralized bio-refinery wherein, it can be used to generate syngas or fuels. This scheme would work mainly because of the fact that the dense bio-oil would be cheaper to transport than that of bulky biomass.sxder

2.3.1 Bio-oil Properties

It is a highly complex mixture of water. More than 300 oxygenated compounds like acids, alcohols, aldehydes, ketones, substituted phenolics, and other complex oxygenates are obtained from biomass carbohydrates and lignin [30].

Table 2.2: Physical properties of bio-oil (pine wood) produced at different temperatures

Bio-oil properties	**Pyrolysis temperature (°C)**			
	425	**450**	**475**	**500**
Density	1174 ± 40	1156 ± 17	1142 ± 26	1138 ± 31
pH	2.1 ± 0.09	2.2 ± 0.08	2.3 ± 0.07	2.4 ± 0.07
Water (wt. %)	20.8 ± 3.9	21.0 ± 4.6	20.3 ± 2.8	20.6 ± 3.9
HHV (KJ/Kg)	18.6 ± 0.8	19.1 ± 1.3	18.4 ± 0.5	19.7 ± 1.2
Ash (wt. %)	0.12 ± 0.09	0.10 ± 0.06	0.12 ± 0.05	0.11 ± 0.03
Solid (wt. %)	0.3 ± 0.17	0.4 ± 0.13	0.5 ± 0.21	0.7 ± 0.36

The different oxygenated compounds present in the bio-oil depend on the biomass types used and the process conditions like temperature, residence time and heating rate. **Table 2.2:** shows the variation in physical properties, such as density, pH, calorific value, water content, solid content and ash content of the bio-oil derived from pine wood with temperature variation. Water is the most abundant component in the bio-oil and results from the original moisture present in the feedstock and the dehydration reaction occurring during pyrolysis. The water content in bio-oil (15-30%) depends upon the feedstock and process conditions. There are different reports available that provide the physical and chemical properties of bio-oil [31, 32]. Bio-oil can be distinguishing between the aqueous and non-aqueous phases. The non-aqueous components mainly include phenols, toluene, naphthalene and other aromatic compounds [28]. The aqueous components mainly include acetic acid, ketones, aldehyde and alcohols [33], which can be used as raw materials for hydrogen production [34, 35].

The chemical properties of bio-oils are different from derived petroleum fuels because of differences in oxygen content, sulfur content, and pH. The main elemental constituents of bio-oil are carbon (C), hydrogen (H), and oxygen (O), and hence its empirical chemical formula is given as $CnHmOk.xH_2O$ [36]. Crude bio-oil carries a substantial amount of water-insoluble materials (>50%), which includes lignin-derived oligomeric phenolic compounds, which are difficult to be reformed [37, 38]. These water-insoluble materials are prone to form carbon over the catalyst surface, leading to the catalysts' rapid deactivation. In light of these limitations, most of the work focuses on the water-soluble and volatile fractions of bio-oil for H_2 generation[39]. Different oxygenated compounds (acetic acid, ketones, various alcohols, and mixtures) were used as models of oxygenated organic compounds found in bio-oil to investigate bio-oil reforming behavior [29, 40-44].

2.3.2 Drawbacks of Bio-oil

Bio-oil is combustible but is not miscible with today's conventional liquid fuels like gasoline or diesel due to its high water content. Because of high water (15-25 wt%) and oxygen content (35-45 wt% on a dry basis), the lower heating values (LHV) of bio-oil are in the range of 14-15 $MJkg^{-}1$. This LHV value is similar to biomass and is 40-45% of that for hydrocarbon fuels [32]. There are a series of identified challenges regarding bio-oil stability, viscosity and solids content. When bio-oil is compared to other fuels, some important differences are its poor volatility, high viscosity, and corrosive nature. Some of the concerns are associated with the low heating value and high water content of bio-oil. The presence of high oxygen content in biomass-derived bio-oils increases its acidity and reduces the bio-oil stability as oxygenates present in bio-oil can polymerize under storage. Polymerization increases viscosity and average molar weight with time. This polymerization might upgrade the bio-oil more difficult as complex molecules, which are more difficult to convert, could be formed. The aging of the bio-oil reduces the volatility and results in phase separation and gum formation [45, 46]. The bio-oil aging process could be accelerated by temperature, oxygen exposure, and UV light exposure [47]. The acidic nature of bio-oil is another problem that could corrode piping and process equipment; hence corrosive resistant materials are needed, which makes the overall process more expensive. Therefore, long-term storage of the bio-oil brings severe changes in its physical and chemical properties. Some efforts have been carried out to enhance bio-oils storage stability by adding additives like methanol [48]. There are numerous issues related to the direct use of bio-oil as a fuel in engines or boilers. Currently, different methods are employed to obtain hydrogen from fossil fuels or bio-oil [49]. There are several ways to produce H_2 from AcOH: (i) SR [50, 51], (ii) catalytic partial oxidation (POX) [52], and (iii) auto-thermal reforming (ATR) [53]. Various reactors were also employed to produce hydrogen from bio-oils and its model compound efficiently, along with different methods. For many years, Steam reforming (SR) has been one of the most popular, relatively low-cost, and frequently used methods compared to other methods.

2.4 Steam reforming (SR)

Steam reforming is a technically viable and most commonly used process for commercially producing hydrogen from organics molecules [54]. It is an endothermic process in which substrate reacts with steam in the presence of a catalyst resulting in a mixture of CO and H_2 followed by a water gas shift reaction [55]. The general chemical reaction scheme for the steam reforming of bio-oil is:

$$C_nH_mO_k + (n-k)H_2O \longrightarrow nCO + (n+m/2-k)H_2 \qquad \Delta H > 0 \qquad (1)$$

$$nCO + nH_2O \longrightarrow nCO_2 + nH_2 \qquad \Delta H < 0 \qquad (2)$$

The overall reaction can be represented as:

$$C_nH_mO_k + (2n-k)H_2O \longrightarrow nCO_2 + (2n+m/2-k)H_2 \qquad \Delta H > 0 \qquad (3)$$

Eq. (1) is highly endothermic, taking more heat than it evolves from water–gas shift reaction. Therefore, overall, steam reforming is an endothermic process. Fig. 2.3 shows the detailed schematic representation of H_2 generation from biomass-derived bio-oil via steam reforming reaction. Thermodynamically, the steam reforming process is favored by high temperatures and low pressures; whereas, high temperatures inhibit water–gas shift reaction. Excess steam favors the reforming reaction, and the steam/carbon ratio of 3.5–4.5 is common in practice, especially in the case of methane steam reforming[55]. The steam reforming reaction for bio-oil has been widely explored via various catalysts, e.g., Ni-based catalysts [40, 56] [44]. Mg-doped catalysts[56] and noble metal-loaded catalysts[40, 57]. Noble metals (Pt, Ru, and Rh) are generally more effective than Ni-based catalysts and show less carbon deposition. They are not used in practical applications because their high-cost specific metals activities are reported to decrease in the order Rh, Ru > Ni, Pd, Pt > Re

> Co. As reported in the literature, organic molecules dissociatively adsorb on metal sites whereby water molecules are adsorbed on the support (metal oxide, i.e., Al_2O_3, MgO, etc.) surface. Hydrogen is produced via dehydrogenation of adsorbed organic molecules and reaction of adsorbed organic fragments with hydroxyl groups, which migrate from the alumina support to the metal/support interfaces [58].

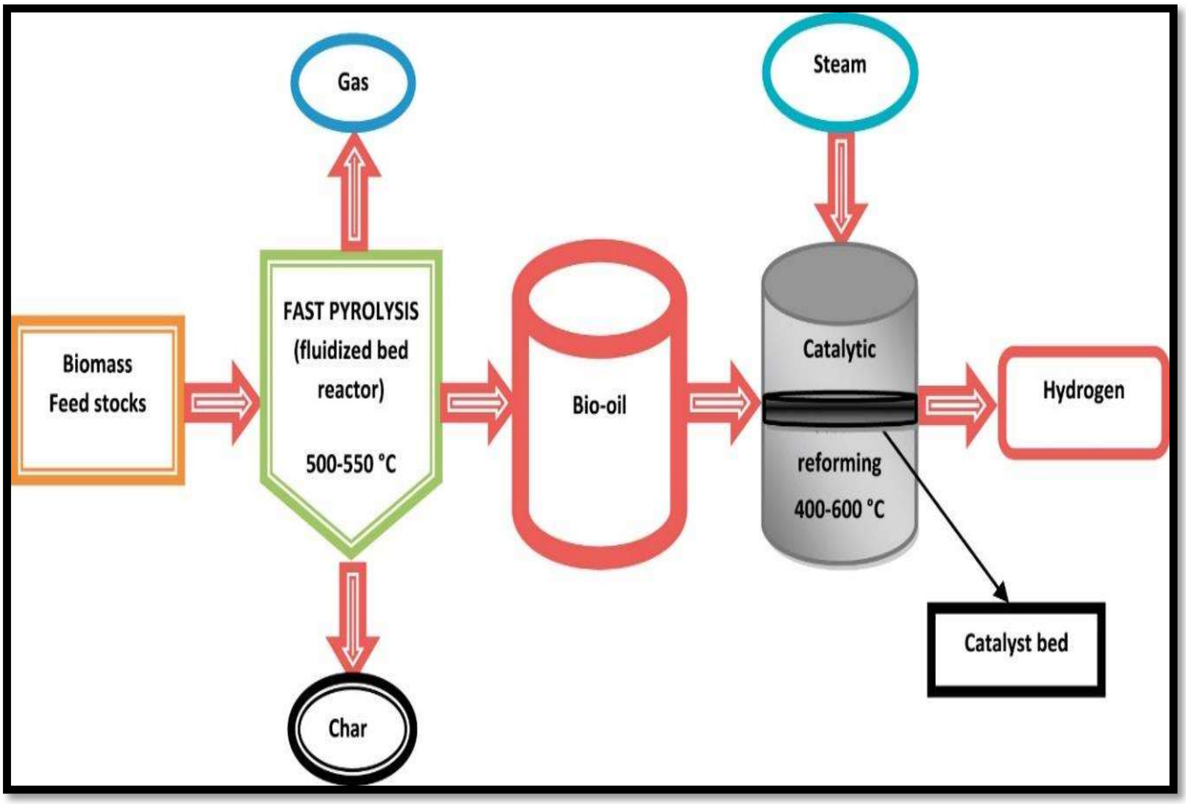


Fig 2.3. Possible route of hydrogen generation from biomass via steam reforming

In comparison to hydrocarbons, bio-oils are more reactive as they carry some C-O bonds. At elevated temperatures, the chance of carbon deposition increases because of the large size and thermal instability of constitutive molecules (cresol, furans, and phenols). A major drawback of crude bio-oil reforming is coke deposition on the catalyst surface, which is mainly due to the presence of heavier molecules of olefins and aromatics. It has been observed that the incorporation of small amounts of K and La as additives prevents sintering and coke formation [59] [60, 61]. The use of ceria as a support modifier in a Ni-based catalyst improves hydrogen yield because of increased metal dispersion over support[62]. The presence of ceria promotes coke gasification, which reduces the catalyst deactivation through coking[63]. The incorporation of MgO to Al_2O_3 support improves the adsorption and H_2O dissociation capacity, keeping the nickel-metal surface free from carbon. Basagiannis AC et al.[64] investigated catalytic steam reforming of the aqueous fraction of bio-oil over a series of $Ru/MgO/Al_2O_3$ catalysts supported on cordierite monoliths, ceramic foams, and γ-Al_2O_3 pellets. Among all the investigated structured materials, catalyst supported on Al_2O_3 pellets showed the best performance because of efficient contact between gas phase and solid phase.

2.5 Partial oxidation (POX)

Partial oxidation is a highly exothermic catalytic/non-catalytic process and a widely used method for producing hydrogen-rich gas from organic molecules[65]. Compared with that in SR, bio-oil can be converted at relatively lower POX temperatures [66]. Catalytic POX is advantageous over the non-catalytic process due to the heterogeneous reaction requiring lower temperatures and low soot formation[67]. The general reaction formula for partial oxidation (POX) is:

$$C_xH_yO_z + (x/2- z/2)O_2 \longrightarrow (y/2)\ H_2 + xCO \qquad (4)$$

$$C_xH_yO_z + (x + y/4- z/2)O_2 \longrightarrow (y/2)H_2O + xCO_2,\ \Delta H << 0 \qquad (5)$$

Poplar wood oil mixed with methanol was used for non-catalytic POX to synthesis gas with a hydrogen yield as high as ~25%[68]. Hu and Lu[60] investigated POX of bio-oil alone and further coupled it with dry reforming (DR) at atmospheric pressure. POX of bio-oil gives almost 100% conversion and ~50% H_2 yield at a temperature of 700 ºC. While coupled with dry reforming, it also gives the same result at the same operating parameters. Rennard et al. [69] performed catalytic POX of bio-oil using ester and acids as a model compound over platinum and rhodium-based catalysts to produce synthesis gas. Products can be readily managed to equilibrium synthesis gas or olefins by regulating the C/O ratio.

Rhodium-based catalysts show higher selectivity to synthesis gas, while Pt catalysts show higher selectivity for olefins and aldehydes.

2.6 Oxidative steam reforming (OSR)

The oxidative reforming process is a combination of endothermic steam reforming (SR) and exothermic catalytic partial oxidation (CPO) reactions[70]. In this process, hydrocarbon fuel is reacted with both air and steam simultaneously to produce hydrogen [71, 72]. The general reaction formula for OSR, using air as the oxygen source and assuming that the products are only CO_2 and H_2, can be expressed as follows:

$$C_nH_mO_p + aO_2 + bH_2O \longrightarrow cH_2 + dCO + eCO_2 + fCH_4$$

$$C_nH_m + x(O_2 + 3.76N_2) + 2(n - x)H_2O \longrightarrow nCO + 2\,(n - x + m/4)H_2 + 2.76x\,N_2$$

The heat generated by this reaction can be controlled directly by adjusting the proportions of fuel, air/ oxygen, and steam in the feed[73]. Oxidative steam reformers are simpler, smaller and lighter than steam reformers. The concentration of hydrogen produced by the OSR reaction is higher than that of POX [74]. In oxidative steam reforming, the POX and SR occur in one reactor, and oxygen facilitates a fast OSR reaction. The presence of oxygen suppresses hydrocarbons' cracking; consequently, long-chain hydrocarbons can also be reformed, otherwise yields coke[69]. The combination of oxidation reaction along with SR improves the reactor temperature control and, in the process, reduces the chances of hot spot formation. It also helps in protecting the catalyst from deactivation by carbon deposition [75]. However, the presence of any amount of O_2 lowers both the experimental and theoretical H_2 yield[76]. The presence of molecular O_2 favors the following reactions that eliminate carbon molecules over the catalyst surface [77].

$$H_2 + \tfrac{1}{2}\,O_2 \longrightarrow H_2O \qquad (6)$$

$$C + \tfrac{1}{2}\,O_2 \longrightarrow CO \qquad (7)$$

$$CO + \tfrac{1}{2}\,O_2 \longrightarrow CO_2 \qquad (8)$$

Vagia and Lemonidou [75] studied the effect of temperature and pressure on H_2 production. They found out that with an increase in pressure from 0 to 20 atm, the H_2 fraction decreases from 0.6 to 0.47. The maximum H_2 yield was obtained at 900 K, along with low CO and CH_4 production. They also observed that at optimum reaction conditions (T = 900 K, P = 1 atm and S/C = 3), 1 kmol of H_2 is produced from 0.245 kmol of simulated bio-oil (acetic acid/ethylene glycol/ acetone), which is 20% lower than the H_2 yield achieved by SR method because part of the fuel is consumed during oxidation.

2.7 Aqueous phase reforming (APR)

Aqueous phase reforming (APR) is, as the name implies, another process to generate H_2 using oxygenated hydrocarbons in an aqueous solution by the use of heterogeneous catalysts at low temperatures (~270 ºC) and high pressures (~ 60 bars). It reduces the thermal decomposition and promotes WGS reaction towards H_2 and CO_2. Similar to steam reforming, the reaction mechanism for the APR is believed to occur by cleaving a C–C-bond forming CH_xO species on the catalyst, which can decompose to CO and H_2. The CO reacts with either water by the WGS or H_2 through the methanation forming CO_2 or CH_4. The C–O bond can also be cleaved, which would lead to the formation of small hydrocarbons like CH_4 or C_2H_6. A suitable catalyst should have high activity in the WGS and the C–C-bond breaking and low activity for the C–O cleaving to ensure that the products are mainly CO, CO_2, and H_2. The reaction mechanisms for C–O and C–C-bond breaking in ethylene glycol are shown in Fig. 2.4.[78]. Davada and co-workers [79] studied silica-supported Ni, Pd, Pt, Ru, Rh, and Ir catalysts at temperatures 483-498 K and high pressure of 22 bar using ethylene glycol for the production of hydrogen. Shabaker et al.[80] studied the APR of methanol and ethylene glycol over Pt/Al_2O_3 catalysts. They observed that methanol and ethylene glycol at constant C/H_2O feed ratios show similar reactivity over Pt/Al_2O_3 catalysts, showing that the C-C bond cleaving for ethylene glycol is not the rate-determining step. However, H_2 generation was found to be higher for methanol in comparison to ethylene glycol. Huber et al. [17] investigated a series of Pt and Ni-based catalysts, including Sn-modified Raney Ni catalyst for hydrogen production from ethylene glycol, sorbitol, and glycerol at a temperature of 225-265 ºC and pressures of 5-26 bar. Results obtained from the experiments depict that the Sn-modified Raney Ni catalyst achieved high activity equivalent to those found for the Pt/Al_2O_3 catalyst. Lehnert and Claus [81] studied the APR of glycerol with different particle sizes (1.6-3.2 nm) of Pt/Al_2O_3 catalyst; with no change in glycerol conversion (20%) however, enhanced hydrogen selectivity was observed for bigger catalyst particles size (3.2 nm) in comparison to smaller ones (1.6 nm), suggesting the structured dependency of the APR reaction.

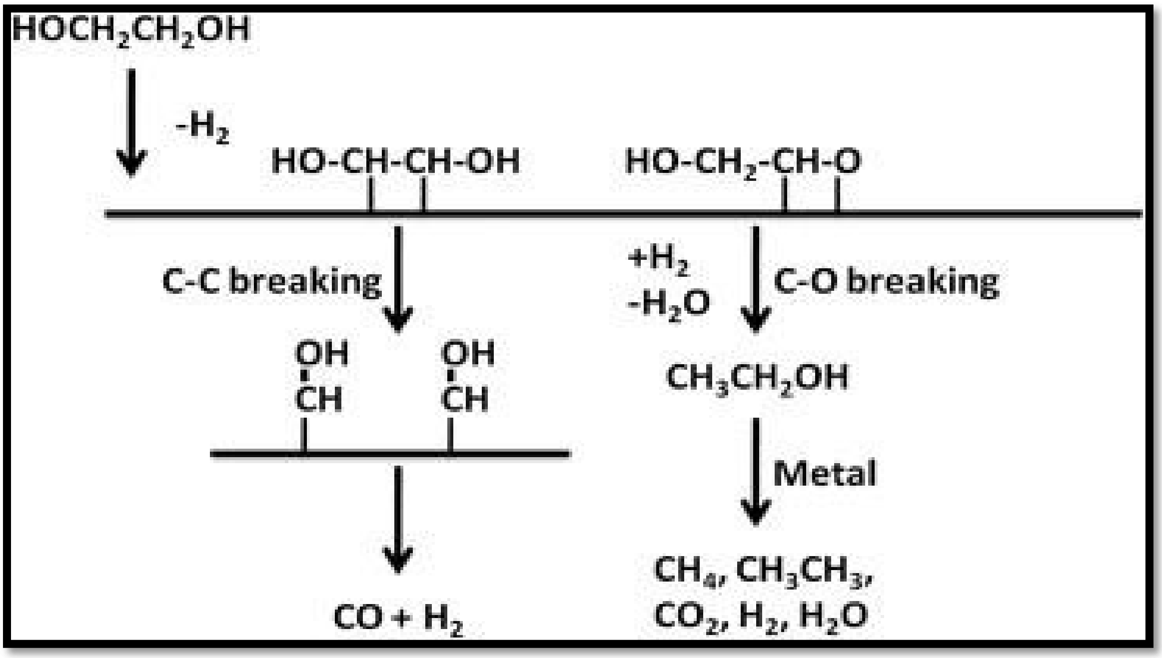


Fig. 2.4. The reaction mechanism for C–C and C–O breaking in the APR of ethylene glycol over a metal catalyst. The horizontal lines represent a metal surface [82].

An increase in particle size increases the number of face atoms of metal crystallites, whereas the number of edges and corner atoms decreases. The low degree of conversion and the low production rate for APR requires large reactor volume and large recycle loops. The Pt-catalyst can be improved by alloying with Ni, Fe, or Co, which could be due to lowering the d-band center, which would cause a lowering of the heat of adsorption for H_2

and CO[83]. Deactivation is also a significant challenge with APR during the processing of heavier compounds[84].

Several reforming methods for hydrogen production: SR, POX, OSR, and APR which have been primarily investigated. The steam reforming process in an active catalyst is the most promising route for sustainable hydrogen production from hydrocarbons and oxygenates over other present techniques. Other reforming techniques are in the early stages of the study along with certain drawbacks and are far from industrial application. Moreover, for the reasons mentioned above related to bio-oil and difficulty related to bio-oil reforming reaction such as catalyst deactivation by sintering, coking and metallic phase oxidation, hydrogen production from bio-oil is also a difficult task. Due to the problems as mentioned above of bio-oil and severe operating conditions of reforming, acetic acid has been selected as a model compound of bio-oil by several researchers to find out the optimum operating conditions and best formulation of catalysts for the production of H_2 via steam reforming [41, 54, 85-90]. The present research investigation involves studies on steam reforming of **acetic acid** as a model compound of bio-oil.

2.8 Acetic acid as a model compound of Bio-oil

There are numerous studies focused on hydrogen production from model bio-oil compounds [91]. **Acetic acid** is one of the most studied model compounds of the aqueous bio-oil for hydrogen production because its concentration is 30%. It is considered a safe (non-flammable), easily transformed and managed hydrogen carrier [92]. For this reason, acetic acid has been selected as a model compound of bio-oil for studying hydrogen via steam reforming. Due to the complexity of the bio-oil composition, model compounds have been used to study the process parameters and selection of catalysts for steam reforming of bio-oils. Certainly, model compound studies are useful since they highlight the structure-reactivity of bio-oil components. Besides, they provide a systematic approach for determining how best H_2 productivity can be maximized while minimizing catalyst coking. Various catalysts have been employed, and a comparative analysis of the performances of different metals and supports has been done for acetic acid as a model compound of bio-oil [93].

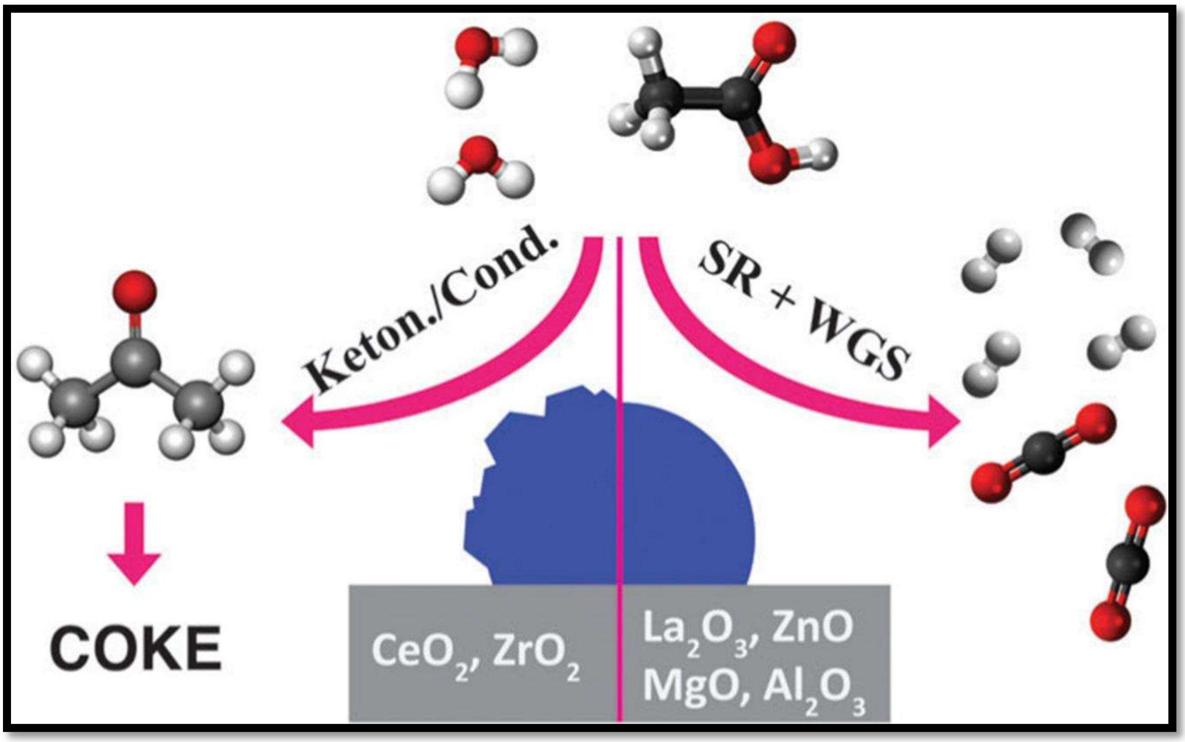


Fig. 2.5. Schematic representation of acetic acid steam reforming

Acetic acid steam reforming **(AASR)** for H_2 generation (Eq. (1)) can take place via acetic acid decomposition (Eq. (2)) followed by water gas shift reaction (Eqn. (3)) respectively[94]. The schematic representation of acetic acid steam reforming containing some main reactions during steam AASR is shown in Fig 2.5.

$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2; \Delta H = 131.50$ kJ/mol (1)

$CH_3COOH \rightarrow 2CO + 2H_2; \Delta H = 213.76$ kJ/mol (2)

$CO + H_2O \rightarrow CO_2 + H_2; \Delta H = -41.13$ kJ/mol (3)

2.8.1 Reaction network and coke formation mechanism of AASR

Acetic acid steam reforming (AASR) reaction pathways involve a complex reaction network due to some secondary intermediates and products formed. For better identification of the reaction mechanism of AASR, the whole reaction mechanism distinguishes into different parts, including main reactions as mentioned above (Eqs. (1)-(3)) [94]. A few of these reactions lead to the generation of undesired products. Furthermore, acetic acid is unstable in the temperature range of 500 - 800 ºC, where coke formation easily occurs because of thermal decomposition and the interaction between intermediate products and catalyst surface, which are likely to take place at mild operating conditions (Eqs. (4) -(6)).

Thermal Decomposition

$CH_3COOH \leftrightarrow 2H_2 + 2CO$ $\Delta H = 213.7$ (4)

$CH_3COOH \leftrightarrow C_2H_4, C_2H_6, C_3H_4,+ \text{gases}(CO, CH_4, CO_2, H_2) + \text{Coke}$ $\Delta H > 0$ (5)

Decarboxylation

$CH_3COOH \leftrightarrow CH_4 + CO_2$ $\Delta H = -33.5$ (6)

There also exist pathways for dehydration reaction Eq. (7) and ketonization reaction of acetic acid on acidic sites over catalyst surface. Acetone, which is formed, is a carbon precursor. Ketonization is a common reaction taking place at low temperatures and especially when support is solely used without active metals (Eq. (8))[95].

Dehydration

$CH_3COOH \leftrightarrow CH_2CO + H_2O$ $\Delta H = 144.4$ (7)

Ketonization reaction

$2CH_3COOH \leftrightarrow (CH_3)_2CO + H_2O + CO_2$ $\Delta H = 16.7$ (8)

These carbon precursors such as ketene, ethylene, or acetone eventually generate coke through condensation reactions on the catalyst's surface, leading to catalyst deactivation and subsequently decreasing the activity. The reaction mechanism of AASR has been proposed in several studies [95-97]**.** The dissociation of acetic acid over the catalyst surface is shown in **Fig. 2.6 and Fig. 2.7,** along with the proposed bifunctional mechanism. Dissociation of acetic acid over the active metal phase occurs by cleavage of C-O and O-H bonds, resulting in acyl and acetate species, respectively. Acetate further decomposes to form adsorbed CO_2 and methyl species. At the same time, the formed species combine with *OH species forming H_2 and CO_2. The CH_x species would then react with adsorbed hydrogen to generate methane. On the other hand, formed acyl species can dissociate to form methyl and CO* (**see figure. 2.8**), further reacting with the methyl group to form acetone. Meanwhile, interaction with acidic support site, ketonization reaction might occur, followed by oligomerization of acetone resulting in coke formation over the support and metal/support interface[98].

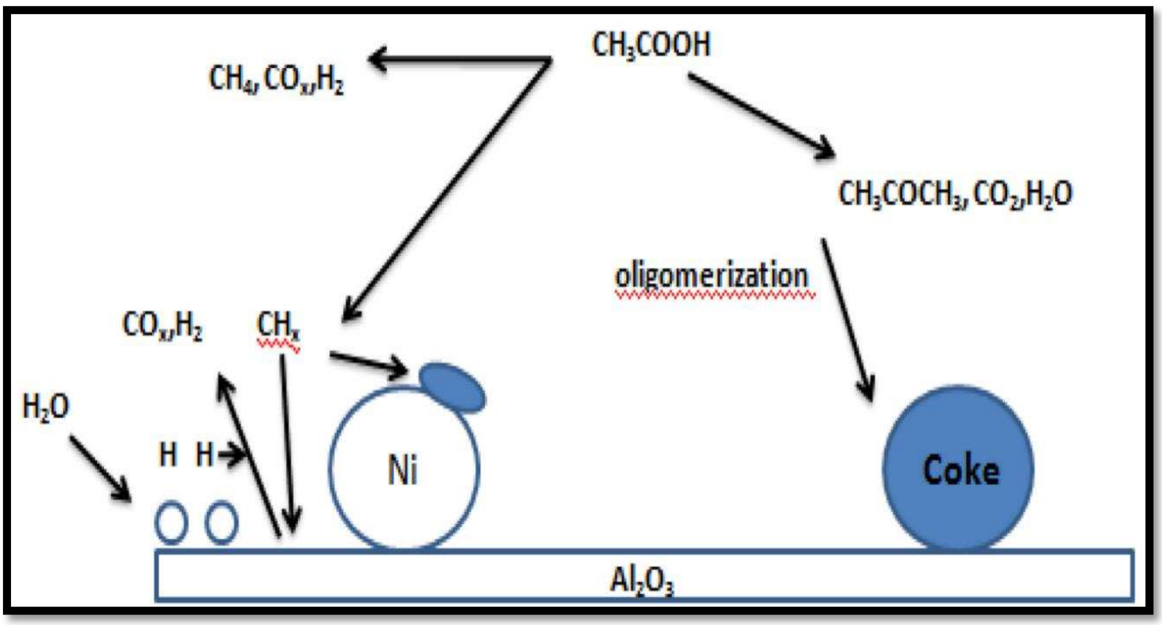


Fig. 2.6. Schematic representation of reaction mechanism for acetic acid steam reforming

Several workers have worked on stable catalysts for steam reforming reactions by improving the surface oxygen mobility that prevents interfacial carbon formation and improves the catalyst activity and stability [99, 100]. However, during AASR, several undesired by-products are generated, which lowers hydrogen yield. For example, CO is one of the main intermediates during the steam reforming process. At lower temperatures, decomposition of acetic acid (Eq. 5.) favors high CO yield. At high temperatures, reverse water gas shift reaction favors (RWGS)[Eq. (9)], which also promotes the production of CO.

$H_2 + CO_2 \leftrightarrow H_2O + CO$ (9)

CH_4 is another main by-product during AASR, which significantly lowers hydrogen yield. Firstly, methane comes directly from the thermal decomposition of acetic acid (Eq. (5)) and secondly, methane may come from the methanation of CO and CO_2 [Eqs. 10, 11 and 12].

Methanation

$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -206.1$ (10)

$2CO + 2H_2 \leftrightarrow CH_4 + CO_2 \qquad \Delta H = -247.3$ (11)

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H = -165.1$ (12)

During AASR Nickel based catalysts favour methane steam reforming at high temperature, resulting in the removal of methane via steam reforming of methane [101].

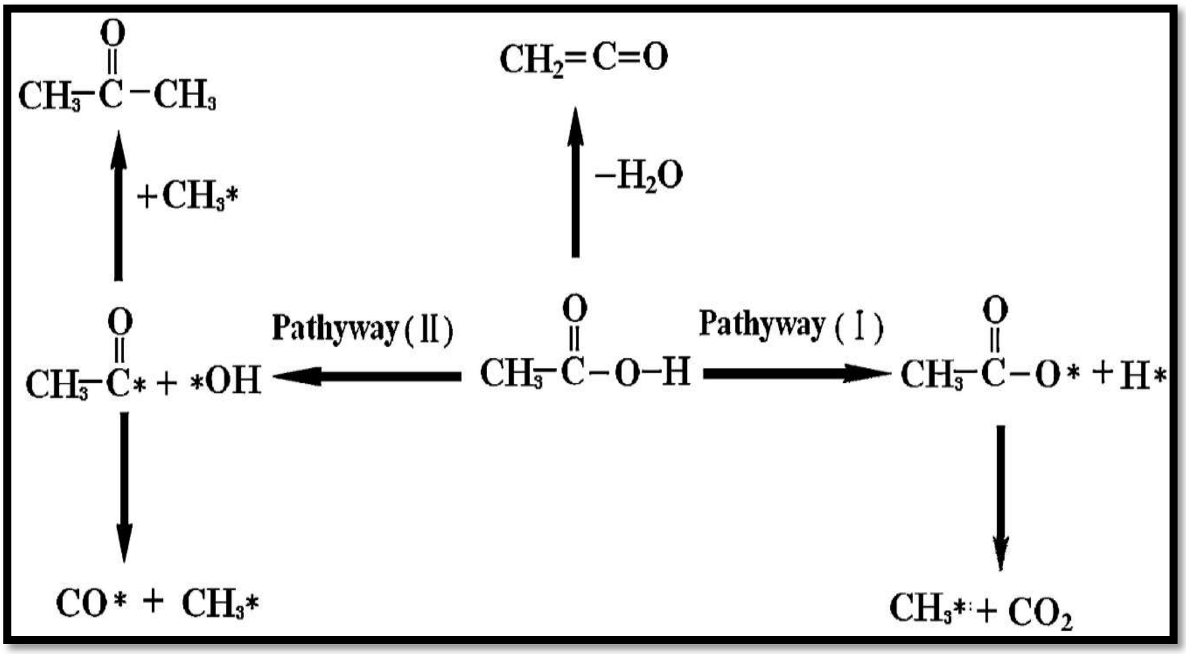


Fig. 2.7. The dissociation patterns of acetic acid on the catalyst surface

Coke formation easily occurs because of thermal decomposition and the interaction between formed intermediate gases and catalyst surface, which are likely to depend on various operating conditions such as temperatures, steam to carbon ratio and space velocity. Temperature plays an essential role in coke formation reactions [102]. Temperature below 400 ºC can facilitate carbon deposition via the "Boudouard" reaction [Eq. 13]. Carbon deposition can also occur via thermal decomposition of CO and CH_4 [Eq. (14) and (15)] at higher reaction temperatures (above 600 ºC)[103].

Boudouard reaction

$$2CO \leftrightarrow C + CO_2 \quad (13)$$

Thermal decomposition

$$CO + H_2 \leftrightarrow C + H_2O \quad (14)$$

$$CH_4 \leftrightarrow C + 2H_2 \quad (15)$$

Irreversible decomposition of acetic acid to coke precursors such as ethylene or other olefins. These intermediates may lead to carbon deposition after polymerization [Eqs. (16) & (17)] [103].

$$2CH_3COOH \leftrightarrow C_2H_4 + 2CO + 2H_2O \quad (16)$$

$$nC_2H_4 \leftrightarrow (C_xH_y)_n \rightarrow Coke \quad (17)$$

Verykios et al. [87] observed that for γ-Al_2O_3 supported catalysts, the reaction temperatures ≤400 ºC triggers ketonization reactions (Eq.(8)), which results in the formation of CO_2 and acetone. Furthermore, acetone undergoes oligomerization reactions resulting in the formation of intermediates such as mesityl oxide, ketene, etc., which are major routes for coke formation. The formation of ketene and mesityl oxide act as coke precursors via CH_3COCH_3 intermediate oligomerization (Eqs.18-20)[95].

Acetone oligomerization

$$2CH_3COCH_3 \rightarrow CH_2COHCH_3 + CH_3COCH_3 \quad (18)$$

$2CH_3COCH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3$ (19)

$(CH_3)_2C(OH)CH_2COCH_3 \rightarrow (CH_3)_2C = CHCOCH_3$ (Mesityl Oxide) + H_2O (20)

Several researchers have also explained coke generation routes [55, 79] and proposed that in the case of Pt/ZrO_2 catalyst, ketonization reaction readily occurs over the ZrO_2 surface, forming acetone which acts as a coke precursor leading towards the coke formation, as shown in **Fig. 2.6, and 2.8.** Different studies conducted over Ni-based catalysts suggest that a mixture of acetic acid and steam in the presence of Ni catalyst triggers catalytic cracking reactions (Eqs. (21)–(23) resulting in the formation of CO, CO_2, CH_4, and H_2 along with intermediate $(CH_{1\text{-}3})$ads. To avoid coke deposition over catalyst surface, formed $(CH_{1\text{-}3})$ads needs to be quickly gasified by H_2O to prevent further oligomerization, which can form coke over catalyst surface(Eq. (24)) [40, 80].

$CH_3COOH \rightarrow (CH_3COO)_{ads} + H_{ads}$ (21)

$(CH_3CO_2)_{ads} \rightarrow (CH_3)_{ads} + CO_2$ (22)

$(CH_3)_{ads} \rightarrow C_{ads} + 3H_{ads}$ (23)

$C_{ads} + H_2O \rightarrow CO_{ads} + H_2$ (24)

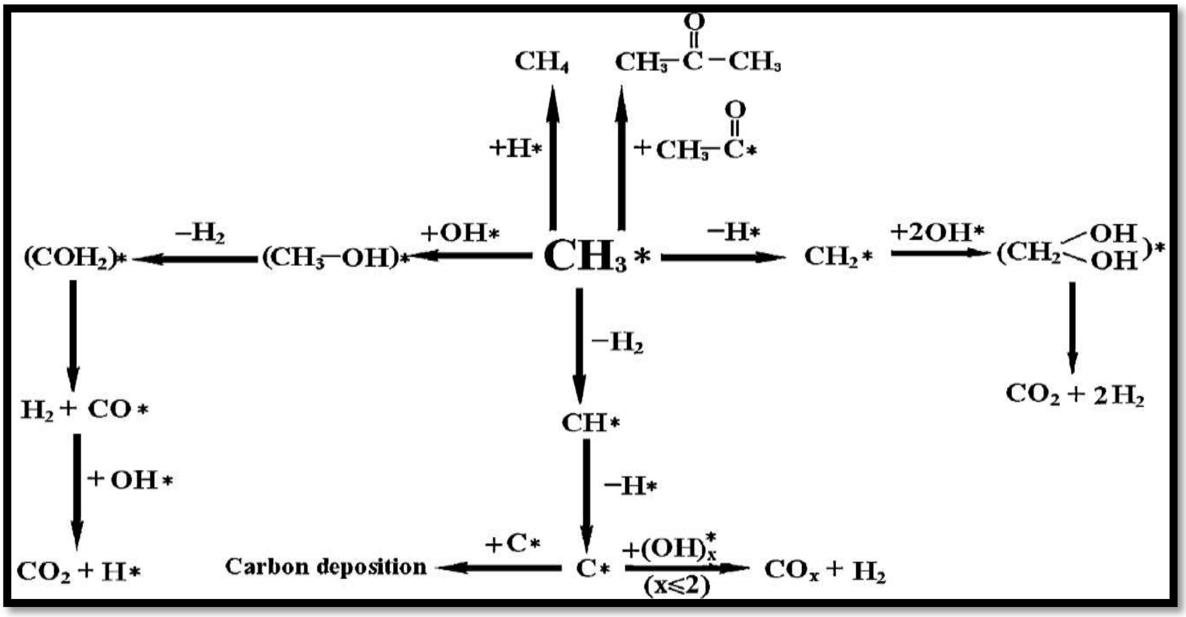


Fig. 2.8. Assumed reaction pathways and carbon deposition mechanism from intermediate methyl group during AcOH during reforming

Hoang *et al.* [104] have concluded that coke formation is caused by the decomposition of acetic acid and acetone produced during AASR. Presently, understanding of coke formation during AASR is typically limited to experimental observations. Researchers also presented theoretical considerations to understand the coke deposition mechanism during AASR by implementing density functional theory (DFT) [105-107]. Wang *et al.*[106] reported the dissociation mechanism of acetic acid over Co (1 1 1) and observed that $CH_3COOH \rightarrow CH_3COO^* \rightarrow CH_3CO^* \rightarrow CH_3^* + CO^*$ was the minimal energy pathway. In contrast, Li e*t al.* [105] proposed that $CH_3COOH^* \rightarrow CH_3CO^* \rightarrow CH_2CO^* \rightarrow CH_2^* \rightarrow CH^*$ was the most favorable pathway and dehydrogenation of $CHCO^*$ is the rate-determining step (RDS). The density functional theory over Ni (1 1 1) surface was investigated by Ran *et al*. [107], and based on DFT calculation, the activation energy (E_a) for the formation of CH_3COO^* was found 45.6 kJ/mol, while activation energy for the formation of CH_3CO^* was 89.5 kJ/mol. The formation of CH_3COO^* from acetic acid decomposition is the preferred route due to low Ea. Further, CH_3COO^* converted to CH_3CO^* by losing one O^*, Ea for which was found 84.8KJ/mol. In another pathway CH_3COO^* formed CH_3^* by losing a CO_2 molecule. The E_a for this reaction was found 194.8 kJ/mol, which is very high compared to the previous reaction. Thus CH_3CO^* formation was preferred intermediate. After losing CO^* radical, CH_3CO^* formed CH_3^* radical [106]. Similar DFT calculation over Ni (111) surface of decomposition of acetic acid was reported by Wang *et al.* and proposed that CH_3COO^* formation is the preferred route compared to CH_3CO^* formation [108]. Furthermore, CH_3^* dissociation by losing H^* step by step to form CH^*. In the steam reforming process, both the CH_3^* and CH^* are the major sources for coking and play a crucial role in coke deposition. For instance, methyl ions (CH_3*) combines with H^* to form the by-product CH_4. It could also dehydrogenate step by step to form C^* species, which would further form coke and deactivate the catalyst and its stability. C^* species could also combine with the OH^* and gasify to form carbon di oxide and hydrogen, as displayed in **Fig. 2.8**. H_2 is not only produced from the recombination of dissociative adsorbed species of acetic acid and steam but CH_3^* and CH^* also dissociate to lose H^* and could integrate to form H_2 and coke. Furthermore, to suppress the by-products like CO and CH_4 and gasify the carbon precursor-like CH_x(x=0-3) species, catalyst surface must have enough *OH species in the vicinity of CH_3^* [109].

2.9 Nature of Carbon deposit (AASR)

Several researchers investigated the development of carbon formation and its nature during the steam reforming of hydrocarbons such as methane [110, 111] and propane [112]. They concluded that there are two types of coke formation, mainly (i) Ni-encapsulating amorphous coke and (ii) structured (filamentous coke), which is also classified as carbon nanotubes (CNT) under certain specific conditions. The mechanism of CNTs generation suggested by Lattore *et al.* [113-115] assumes that methane resides as a metastable carbide form, which eventually leads to the generation of carbon atoms diffusing through the interphase of metallic nanoparticles and forming nanotubes after the nucleation stage. Two major types of coke formation were also observed during the reforming of oxygenated compounds, such as acetic acid[116, 117], ethanol[118-120] and bio-oil[121]. Carbon deposition behavior is significantly different for different catalysts. Iwasa *et al*. [89] reported that after AASR, an amorphous type of carbon was formed on the surface of the Pt/Al_2O_3 catalyst.

On the other hand, fiber-like structures were observed over Pt/smectite. On Pt/CeO_2 catalyst, acetone acts as a coke precursor produced from acetic acid condensation/dehydration and further converts to oligomeric coke species. Condensation of oxygenated reaction intermediates plays a significant role in the evolution of amorphous and encapsulating coke, while structured coke generation is due to dehydrogenation of CH_4

along with Boudouard reaction. Three types of surface carbonaceous species (amorphous, filamentous and graphitic) are generated during CH_4 decomposition. The first one, highly reactive carbidic species, which acts as an intermediate for filamentous carbon formation (hydrogenable at temperature ≈323K), is formed via dissociation of methane after that it convert to graphitic carbon at high temperature, and it is also favored over Ni catalyst [122, 123]. The spectroscopic studies suggest that carbon formation over Ni (100) requires a lower decomposition temperature than Ni (111) surface during the hydrogenation of carbidic carbon. The difference in surface energies at different Ni surfaces (100) and (111) affects the local CH_x species growth, which causes an observed difference in thermal stability over the Ni surface [124].

On the other hand, nickel carbide readily decomposes into metallic form and graphitic carbon forms at temperatures >873K [125]. The second one is amorphous carbon, which is developed via polymerization of carbidic carbon and promotes carbon whiskers' formation. The third one is the graphitic carbon hydrogenable at temperature ~ 673K and shows variable reactivity for oxidation and hydrogenation reaction [125]. Nogueira *et al.* [126], through TGA and DTA analysis, investigated the oxidation behavior of different carbonaceous species formed during AASR reaction over 15NiAl and 15NiMg/Al catalysts, respectively (**Fig. 2.9)**. They reported that for the 15NiAl catalyst, oxidation of carbon started at 400 ºC and continued till at 670 ºC. On the other hand, for 15NiMg/Al catalyst, carbon oxidation started at 100 ºC and ended at 670 ºC. For both the samples, most of the deposited carbon remained over the catalyst surface at 500 ºC. The peak at 350 ºC was due to removing readily oxidizable carbon species and desorption of H_2O and CO_2 from the catalyst surface. Whereas the peak at temperature > 500 ºC was assigned to oxidation of graphitic and filamentous carbon species. Generally, amorphous and filamentous types of coke are formed over Cu-based catalysts. However, Ni-based catalysts

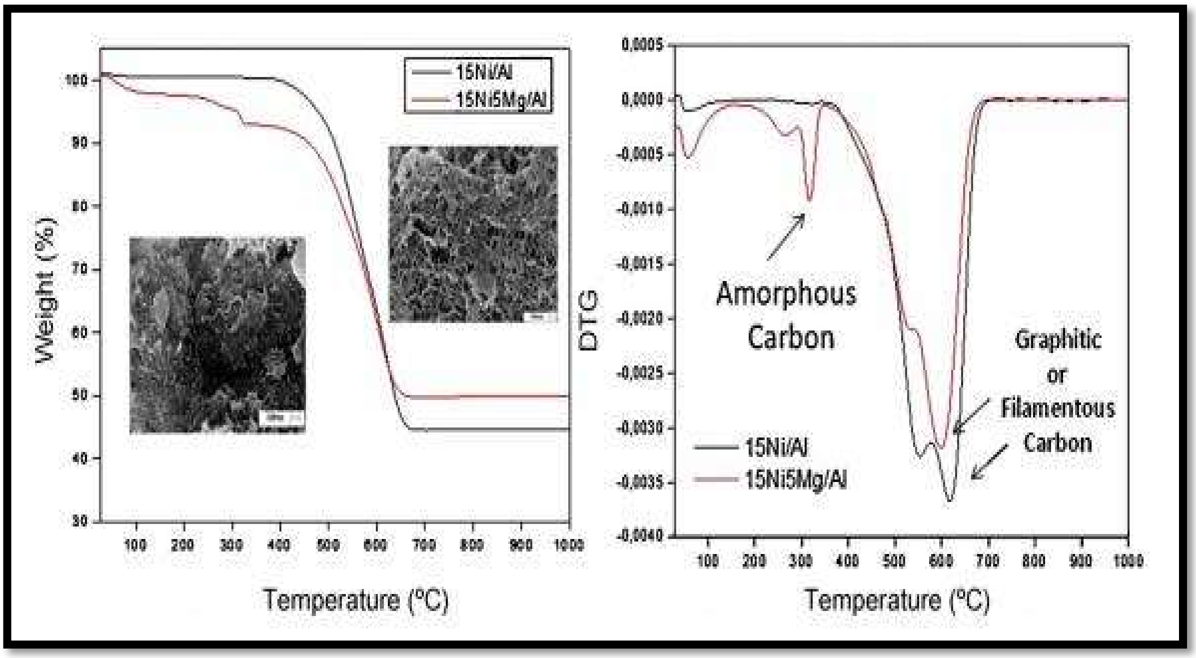


Fig. 2.9. (a) TGA of used 15Ni/Al (inset, SEM micrographs of 15Ni/Al catalyst after reaction) and 15Ni5Mg/Al (inset, SEM micrographs of 15Ni5Mg/Al catalyst after reaction) catalysts performed under airflow and (b) derivative thermograms for used 15Ni/Al and 15Ni5Mg/Al catalysts

deactivate by the formation of filamentous and graphitic carbon[116, 117]. For Ni/γ-Al_2O_3 catalyst, increase in Ni loading increases the catalytic cracking reaction at the ketonization reaction cost. An increase in Ni loading also increases the deposition of the graphitic form of carbon deposition over the catalyst surface at the expense of amorphous carbon. A DTA analysis (**Fig. 2.10**) of spent catalysts (Ni and Cu supported on mesoporous support) was carried out to determine the characteristics of coke formed during AASR. Three types of carbon formation (amorphous, filamentous and graphitic) on the catalyst surface were observed. At a low temperature, around 400 °C DTA peak corresponded to the amorphous carbon. The filamentous type carbon is generally oxidized around 550 °C.

Moreover, higher temperature oxidation peaks over 700 °C correspond to the graphitic type carbon [117]. The nonfilamentous carbon formed blocks the nickel active sites[120, 127]. On the other hand, the filamentous carbon formed via CO and CO_2 resulted in the separation of support and the active nickel sites. During the reaction, the amorphous coke

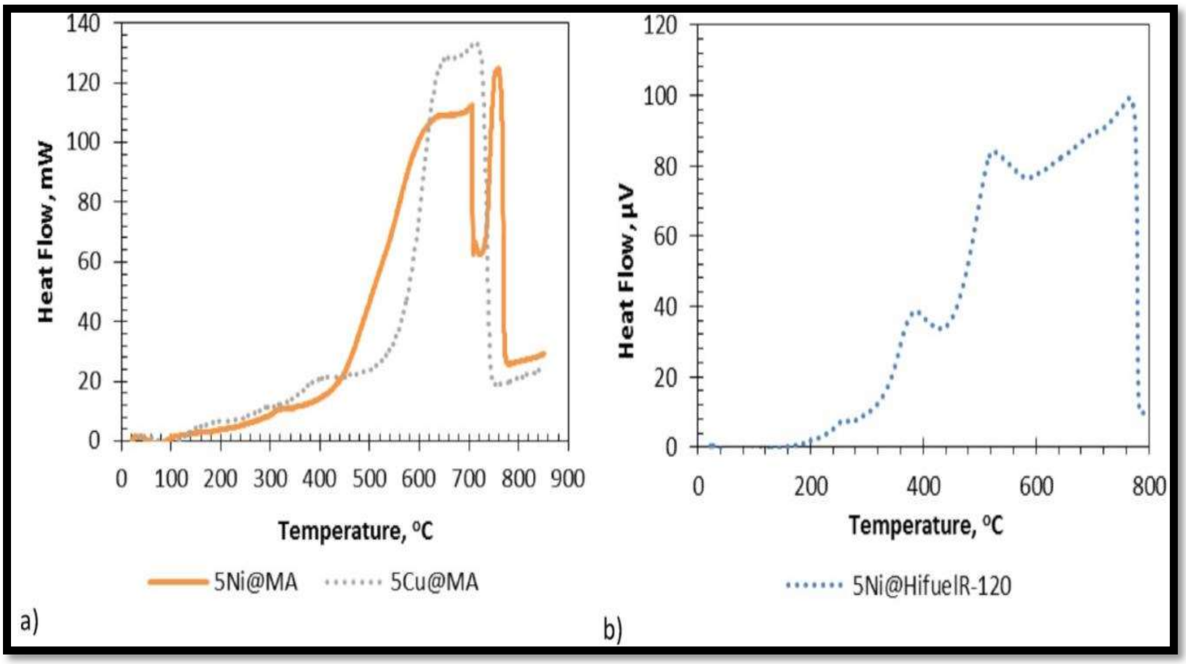


Fig. 2.10. DTA analysis of used catalysts (a) 5Ni/MA, 5Cu/MA (b) 5Ni/ HifuelR-120

could cover catalytically active sites, resulting in deactivation of the catalyst species. The filamentous coke grown over metallic species shows relatively less effect than amorphous coke on catalytic activity[127]. De Bokx *et al.* investigated the formation of filamentous carbon from CO and CH_4 in the temperature range of 600-1000K over nickel and iron catalysts. They observed that carbon is initially deposited in the form of a metastable carbon intermediate that thermally decomposes to form filamentous carbon [128]. The relatively high mechanical strength of filamentous carbon makes it compatible enough to disintegrate active metal from catalyst support [129] completely. Reports suggest that amorphous carbon resulted in severe deactivation compared to filamentous carbon [129][105]. The graphitic form of carbon is formed by direct deposition of carbon in the vapor phase and via heat treatment of amorphous carbon [130]. At lower temperatures, coke formation occurs mainly due to the catalytic cracking reactions, whereas at high-temperature, CO disproportionation reaction is responsible for the coke formation [116]. The typical SEM of graphitic-like carbon formed on the deactivated Ni/CeO_2-ZrO_2 catalyst is shown in **Fig. 2.11.** [131].

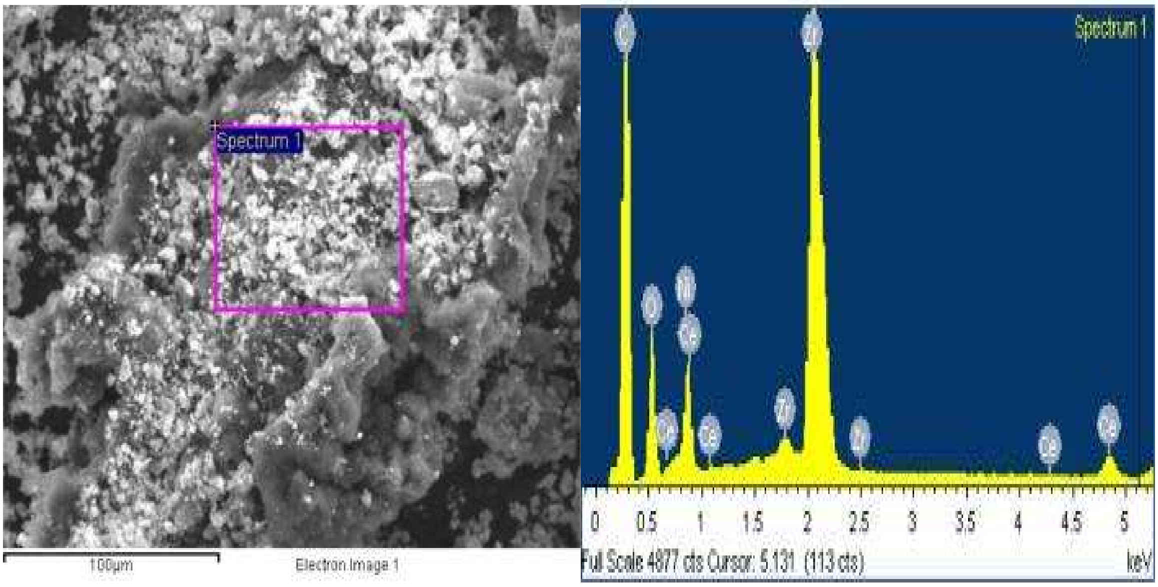


Fig. 2.11. Scanning electron microscopy and EDX scan of the used 12%Ni/CeO_2–ZrO_2 catalyst

Cheng *et al.* [132] also have reported two different carbonaceous sites for coke deposition over the catalyst surface. The lower temperature peak at 330 °C in TPO was attributed to the carbon deposition on the active metal, whereas the higher temperature peak [550 °C], the (significant one) was attributed to carbon deposition over the support surface. Many workers have concluded that the lower temperature peak represents polyaromatic compounds, whereas the higher temperature peak represents a pseudo graphitic structure [132-134].

2.10 Kinetics study of steam reforming

2.10.1 Effect of operating parameters on reforming reaction

Different studies in the literature showed that operating parameters such as temperatures, water to the acetic acid ratio (S/C), and catalyst to acetic acid flow rate (space velocity) affected the product distribution and the carbonaceous deposition during steam reforming reaction. Studies have shown that the molar ratio of acetic acid and water significantly affects hydrogen production and the mitigation of coke deposition in AASR [54, 86]. Operating parameters such as high steam to carbon ratio and temperatures promote removing by-products and carbonaceous deposition and favor the hydrogen generation during AASR[29]. These parameters also play a crucial role in the formation of intermediate products (CO, CH_4, C_2H_4, CH_3COCH_3), which are responsible for coke deposition via different reactions as shown in Eq. ((13)-(20)). Hoang et al. investigated the AASR on Ni/HT catalyst in the temperature range of 600-700 ºC. They have reported that the conversion of acetic acid and yield of H_2 strongly depended on the reaction temperature. They showed that the activity of catalysts drastically decreased due to deactivation by coke deposition. They concluded that the catalyst's initial deactivation was strongly influenced by the formation of acetone at lower temperatures [135]. Carbon depositions are also regulated by different types of reactions that occur at different temperatures. Verykios et al. have reported that during AASR, the nature of carbonaceous species formed over catalyst surface was different at different reaction temperatures. They explained that at a lower temperature (500 ºC), CH_x type of carbonaceous species formed via acetone intermediate, whereas at high temperature (700 ºC), only carbon exists on the catalyst surface[88]. Cheng et al. described below 650 ºC reaction temperature; a huge amount of coke deposition occurs on the reactor wall generated via the Boudouard reaction. Increasing the temperature to 650 ºC or above, carbon deposited on the reactor's wall was removed[132].

Hoang et al. have also reported that the steam/carbon ratio strongly impacted the catalyst's conversion and deactivation. They reported that acetic acid conversion dropped from 100 to 76% when the S/C ratio lowered from 14 to 5. In addition, a higher S/C ratio enhanced WGS reaction. Both feedstock and steam compete for active sites over catalyst surfaces during the steam reforming reaction [136]. The high steam to carbon ratio promoted the adsorption of steam on the active sites and consequently suppressed the feedstock's decomposition or degradation. High steam partial pressure also promotes water gas shift reaction to remove intermediate CO resulting in a higher hydrogen selectivity [137]. A typical result showing the effect of the S/C ratio is given in Table 2.3.

Table 2.3. Effects of S/C on acetic acid conversion and selectivities of gaseous product at T = 673 K; the heavy feedstocks: T=973 K LHSV = 10.1 h^{-1}; P = 1 atm [97]

S/C	Conversion	Product selectivity (%)					Carbon Balance
	(%)	H_2	CO_2	CH_4	CO	Others	%
1	57.3	42.6	40.3	21.4	9.5	12.1	88.8
3	70.9	61.6	54.2	17.2	8.6	10.2	90.6
6	85.4	79.1	79.7	11.7	1.1	4.6	94.3
9	100	90.5	91.8	1.6	0.9	0.5	99.2

2.11. Reactors

Choice of reactor plays an important role in steam reforming of bio-oil and its model compound. The generation of carbonaceous species is one of the major operational challenges that result in catalyst deactivation, especially for nickel-based catalysts used in steam reforming. Furthermore, during the reforming process of bio-oil and any of its model compounds, there always exists a high possibility of coke formation, which deactivates the catalyst and fouls reactors. Therefore, for the same reason, various types of reactors have been employed during the reforming process.

Fixed-bed reactor

A fixed bed reactor is a commonly used reactor for steam reforming reactions with liquid and gas feeds [41, 97]. The design of the reactor is very simple. The reactants pass through a catalyst bed heated at a certain reaction temperature for the steam reforming reactions. A typical scheme depicting the reactor is shown in Fig. 2.12 [132]

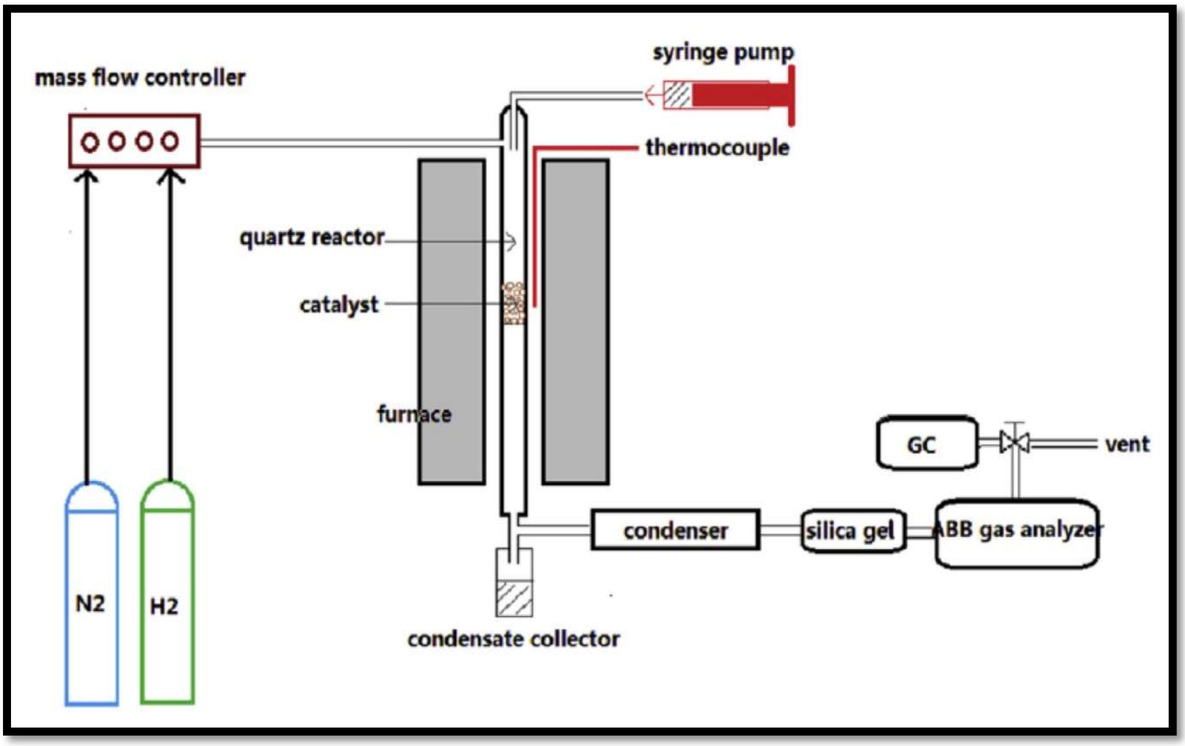


Fig. 2.12. A typical schematic diagram of a fixed-bed setup for steam reforming of acetic acid

Sequential cracking/two-stage reactor

It appears that carbon deposition on the catalyst surface is a key issue in bio-oil steam reforming. Therefore, a different concept has been applied. In this process, two steps were investigated for the conversion of bio-oil for H_2 production. In the first step, bio-oil is converted into synthesis gas without water, followed by catalytic steam reforming of generated gases [30, 138]. Davidian et al. studied acetic acid decomposition for syngas production in a two-reactor system, as shown in **Fig. 2.13.** [139]. The decomposition of acetic acid at high reaction temperatures produces a heavy coke deposition on the catalyst's surface. The coke has to be burned off, and the catalyst has to be reduced to regenerate frequently. Two parallel fixed-bed reactors were used to achieve continuous operation by switching the steam reforming and regeneration steps alternatively. The heat from the burning of the coke can be used for the endothermic steam reforming reaction. In some cases, thermoneutrality may be achieved by the integration of the two processes.

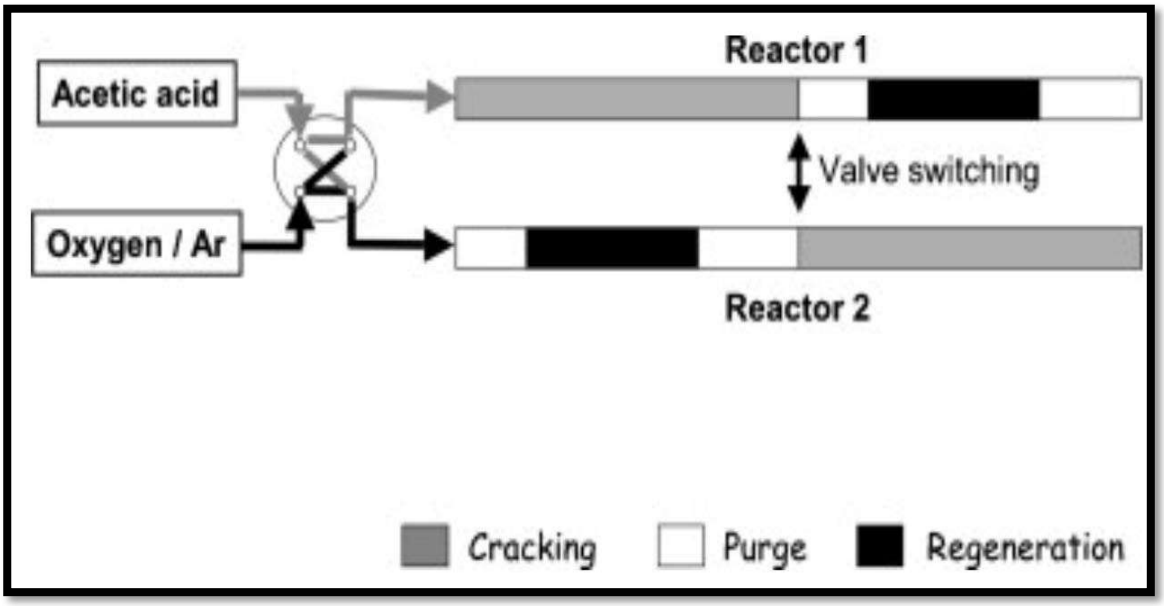


Fig. 2.13. Schematic diagram of the two-stage reactors performing AcOH cracking/regeneration sequences in opposition for continuous hydrogen production

Using two parallel fixed-bed reactors instead of one would increase the process's cost, which must be carefully calculated to balance the energy input and output. In addition, the hydrogen productivity in sequential cracking is lower in comparison to continuous steam reforming. However, catalyst regeneration due to coke deposition is comparatively easier in two-stage reactors [140].

Fluidized Bed reactor

Coking lowers the hydrogen yield and causes severe catalytic deactivation, especially at the upper layer of the catalyst bed, and reactor blockage limited the reforming time, subsequently needs regeneration of catalysts. The limitations of a fixed bed with steam reforming of the whole bio-oil are more problematic and require a longer time due to the regeneration process. An advantage of a fluidized bed is that, in a well-mixed regime, the feedstock is in contact with all of the catalyst particles, not only with its upper layer, as is the case in fixed-bed mode. Also, carbon deposits on the particles are better exposed to steam and can be gasified more quickly. Consequently, a fluidized-bed reactor should extend the catalyst's reforming activity duration and shorten the regeneration cycle [19]. A fluidized-bed reactor's advantage is that carbon deposits on catalyst particles can be gasified easily, allowing for a more continuous operation. They can be operated continuously by gasifying carbonaceous deposits on the catalyst surface [38, 141]. For the same reason, fluidized beds perform better than fixed ones for the continuous process of AASR [142]. Kechagiopoulos et al. [143] investigated the steam reforming of ethylene glycol, acetic acid, and aqueous phase bio-oil over Ni/olivine catalysts over a pilot-scale spouted bed reactor as shown in **Fig. 2.14.**

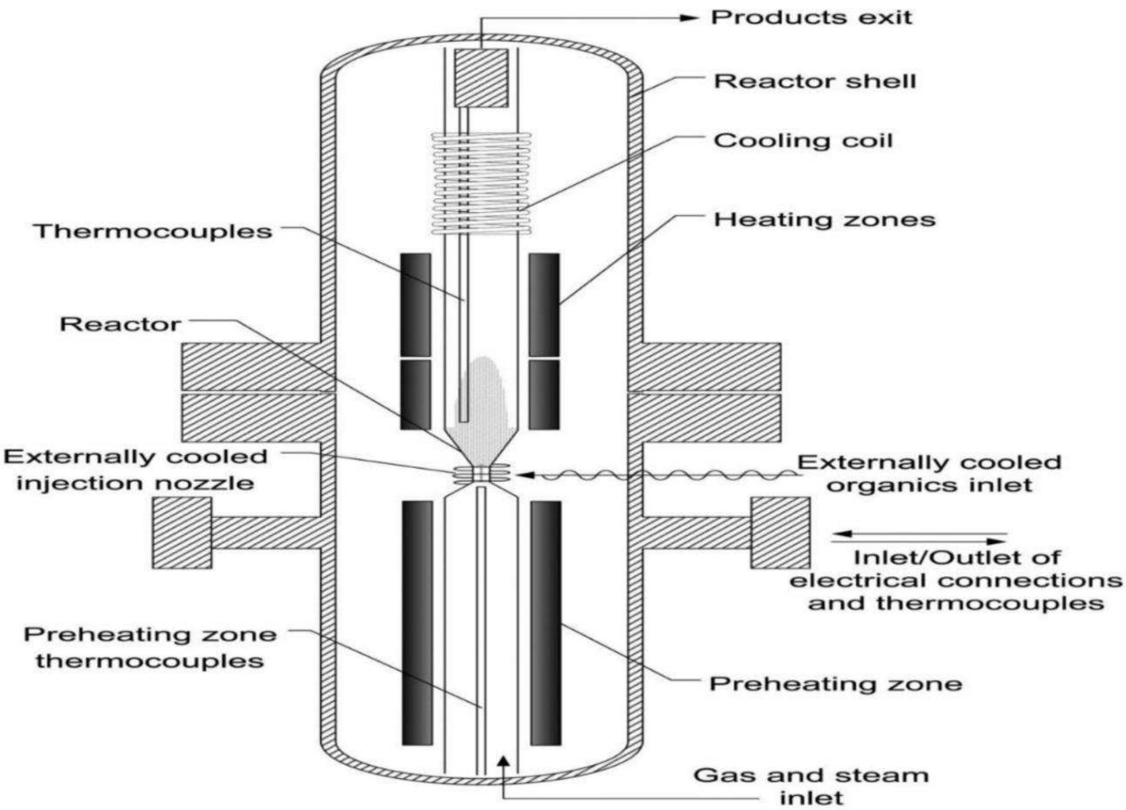


Fig. 2.14. Schematic diagram of the spouted bed reactor

The design of the spouted bed reactor follows the philosophy of a fluidized reactor system. The catalyst in the catalyst bed was fluidized by a mixture of steam, gas and organic reactants. The catalyst was continuously fluidized, and thus they have a similar chance to contact reactants. In a spouted bed, rapid and sufficient mixing of hot particles and cold injected reactants and continuous cyclic movement of solid particles lowers the coke build-up over the catalyst surface and increases the H_2 yields compared to a fixed bed reactor.

[144]. However, fluidized bed reactors enhance the hydrodynamics of catalyst and remove coke deposition in contrast to fixed bed, and there are two drawbacks, attrition of catalyst and usage of the high amount of carrier gas to fluidize the particles of catalyst. Attrition of catalyst particles with the reactor wall occurred due to the fluidization. Therefore, in a fluidized bed reactor, the catalyst should have high mechanical strength. Moreover, to maintain fluidization in the reactor, a significant amount of carrier gas is blown, which dilutes the H_2 production and increases the operating cost in the separation process.

Sorption enhanced reactor (SER)

Recently, the sorption-based reactor has attracted much attention in the steam reforming of acetic acid. The primary characteristics of this process are that CO_2 generated during steam reforming can be removed in-situ by using CaO as an adsorbent hence, produced much-purified hydrogen. Furthermore, CO_2 produced during reaction combined with CaO formed $CaCO_3$ that could be decarbonated further in another reactor. Therefore, CaO and $CaCO_3$ need to be circulated in a time interval. Hence, for the sorption enhanced reactor, some modification is a need in a fixed bed reactor. A typical schematic representation of sorption enhanced assembly for AASR is shown in **Fig. 2.15.**

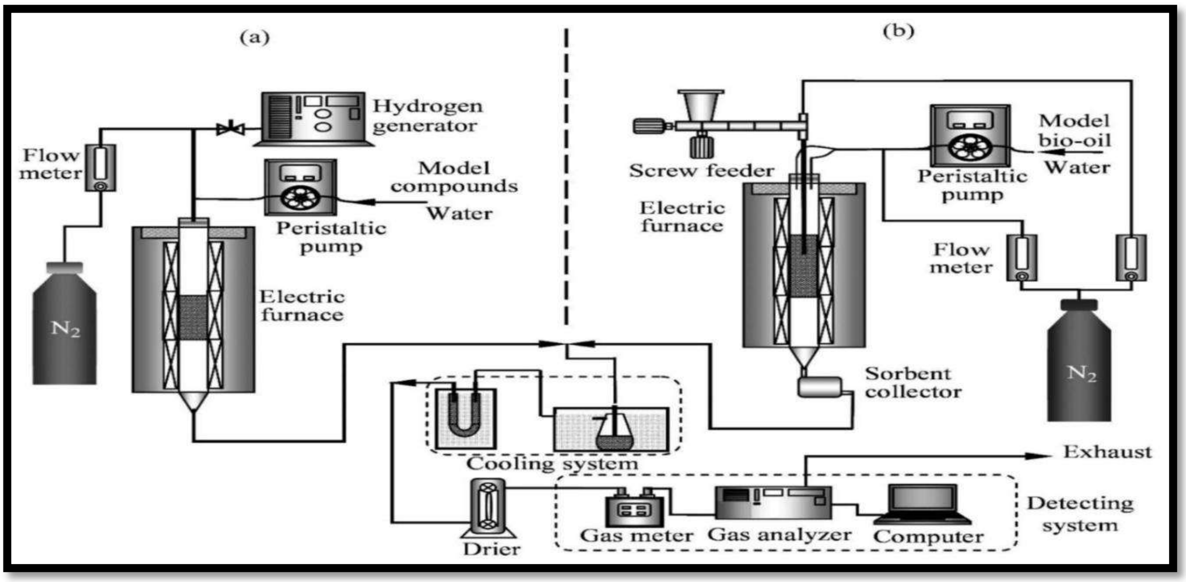


Fig. 2.15. A typical schematic representation of sorption enhanced assembly for AASR

The configuration of SER is primarily similar to the fixed bed reactor. The major difference between these two is that a screw feeder and a sorbent collector are also required. Another reactor assembly or unit is required to decarbonate $CaCO_3$ to complete the cycle. Fermoso et al. reported a novel catalyst assembly to decarbonate $CaCO_3$ in-situ in the reactor cycle. [145]. The sorption enhanced steam reforming of acetic acid is a promising technique to generate high-purity H_2. The overall concept is simple; however, the main challenge for implementing the idea will be developing an efficient unit while reducing the cost to operate sorption-enhanced steam reforming reactions cost-effectively.

2.12 Catalysts consideration for acetic acid steam reforming

Formulation of the catalysts used in AASR generally includes the metallic species acting as the active sites for the reforming reactions, the additives to aid catalytic performances, and the carrier to support metallic species and additives. Several catalysts with distinct formulations have been employed or developed for steam reforming of acetic acid, reviewed from the following three categories: metals, additives, and supports. Thus, for acetic acid steam reforming, formulation of such types of catalysts that are more effective and stable against coking, sintering, and capable of providing high H_2 yield has ever been a research subject.

Active metals

The chemical nature of an active metal plays a major role in defining the catalyst's catalytic activity and stability. A strong basic characteristic of active metal assists in CO_2 adsorption (a molecule with acidic characteristics) and helps in gasifying the formed carbon deposits over the catalyst surface. However, those active metals possess acidic nature to assist in coke deposition [146]. Nabgan et al. estimated the basicity of a catalyst via CO_2-TPD-based peak area and reported that strong basic sites present in active metals become an active oxygen source species with high activity and act as the inhibitor for coke deposition on catalyst surface [147]. Furthermore, the acidic behavior of the catalysts varies with the nature and the proportion of active metal. Various types of catalysts have been reported in the literature as active metal sites for acetic acid steam reforming. It includes noble metals (Pt, Pd, Rh, Ru, Ir) [96, 148-154], transition metals (Cu, Co, Fe and Ni) [54, 85, 117, 155] [156], and also a combination of both transition metals and noble metals [94, 157-161].

Noble metals have shown great activity towards the conversion of acetic acid into gaseous products. During AASR generally, these metals require high reaction temperatures (>600 ºC) to attain a complete conversion. The main reason for the high reaction temperatures is directly linked with these metals' low loadings on supports. However, low loadings of metals could be the reason for high dispersion, and the total active sites available for the reaction would be decreased. Eventually, a high reaction temperature is needed to increase the turnover frequency over the limited metal sites to enhance the acetic acid conversion. More active sites would facilitate the conversion of acetic acid. However, the specific activity based on the metal surface area decreases in Ru > Pd ~ Rh > Pt > Ni for steam reforming of acetic acid.[162]. In addition, noble metals show more resistance to coke deposition than transition metals Verykios et al. [154] compared nickel with noble metals; they concluded that noble metals showed lower activity but more stable behavior towards coke deposition. They also proved that Rh was the most active noble metal among noble metals compared to Ru, Pt, and Pd. Rh has the capacity of scission both C-C and C-H bond. The main drawback of noble metals-based catalysts is that they are too costly and not economically viable for this industrial reforming process. Combining noble metal with transitional metal could be a solution to overcome the above issue, and the synergistic interaction between two metals might have a beneficial effect on preventing the coking and the increased H_2 yield. Fermoso et al. reported that Pd could significantly enhance the reduction of Ni and Co oxides to metallic nickel, consequently improved the reforming activity [145].

Transition metals (Cu, Fe, Co, and Ni)[54, 85, 117, 155, 159]. These metals have been extensively examined using various supports such as Al_2O_3, ZrO_2, La_2O_3 and CeO_2.[104, 163, 164]. Hu et al. studied acetic acid steam reforming over different transition metal catalysts supported over alumina and concluded that Ni and Co catalysts exhibited much better activity and stability than Fe and Cu catalysts. Besides, Ni and Co also showed different reaction networks and product distribution. Moreover, the Ni catalyst showed the lowest coke deposition, metal sintering, and active metal oxidation rates, ensuring its stability. Fe and Cu metal catalysts showed lower activity and hydrogen selectivity and did not effectively cleavage C-C bonds during AASR. Consequently, condensation to heavier organics but not the cracking to gaseous products was the dominant reaction pathway when the Fe and Cu catalysts were used [155]. Hu et al. reported that Cu-Zn-CO showed a better activity and H2 yield at lower temperatures and resistivity towards coking due to the synergistic effect. Whereas Cu and Zn were not much active for acetic acid steam reforming at lower temperatures. [165]. Cu has been identified as an active metal for the methanol steam reforming due to cracking C-H bonds effectively. C-C bonds are also required in oxygenated hydrocarbons such as ethanol and acetic acid cracking of the C-H bond. Mohanty et al. reported that the Cu–Zn/Ca–Al catalyst showed significantly high H_2 yield (80%) at temperatures above 600 ºC during AASR.[166]. At higher temperatures, thermal decomposition of acetic acid occurred, and therefore, Cu could effectively catalyze the acetic acid and produce hydrogen at this condition.

Cobalt

Cobalt-based catalysts have relatively high activities towards water gas shift reactions at low temperatures [147, 167]. Cobalt catalysts are also low-cost catalysts compared to noble metal catalysts and can break C-C bonds at lower temperatures. Nonetheless, the performance of metallic cobalt-based catalysts suffers severe deactivation due to carbon deposition [54]. Mizuno et al. reported that the Co catalyst remained oxidized and inactive at a lower temperature. A lower carbon deposition was observed when Co was combined with Ni catalyst due to a higher rate of oxidation of C* by O and OH and the presence of CoO on metal cores of Co and Co-Ni catalysts[168]. Xun et al. showed that Co/Al_2O_3 catalyst was more active in the thermal decomposition of acetic acid, and higher amounts of CO were formed compared to Ni/Al_2O_3 [169]. The metallic cobalt phase is an active phase for the steam reforming reaction. Oxidation of these species causes catalyst deactivation, which further leads to coke formation reaction [170]. Co-supported alumina showed strong interaction with the support and resulted in cobalt aluminate formation, which was difficult to reduce. As a result, it exhibited low activity during the reforming reaction [171].

Nickel

Nickel is the most extensively used metal catalyst for steam reforming acetic acid due to its excellent ability to facilitate cleavage of C-C, O-H and C-H bond and dehydrogenation reactions [172-174]. Similar to cobalt, nickel-based catalysts require lower reaction temperatures and exhibit high activity. Activity of the base metal decreases in the order Ni > Co > Fe > Cu [155]. The main advantage of Ni-based catalysts compared with those of noble metals is their high activity towards C-C bond cleavage and high selectivity for the H_2 generation at a substantially lower cost [141, 175-178]. However, Ni-based catalysts are more vulnerable to coke formation [85]. Hence, the development of Ni-based catalysts, having more resilience towards coke deposition, remains a major challenge [117, 141]. Ni in its metallic form is considered an active state for steam reforming reaction; on the other hand, Ni (NiO) 's oxide form does not catalyze the reaction[179]. Therefore, the catalytic activity of Ni/Al_2O_3 catalyst is mainly determined by the characteristic of metallic Ni species over Al_2O_3. The amount of Ni loading over Ni/γ-Al_2O_3 catalyst affects the carbon deposition species and coke formation. With an increase in Ni loading 10 to 20 wt%, stability is enhanced due to the catalyst's resistance towards coke formation. The increase of Ni loading does not increase the catalyst activity while it only alters the properties and structures of the coke formed. Fibrous structures were formed over the 20 wt% Ni/Al_2O_3, while 10 wt% Ni/Al_2O_3 catalysts showed the amorphous type of coke on catalytic sites. Moreover, 20 wt% Ni/γ-Al_2O_3 catalyst had more aromatic and carbon nanotube structured coke species, which was not noticeable over 5 wt% Ni/γ-Al_2O_3 catalyst [127]. Piscina et al. observed an increase in graphitic-like species when Ni loading was increased from 9 to 15%[123]. The coke formation study of steam reforming reaction over Ni-based catalysts showed (Fig. 12) that catalyst deactivation was because of encapsulation by nonfilamentous carbon, which blocked the active catalyst sites [180]. Filamentous carbon formed from CO and CO_2 does not lead to catalyst deactivation but results in detachment of active nickel sites from the support [120, 179]. Medrano et al. investigated the influence of calcination temperatures (750, 850 and 900 ºC) on Ni/Al catalyst and observed an increase in spinel phase formation ($NiAl_2O_4$) at high calcinations temperature, which was difficult to reduce. Hence, the catalyst calcined at 900 ºC temperature showed lower activity than catalyst calcined at 750 ºC and 800 ºC [181]. At the same time, Zhang et al. reported that calcination temperatures affected the interaction between support and Ni metal and concluded that catalyst calcined at high temperature could improve the catalytic stability due to enlarged mean pore size, which enhanced the mass transfer efficiency [182]. Goyal et al. observed that 12 wt% Ni-Al monolithic catalyst was more stable than 12 wt% Ni-Al pelletized catalyst [183].

Active metal sintering

In addition to coke deposition, sintering is another important cause for catalyst deactivation during the steam reforming reactions [184]. The reason for sintering is the minimization of the surface energy after reducing the surface area resulting in agglomeration of small particles, leading to increased average particle size. Its effect is pronounced in the case of supported nickel catalysts during steam reforming[185]. Nogueira et al. described the above phenomenon over 15 Ni/Al catalyst by high-resolution transmission electron microscopy, in which sintering of nickel particles was observed **Fig. 2.16.** [186]. Sintering of nickel catalysts during steam reforming has been investigated extensively in

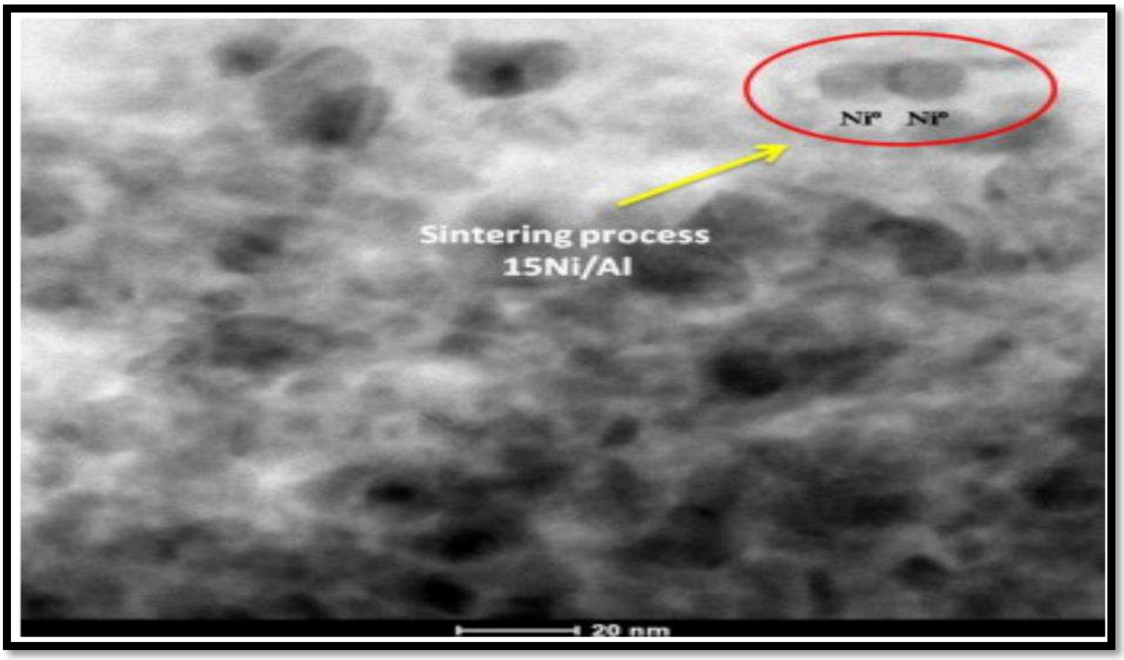


Fig. 2.16. HRTEM image of 15 Ni/Al catalyst (sintering process)

H_2O/H_2 model atmosphere [180, 187-189] is appropriate for steam reforming reaction. It has been observed in the reforming process that partial pressures of steam and hydrogen are exceedingly important and most likely control the rate of sintering [185]. Sehested et al. reported Ni/Al2O3 catalysts typically sintered in a severe hydrothermal environment because of the large loading and formation of $NiAl_2O_4$. At the same time, the addition of a small amount of magnesium and potassium resulted in the formation of $MgAl_2O_4$ and $K_2Al_2O_4$, which suppressed the nickel segregation on the support surface and formation of $NiAl_2O_4$ and consequently prevented the sintering [190]. Pu et al. investigated a fresh and a spent catalyst by XRD analysis and concluded that after the AASR, crystallite sizes of the Ni_ estimated by Scherrer equation increased due to the sintering of nickel crystallites[191]. The addition of Mg, Zr, Ce, and La to the γ-Al_2O_3 support also affects the catalytic activity as well as reduce coking and active metal sintering during steam reforming

Additives

Basic alkali metal additives such as (Li, Na, K, and Cs) have been reported to neutralize the acidic sites of alumina and enhance the catalytic activity & stability by preventing coke formation over the catalyst surface. They can modify the electronics and geometric properties of the active nickel particles, thus improving its coke resistivity and sintering of active metal [125]. These additives can efficiently disperse the active metal and prevent the formation of less active NiAl2O4 and inhibit sintering [192, 193]. Hu et al. reported that the addition of K to cobalt catalyst significantly enhanced hydrogen production via effectively diminishing the methane formation during AASR and high catalytic stability by resisting the coke formation [170]. Potassium also suppresses the CH_4 dehydrogenation and slows down the coke formation over nickel-supported catalyst [194]. Hu & Lu. [195]reported the effects of alkali metals like Li, Na, K, and Mg in Ni/Al_2O_3 catalysts during AASR. They observed that alkali metals modified catalysts effectively and restrained methane formation, especially with Ni-K/Al_2O_3 catalyst.

Support effect

Support is an important component in a reforming catalyst. The typical work investigating the effects of support and active metals on steam reforming of acetic acid has been extensively carried out. Besides active metals, support materials also affect the catalytic activity, selectivity of products and coke formation during steam reforming reaction. Generally, both porous and non-porous types of supports could be employed as support in reforming reactions. Therefore, a large number of materials including oxides such as Al_2O_3, La_2O_3, CeO_2, ZrO_2, MgO, mixed oxide CeO_2-ZrO_2, Al_2O_3-La_2O_3, MgO-Al_2O_3, La_2O_3-CeO_2-ZrO_2 metal composites normally used $MgAl_2O_4$, mesoporous materials such as SBA-15, MCM-41, mesoporous alumina and MgO and different types of minerals typically olivine, H-ZSM, coal ash have been investigated by several researchers. A detailed comparative study of conversion, selectivity, stability, and amount of carbon deposition during the AASR uses various support and catalysts in **Table 2.4**. (Given in appendices)

The support also plays a crucial role in the dispersion of active metal and participates in catalytic reactions [196, 197]. As mentioned in the literature, supports material takes part in steam reforming reactions by dissociating H_2O into ions. Water adsorption capability of support decides the steam reforming reaction pathway involved. It promotes product selectivity followed by coke gasification [96] [198, 199]. For example, during AASR over Pt/ZrO_2, Pt as an active metal actively participates in reforming reaction, but ZrO_2 is also involved via dissociation of adsorbed steam, which significantly improved catalytic activity. Cracking of C-C, C-H bonds in acetic acid is favored by Pt active sites, while ZrO_2 is active for dissociative adsorption and responsible for the activation of steam in reforming reaction. The steam reforming reaction over the catalyst showed bi-functional behavior shown in **Fig 2.6,** and both active metal and the support are responsible for steam reforming reactions [95]. Goicoechea et al. investigated and reported that catalytic performance and stability are strongly dependent on the support surface, chemistry and strength of metal-support interaction [54]. Redox ability and basicity of the support materials are the major factors that influence the coke resistance during steam reforming reaction. Catalyst support composition also affects the coke resistivity of catalysts [200]. Wang et al. carried out steam reforming of acetic acid over Ni/nano-Al_2O_3 catalyst and observed that nano-sized Al_2O_3 support exhibits excellent activity and stability (more than 10 h) in comparison to commercial γ-Al_2O_3 due to a high surface area which resulted in better dispersion of active metals [201].

Alumina

Among the different supports available, alumina is extensively used as a support in steam reforming reaction due to high surface area for active metal dispersion, and also it exhibits high chemical and thermal stability. Al_2O_3 supported metal catalysts showed high selectivity towards hydrogen generation during steam reforming of acetic acid. On the other hand, the acidic property of Al_2O_3 also catalyzes dehydration reaction, which subsequently leads to the deactivation of the catalyst due to coke formation. Verykios et al. compared carbon deposition behavior over Al_2O_3 support and concluded that Al_2O_3 being acidic favors decomposition and subsequent polymerization reactions, resulting in the generation of a considerable amount of graphitic carbon deposition over support during the AASR [87]. Chen et al. investigated the influence of the crystalline phase of Al_2O_3 over Ni-based catalyst during AASR and concluded that coke deposition was different on all four phases (α, β, γ, θ) of alumina. They inferred by the TGA analysis that Ni/α-Al_2O_3 showed better stability compared to other Ni/x-Al_2O_3 catalysts (x = α, β, γ, θ)[116] [202].

The Ni-supported γ-Al_2O_3 catalysts' activity and stability were enhanced by adding basic La_2O_3 and CeO_2 in ZrO_2 support to lower the coke formation [100, 135, 203].

ZrO_2

ZrO_2 is an amphoteric oxide, where both acidic/basic sites co-exist. This property assists in the adsorption of steam and carbon oxides onto the catalyst surface and promotes the dissociation of water over the catalyst surface [204] [205]. During reforming reactions,

ZrO_2 (without any catalyst) decomposes acetic acid into acetone, carbon dioxide and methane as primary products with no hydrogen [97] [204]. Consequently, Pt and Ni's active phase was explored for high conversion and selectivity towards hydrogen from acetic acid. ZrO_2 was utilized as support material by Takanabe and co-workers for the Pt-based catalyst during steam reforming reactions [97]. However, they reported severe deactivation of the catalyst due to blockage of the active site even in the presence of higher steam to carbon ratio via the formation of coke/oligomers. Whereas, ZrO_2 was solely used as a support; the main drawback is its low surface area and mechanical stability, which make ZrO_2 unsuitable as support for AASR [206]. Some reports suggest that modification of Ni/ZrO_2 catalyst with CeO_2 makes catalyst more resilient towards coke formation, and the Ni/CeO_2-ZrO_2 catalyst provide 83.4% of the maximum hydrogen selectivity and 0.39% of minimum methane selectivity at 650 ºC, which are much better in comparison to commercial catalysts [92, 207].

CeO_2

It was observed that the incorporation of CeO_2 increases the activity and the stability of the catalyst by increasing the active metal dispersion and oxidation of carbon deposited over the catalyst surface [208]. The redox properties of CeO_2 are due to the presence of oxygen vacancies on its surface or metal-ceria interface; consequently, high oxygen storage capabilities qualify CeO_2 as active support during AASR [209, 210]. The $CeO_{2,}$ when used as catalyst support, significantly promotes the elimination of coke deposition formed over catalyst surface owing to high oxygen storage capabilities and facile redox properties, but it is unstable at higher temperatures [211]. **Fig. 2.17** displays that a sufficient amount of oxygen vacancies are present on the surface of CeO_2 or the metal-ceria interfaces. Therefore, the water gas shift reaction gets promoted by the addition of CeO_2 [Eq. 3] [191, 212]. The main drawback of the CeO_2 catalyst is its low surface area. One possible route may be that CeO_2 might be incorporated with high surface area support like γ-Al_2O_3 support [191].

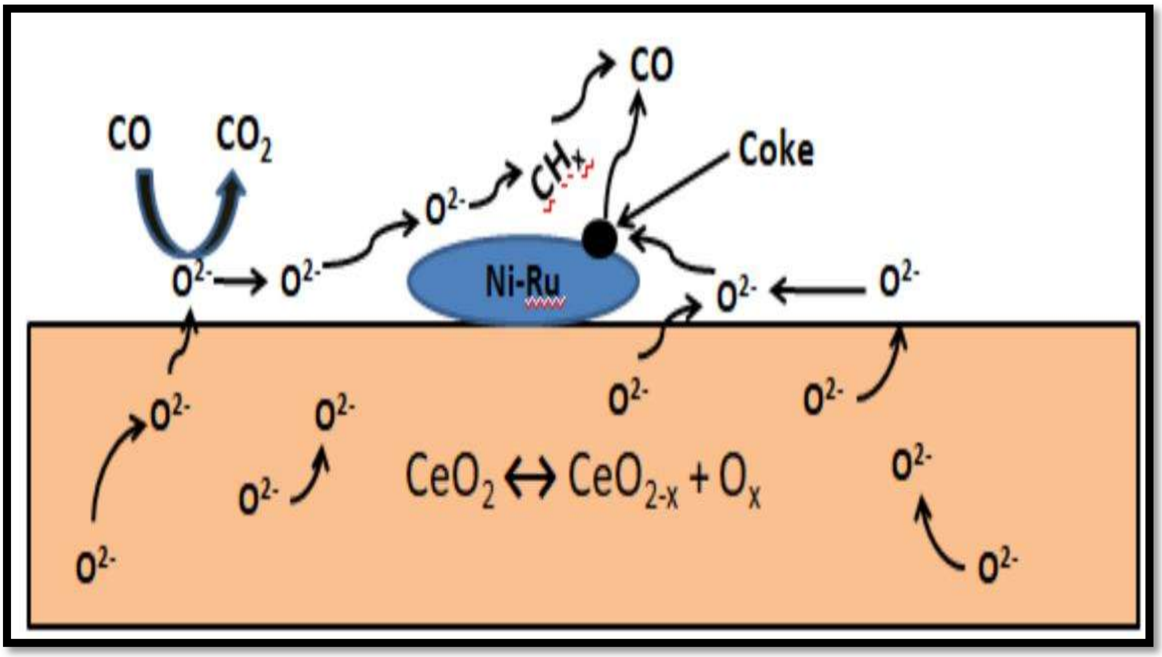


Fig. 2.17. The oxidation of CO, coke and coke precursor via migrated oxygen vacancies in the lattice of CeO_2 during the steam reforming of acetic acid

It is also well known that the incorporation of CeO_2 enhances catalyst activity by improving the Ni dispersion over bimetallic Ni-Ru supported catalyst surface [111][165]. Furthermore, Jianglong *et al*. have reported that the coke deposition is significantly reduced by the addition of ceria in the case of bimetallic Ni-Ru/Al_2O_3 catalyst because of oxygen storage and release property of ceria as explained by the following reaction:

$$CeO_2 \rightleftarrows CeO_{2-x} + O_x \qquad (21)$$

where O_x represents the mobile lattice oxygen present over the CeO_2 surface.

The mobile oxygen present in the CeO_2 lattice can be transferred from the oxygen vacancies to the surface of the catalyst, and oxygen is further transferred to the metallic surface and accelerates mitigation of coke precursor oxidation by following reactions:

$$C_x H_y + O_z \longrightarrow C_{x-1}H_y + CO + O_{z-1} \qquad (22)$$

where C_xH_y represents the coke species on the catalyst surface.

Therefore, coke generation is reduced by bringing down the growth of coke precursors [191]. CeO_2 also acts as an oxygen buffer by reversible redox oxidation state (Ce^{4+}/Ce^{3+}) to exchange oxygen efficiently[212, 213]. Ce^{3+} ions over the CeO_2 surface affect the coke generation over the catalyst surface due to the presence of mobile lattice oxygen [191]. Moreover, the existence of migrated oxygen over the metal surface improves coke precursor oxidation, represented by the reaction below [214].

$$C_{(s)} + O_x \qquad\qquad CO + O_{x-1} \qquad\qquad (23)$$

where $C_{(s)}$ is the coke species on the catalyst.

La_2O_3

Generally, γ-Al_2O_3 is used as catalyst support in the different thermochemical processes because of its low cost and excellent thermal stability and high surface area. However, its high acidic nature makes it susceptible to coke deposition on its surface, and consequently, catalyst activity and stability by deactivation of catalysts are lowered. Hence, the addition of basic promoters, e.g., La_2O_3, has been proposed to neutralize the acidic sites of γ-Al_2O_3. Garbarino et al. reported that the addition of La2O3 lowers the support's acidity by associating with acidic sites present on the Al_2O_3 surface and enhancing the hydrogen selectivity and catalyst stability[215]. In addition, Basagiannis & Verikios et al. reported that acetic acid showed stronger interaction with the Al_2O_3 than La_2O_3 [156]. Therefore, the addition of La_2O_3 with alumina could significantly minimize the coke deposition by preventing side reactions during AASR [41]. Reports suggest that the incorporation of La_2O_3 in nickel-based catalysts causes the interaction between Ni and La atoms which prevents the formation of $NiAl_2O_4$ [216]. The small amount of La_2O_3 prevented the coke deposition effectively over the catalyst surface because La_2O_3 could combine with CO_2 generated during AASR. Due to the adsorption of CO_2 on La_2O_3, the formation of oxygen-containing species ($La_2O_2CO_3$) occurred. Which finally prevents the coke deposition via the following reactions given below [109].

$$La_2O_3 + CO_2 \longrightarrow La_2O_2CO_3 \quad (24)$$

$$La_2O_2CO_3 + C \longrightarrow La_2O_3 + 2CO \quad (25)$$

The lanthanum modified Ni/ZrO_2 catalyst was investigated by Guell et al. They reported that the use of La_2O_3 as additives enhanced the conversion and hydrogen yield and increased catalyst stability AASR [163]. Sanchez-Sanchez et al. examined Ni/x%La_2O_3-Al_2O_3 (x = 3, 6, 15) catalyst with a different La_2O_3 loading over the γ-Al_2O_3 surface and reported that incorporation of lanthanum not only decreased the acidity but also increased the dispersion and stability of nickel-metal by inhibiting the coke formation. It also influenced the interaction of support and Nickel metallic phase, with high Ni and La atoms interaction resulting in nickel aluminates ($NiAl_2O_4$) [217]. AASR was carried out over Ni/La_2O_3, Co/La_2O_3, and Ni-Co/La_2O_3 catalyst by Nabgan et al. They observed that at all the investigated temperature ranges lanthanum supported Ni catalyst exhibited excellent performance in terms of both high hydrogen yield and stability by reducing carbon deposition over the catalyst surface [147]. Moreover, La_2O_3 is also known to prevent metal oxide formation and metal particles sintering at severe reaction conditions [218]. Therefore, to prepare the highly active and stable catalyst, the addition of La_2O_3 is widely used as an additive over γ-Al_2O_3 [87, 94, 142, 154, 217, 219].

Effect of Alkali and Alkaline earth metals

Alkaline earth metals (CaO, MgO) are also extensively reported in the reforming reaction in order to neutralize the acidic sites of γ-Al_2O_3 and enhance the performance of the catalyst by inhibiting the coking of the catalysts [220-222] [166]. Moreover, adding alkaline earth metals favors the adsorption of H_2O and OH^- mobility over catalyst surface significantly, which facilitates carbon oxidation and inhibits coke formation over catalysts surface[166, 223, 224]. Pant *et al.* reported that coke generation over the support (Ca_{-12}/Al_{-7}) surface was insignificant because of excess oxygen present in the $12CaO{\cdot}7Al_2O_3$ phase[166]. Incorporation of CaO and MgO to support materials results in diminishing the quantity of coke deposition and changed the nature of coke[225]. Initially, the coke formation rate over the catalyst surface accelerated for the incorporated promoters (Mg and Ca) with the catalyst. Whereas, after a long time on stream (TOS) reaction, the coke deposition rate over catalyst surface with promoter was less in comparison with the catalyst without promoter [226]. Basic oxides help in lowering down the coke deposition over the catalyst surface. Alkaline earth support increases the concentration of basic sites and strengthens the adsorption of CO_2 on the catalyst. This adsorbed CO_2 reacts with carbon species, resulting in suppressing the deposited carbon by the following reaction

$$CO_2 + C_{(A)} \longrightarrow 2CO \qquad [26]$$

Where $C_{(A)}$ represent the amorphous carbon. ($\Delta G°_{600°C} = -4.4 kJ\ mol^{-1}$) [227].

Passos et al. reported that among basic earth metals, the addition of Ca and Mg to Ni/α-Al_2O_3 improves the catalyst's overall activity and stability. However, Mg only was accounted for the Ni particles size dilution due to the attachment of nickel particles with Mg since Mg obstructs the graphene nucleation pathway and, in that process, helped in less reactive coke formation. In contrast, the addition of Ca showed advanced characteristics because of its capacity to gasify adsorbed carbon species [225]. It was observed that the integration of MgO to Ru/Al_2O_3 exhibits a beneficial effect towards coke deposition, which was attributed due to the formation of magnesium aluminate spinel structure, which enhances O and ^{-}OH anion overflow from the carrier onto the Ru particles and hence improves the carbon gasification rate, thus increasing the catalyst life [41]. The incorporation of MgO as an additive in Ni/Al_2O_3 catalyst improved catalytic performance for H_2 yield and carbon conversion [228]. Xu *et al.*[229] have reported that the addition of

MgO in Ni-CeO_2/olivine promoted the steam adsorption capability, improved the activity, and lowered the coke deposition. Yang *et al.*[230] investigated acetic acid steam reforming over Ni/MgO-m (mesoporous MgO) and observed that MgO as support showed the highest catalytic activity and stability. Ni-Co bi-metallic MgO-based catalyst was tested in AASR for hydrogen production. $Ni_{0.2}Co_{0.8}Mg_6O_{7\pm\delta}$ catalyst showed high resistance towards coke formation [231]. NiO forms a solid solution into the MgO matrix and helps inhibit Ni particles' growth over the surface of Ni-based catalysts [230]. The addition of promoters may also prevent the coke formation on Ni-based catalysts. During steam reforming of methane, the incorporation of alkali and alkaline earth metals, K, Na, Ca and Mg, over the supports improved catalytic activity and stability of Ni catalysts [232, 233]. Recently, Medrano *et al.*[234] investigated that the addition of Mg to Ni/Al catalysts enhanced the catalytic activity and stability during AASR. Mg incorporation in Ni/Al catalyst with a Mg/Ni molar proportion of 0.26 gave an excellent performance during steam reforming without deactivation. Hu *et al.* [195]reported the effect of alkali metals like Li, Na, K, and Mg in Ni/Al_2O_3 catalysts during AASR. They observed that alkali metals modified catalysts restrained methane formation, especially with Ni–K/Al_2O_3 catalyst. Moreover, the presence of K also enhanced the stability of the Ni catalyst through the inhibition of carbon formation. Many researchers have reported different promoters for the steam reforming process [56, 178, 225]. Among them, calcium has been utilized as a promoter for nickel-supported alumina catalysts for dry reforming of CH_4 [235] [236, 237], and some researchers explained its utilization in steam reforming reaction, enhancing the stability of nickel phases in hydrocarbon cracking processes [146, 238]. Mg-modified nickel-alumina catalysts enhance the strength of catalyst and improve the adsorption of steam; improving carbonaceous species gasification and stabilizing active nickel sites by preventing their sintering [56, 239][143, 225]. Hence, both (Mg and Ca) enhance the stability of the catalyst by reducing its acidity and also lower down the cracking and polymerization reactions[238].

2.13 Summary of Overall Literature Review

Metal-Organic Frameworks (MOFs) based on new catalysts have shown outstanding potential because of their controllable structure, unique properties and large surface areas. MOFs are usually synthesized through the coordination of the metals with ligands. A large number of metals particularly, transition metals, are used to synthesize the MOFs. In addition, 2, 2′-bipyridine is found the most widely used ligand because of its ease of functionalization and robust redox stability. MOFs as catalysts have shown great potential for green energy and environmental applications. However, in many applications, direct use of MOFs as catalysts is not possible due to their relatively limited thermal and chemical stability. To overcome these issues, several researchers have prepared heterometallic catalysts via metal-organic frameworks (MOFs). These methods have significantly improved the efficiency, stability and reusability of catalysts. Besides this, several researchers also tried to combine the MOFs to thermal stable supports. However, limited data are available in this respect.

Prevention of the coke deposition over the catalyst surface during acetic acid steam reforming is also a big challenge for the AASR process—encapsulation of catalyst surface with the coke results in severe catalyst deactivation. Industries practice different techniques to control the coke formation, among which coke gasification to convert into CO and CO_2 is the most practiced one. The above review summarized a broad analysis for reducing carbon formation using suitable catalysts and supports, types of reactors etc., to increase catalyst life. Reduction in carbon formation rate during reforming reaction is also a technique to improve the catalyst life but not a permanent solution. Modification of active metal and support or both is the best approach to prevent carbon formation. The present review also discusses the potential reaction pathways, carbonaceous deposition mechanism over catalyst surface and different intermediate reactions during AASR, which are the major deactivation routes during the AASR process. Different types of active metals facilitate a defined reaction pathway, which may or may not produce carbonaceous species. Rh and Pt-based catalysts exhibited excellent catalytic activity, long-term stability, and lower coke formation among available catalysts. However, their high cost prevents the utilization of noble metals on an industrial scale. Among different transition metals, nickel-based catalysts are cheaper and exhibit high performance towards hydrogen generation. However, deactivation due to coke formation over the nickel-based catalyst is the major issue. Traditionally, oxide support such as Al_2O_3, CaO and MgO is used for steam reforming reaction, but all supports suffer severe coke deactivation problem.

Therefore, for longer stability CeO_2, ZrO_2 are identified as oxide supports because of their high redox property and basic character on the catalyst surface. Rare earth metal oxide La_2O_3 also exhibits excellent coke resistance nature by forming $La_2O_2CO_3$. Utilization of mixed oxide support and alkali and alkaline earth metals such as Mg and K over Ni/Al_2O_3 catalyst promotes oxygen mobility and easy coke gasification by increasing the reaction between steam and coke deposited over the catalyst surface and, in the process, reduces the carbon polymerization. Hence, nickel-based catalysts supported over $Al_2O_3/CeO_2/LaO_2$ oxide support might be promising catalysts. Incorporating small amounts of oxygen during the reforming reaction also helps to minimize the coking by gasifying the carbon deposited over the catalyst surface. The combination of proper reactor design and suitable catalyst formulation also plays a significant role in minimizing carbon formation. A fluidized bed reactor and a dual bed system in series during AASR showed lesser coke deposition than the fixed bed reactor.

2.14 Objective of the present work

Development of efficient nano nickel supported catalysts and its activity evaluation in steam reforming of acetic acid reactions. Keeping in mind, the aim and scope of this work, the following specific objectives have been set:

1. Synthesis of a high surface area γ-Al_2O_3 support with incorporation of La_2O_3 and CeO_2 in order to avoid metal sintering and suppress coke deposition during steam reforming reaction.

2. Development of a process of catalyst preparation using metal-organic precursors and compare its microstructure, activity and stability with the catalysts prepared via wet impregnation methods for acetic acid steam reforming reaction for the production of hydrogen.

3. Optimization of operating variables, viz, temperature, space velocity, steam to carbon molar ratio (S/C), and to study the stability of prepared catalysts.

4. Establish the optimum loading of Ni in catalysts for the best performance with respect to hydrogen production.

5. Study the deactivation of catalysts and coke formation during steam reforming of acetic acid.