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Review Article

Short Review: Cu Catalyst for Autothermal Reforming Methanol for Hydrogen Production

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Abstract

Hydrogen is a promising alternative energy sources, hydrogen can be used in fuel cell applications to producing electrical energy and water as byproduct. Therefore, fuel cell is a simple application and environmentally friendly oriented technology. Recent years various methods have been conducted to produce hydrogen. Those methods are derived from various sources such as methanol, ethanol, gasoline, hydrocarbons. This article presents a brief review a parameter process of that affects in autothermal reforming methanol use Cu-based catalysts for production of hydrogen. Copyright © 2012 BCREC UNDIP. All rights reserved.

Keywords: Authothermal; Methanol; Reforming; Hydrogen; Cu; Fuel Cell

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1. Introduction

The growing world population has had a large effect on the demand for energy. To date, fossil fuels have been used as the main energy sources to support such demand. Unfortunately, fossil fuel reserves are expected to last no longer than 50-100 years [1]. The shortage of energy is thus becoming an important problem for mankind, prompting worldwide searches for alternative energy [1,2].

Environmental pollution became a major topic in recent years. Emission from motor vehicles and electric power generation plants are two of the largest sources of air pollution [3]. For controlling emissions from internal combustion engines [4] and high Efficient [5] are of utmost importance to search alternative power sources for vehicles.

Recent global energy shortage and more stringent emission regulations have stimulated research and development in fuel cell area [7]. Hydrogen fuel cell seems to be a promising solution to these global environmental and energy problems as using hydrogen in fuel cells produces useful energy at high efficiencies and generates only heat and water as emissions [6].

In this future, hydrogen is to become a major source of energy [10], fuel [11], an alternative source of energy [12], an important chemical material that is utilize in large amounts in synthetic chemical industries [8], and raw materials for petroleum and petrochemical industries [9].

Hydrogen has potential for use as a localized energy source to replace batteries inside electronic devices or to power vehicles [13] and used for

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energy purposes in fuel cells is a topic of large and growing interest [14]. Hydrogen is produced from various energy sources, stored, transported and used in industries, homes, automobiles, airplanes and factories or used as electricity generations, and will be used more and more if the research and development of it, is continued [10].

The interest on fuel cells has increased, however the main difficulty on hydrogen utilization is about production cost, in this context, a cheaper production alternative could make viable the hydrogen utilization in fuel cells [15]. The production of hydrogen as a fuel from a suitable carrier is a necessary step in light of the difficulties faced in hydrogen transport and storage [14].

This work summarizes about the fuel cell and hydrogen as a fuel, include the latest developments of hydrogen production from several authors. In each section will describe some of the results of previous studies on the production of hydrogen from autothermal reforming of methanol use Cu-based catalyst, and process parameter that influences for this reaction .

2. Fuel Cell

Fuel cells are one of the most promising energy conversion devices due to their high intrinsic efficiency and ultra low emissions [20]. Fuel cell technology is rapidly on the rise. With an increased demand for fuel and energy efficiency over the modern combustion engine, fuel cells are a viable alternative [21].

Fuel cell by definition is an electrical cell, which unlike storage cells could be continuous feed with a fuel so that the electrical power output is sustained indefinitely [16]. Fuel cells can also be used to provide power for home, car, machine in plant, by producing electricity and significant amounts of waste heat.

Due to thermodynamic limitations, the efficiency of a typical combustion engine is usually less than 30%, but a fuel cell can reach above 80% [2]. Fuel cell is a clean burning and highly reactive fuel that offers high thermal efficiencies of 35–45% in comparison with 25–30% typical of normal petroleum fueled engines. Therefore, under development in an effort to reduce CO_2 emissions that accelerate global warming [22].

Fuel cell powered electric vehicles and power plants using hydrogen as fuel [23]. Fuel cell unit generates electrical energy from an electrochemical reaction of hydrogen with oxygen, yielding an environmentally benign by product, water [1]. Fuel cells work by absorbing oxygen and hydrogen gases to generate chemical reactions, and the products of the reactions are water and electricity. Oxygen can be absorbed directly from the atmosphere due to its abundance in the atmosphere. However, because hydrogen is less abundant content in the atmosphere, a mechanism for supplying hydrogen must be developed [2], and hydrogen are extremely difficult to store [18].

Fuel Cell reaction as a follow [24]:

Anode Reaction : $2H_2 \Rightarrow 4H^+ + 4e^-$ (1)
Overall Cell Reaction: $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$ (2)
Overall Cell Reaction: $2H_2 + O_2 \Rightarrow 2H_2O$ (3)

Fuel cells have been designed that can directly oxidize fuels such as methane, methanol, dimethylether, etc [25]. The permeable membrane was between anode and cathode. After hydrogen and oxygen would reach fuel cell of anode and cathode, respectively and thus the hydrogen atom of anode would be decomposed to form hydrogen protons and electrons by catalysis. Finally, hydrogen protons have been attracted into other side membrane by oxygen, and the electron that

Table 1. Data of Different type of Fuel Cell

Fuel Cell Type	Mobile ion	Operating Temperature	Applications and notes
(AFC)	OH^-	50–200 °C	Used in space vehicles, e.g. Apollo, Shuttle.
(PEMFC)	H^+	30–100 °C	Vehicles, mobile applications, and for lower power CHP systems.
(DMFC)	H^+	20–90 °C	Suitable for portable electronic systems of low power, running for long times.
(PAFC)	H^+	~220 °C	Large numbers of 200-kW CHP systems in use.
(MCFC)	CO_3^{2-}	~650 °C	Suitable for medium- to large-scale CHP systems, up to MW capacity.
(SOFC)	O^{2-}	500–1000 °C	Suitable for all sizes of CHP systems, 2kW to multi-MW.

Rewrite from Fuel Cells System Explained book, page 15 2003 [27] would produce electric current by outside-circuit. The hydrogen protons, electrons and oxygen are transformed into water molecule by using cathode catalyst. Hence, water is the only product waste [24].

Fuel cells have difference electrode that would be several kinds of fuel cell. Generally, it has five types such as Alkaline (AFC), Phosphate Fuel Cell (PAFC), Melt Carbonate Fuel Cell (MCFC), Solid Oxide Fuel Cell (SOFC) and Proton Exchange Membrane Fuel Cell (PEMFC) [26] as found in Table 1.

Until now fuel cell still expensive to produce and electrical energy that produce still low voltage. Hydrogen as a fuel still has any problem in a production, because still produce harmful exhaust gases such as CO. After hydrogen is generated then hydrogen must be collected and stored, until recently some researchers are still conducting research on the proper mix of materials as construction materials for hydrogen storage, and still not found the right method to transport and distribute hydrogen, because hydrogen is explosive, and hydrogen can cause a number corrosion problem.

3. Hydrogen Production

There were six types of methods to produce hydrogen for different source feedstock:

3.1. Steam reforming

Hydrogen production from hydrocarbon steam reforming is a cost-effective method in providing hydrogen for fuel cells [28]. Steam reforming processes using the steam reforming to produce hydrogen from methane, methanol and other carbohydrate [24]. Reactant is mixed with steam in the presence of a base metal catalyst to produce hydrogen and carbon monoxide.

3.2. Electrolysis

Hydrogen produced from the electrolysis of water in electrolysers. Electrolysers use electricity to divide water (H_2O) into hydrogen and oxygen [27]. Conventional water electrolysis, such as an alkaline water electrolysis, high-pressure electrolysis, and solid polymer electrolyte water electrolysis, is basically applied to produce hydrogen if a cheap source of electricity is available. In the alkaline water electrolysis, the cells use aqueous solutions of KOH, NaOH or NaCl as the electrolyte. This technology is well developed but the overall hydrogen production efficiency is too small, about 27% [29].

Water electrolysis is technologically simple, environmentally clean and generates very high purity gases (hydrogen and oxygen) from water. Unlike other technologies, water electrolysis does not require large, centralized plants and the cost of hydrogen production scales well from the larger to smaller systems. In an alkaline medium, the half reaction at the anode is [30].

$$4\,OH^- \rightarrow O_2 + 2\,H_2O + 4\,e^- \qquad (4)$$

One of the major limitations of water electrolysis for hydrogen production is the poor kinetics of oxidation of hydroxyl ions to oxygen at anode [30].

3.3. Steam electrolysis

Steam electrolysis is a variation of the conventional electrolysis process. Some of the energy needed to split the water is added as heat instead of electricity. Water decomposes into hydrogen and oxygen.

The high-temperature steam electrolysis offers a promising method for highly efficient hydrogen production. Operation at high temperatures reduces the electrical energy requirement for the electrolysis and also increases the efficiency of the power generating cycle. In addition, high-temperature systems can promote electrode activity and lessen the over potential. Therefore, it is possible to increase the electric current density and consequently decrease the polarization losses at high temperatures, which improves the hydrogen production density and the electrolysis efficiency [31].

3.4. Thermochemical water-splitting

Hydrogen could be produced by thermochemical water-splitting, a chemical process that effects the multistep decomposition of water. Water and heat are the inputs. Hydrogen and oxygen are the only outputs. The other chemicals and reagents are recycled in a closed cycle [32]. Heat can be produced by chemical, solar, nuclear. A thermochemical cycle effects the multi-step decomposition of water into hydrogen and oxygen using only heat [33].

Solar thermochemical water-splitting, in which water is used as the chemical source for hydrogen production and high temperature solar heat is used as the energy source, provides one of the most promising ways to realize hydrogen production from water [34]. Because it’s much more environmentally since hydrogen produced by thermo-chemical water-splitting does not contain contaminants, it could be used directly in fuel cells [32].

In addition to reforming and thermochemical water-splitting, electrolysis produces pure hydrogen. But this latter method suffers from thermodynamic inefficiencies. The efficiency of electrolysis is currently about 70% and the efficiency of heat conversion to electricity is usually 33% (with current technology nuclear heat). Thus, the current combined efficiency does not exceed 20–25% [32].

3.5. Photocatalyst processes

Production of electricity and hydrogen by photocatalytic degradation of organic wastes in a photoelectrochemical (PEC) cell is an attractive project with double environmental benefit: waste material can be consumed and solar radiation can be converted into useful forms of energy, such as electricity and hydrogen [35].

Photoelectrochemical production of hydrogen is produce in a PEC cell. The following three components are the main components of a PEC cell: (a) the anode electrode, which carries the photocatalyst and thus it is usually named "Photo anode". When the photo-catalyst is an n-type semiconductor, which is almost the exclusive case, the photo anode produces electrons, it is the negative electrode, Oxidation reactions take place at the photo anode, (b) the cathode electrode, which carries the electro catalyst, material, which facilitates transfer of electrons from the cathode to the liquid phase. Reductive interactions take place at the (dark) cathode, for example, reduction of hydrogen ions to molecular hydrogen, (c) The electrolyte, which is added in order to increase conductivity and define the pH [35]. Thus the photocatalytic and photoelectrochemical routes are similar. The only difference is that, in the second case, the site of molecular hydrogen evolution is spatially separated from the site of target substance oxidation. By inversing this statement, we may accordingly say that a photocatalyst with deposited metal is a miniature photoelectrochemical cell [36].

Photoelectrochemical processes use two types of electrochemical systems to produce hydrogen. One uses soluble metal complexes as a catalyst such a TiO_2, La_2Ti_2O7, CdS/TiO_2, and Fe_2O_3 [86], while the other uses semiconductor surfaces such as non-oxide semiconductors, e.g., Si, InP, CdTe, GaAs, etc [37].

The photocatalytic process has been criticized as being uneconomical compared with other hydrogen production systems, due to its inherently low efficiency and other limitations [38].

3.6. Photobiological processes

Photobiological is production hydrogen from renewable source such as solar heat from sunlight and water. Hydrogen-production includes processes such as: (i) direct biophotolysis of water by microalgae and cyanobacteria, (ii) photo-fermentative nitrogen fixation and the attendant hydrogen production by photosynthetic bacteria, (iii) non-photosynthetic hydrogen production from organic compounds by obligate anaerobic bacteria, (iv) nitrogen fixing fermentative bacteria [39].

These processes can be beneficial in two ways: firstly by removing the green house gases (mostly CO_2) which are responsible for global-warming and production of nonpolluting, renewable potential energy carrier (biophotolysis by green algae and cyanobacteria) and secondly using waste materials that potentially create ecological hazards, as substrate (photofermentation by photosynthetic bacteria) [40].

Photobiological hydrogen production has several limitations and the yield is very low compared to thermochemically and electrochemically produced hydrogen [82], relatively low efficiency of photosynthesis in practice [41].

One of the weakness of hydrogen production from raw water, is a must keep the clean process from initial to the end of process, because water contains corrosive substances. So it can increased energy used in the process.

Hydrogen production based on biology process is very interesting to study further, but until now, the biological process is still an expensive process, because it requires expensive enzymes, bacteria, and not a short process time, and requires the separation of the product at the end of the process.

Steam reforming is a more economical process than the others, because less production cost, short time in a process, not used high pressure steam, high selectivity and less exhaust emissions.

4. Steam Reforming

Conventional methods for hydrogen production are based on gasoline [29-31], natural gas [42-44], methanol [45, 23, 22, 46-51, 52], ethanol [12, 15, 53, 54-58], and a renewable raw material [59-63].

An important issue in gasoline reforming is the deactivation of the catalyst by coke formation or by sulfur compounds present in the feed. Gasoline contains different types of sulfur compounds (thiophene, benzothiophene) at a concentration of a few ppm. These sulfur compounds can interact with the catalyst surface and may alter the chemical and structural properties of the active sites, which results in the deactivation of the noble metal catalyst [64].

The development of onboard reformer or partial oxidation processor of gasoline to hydrogen and CO_2 inevitably release a large quantity of CO_2 and an unacceptable level of CO [65].

Natural gas is the resource most commonly used for hydrogen production. Typically, natural gas (which consists mainly of methane) is converting to hydrogen through steam methane reforming (SMR) [42]. Natural gas is clean hydrocarbon fuel, abundant, and well distributed, is considering one of the ideal fuels for hydrogen source for fuel-cell stationary applications [44]. However, liquid feedstocks are used. In particular, carbon deposition and poisoning by sulfur and other electronegative atoms (Cl, P) determine loss of catalyst activity, especially when petroleum-derived liquid fuels are used [43].

Ethanol is a promising source of hydrogen as it is a renewable source when obtained from biomass [54]. Ethanol also capable to produce hydrogen from steam-reform, its advantages are clear: ethanol is liquid, has low toxicity and its production is simple and cheap [15]. Direct production of H_2 from carbohydrates catalytically has been demonstrated, but the process requires long reaction times and has shown only ~50% selectivity to H_2 from glucose [67].

Among the hydrocarbon fuels examined. Methanol is one of the best source [17] and promising candidate fuels [20], Methanol is a renewable resource, low boiling point, high H/C ratio[17], safe handling/storage materials [45], sulfur-free, can be activated at relatively low temperature (under 300 °C) [10], high ratio of hydrogen [24]. Methanol also offers a high conversion rate and produces fewer by-products, other hydrocarbon fuels [2].

Methanol has high H/C ratio and no C–C bonds, hence minimizing the risk for coke formation. Moreover, as methanol can be produce from renewable sources, its reforming does not contribute to a net addition of CO_2 to the atmosphere [66]. The decomposed methanol is a cleaner and more efficient fuel than gasoline and undecomposed methanol for internal combustion engines of automobiles [3].

Methanol, compared to natural gas or other hydrocarbons, is a more efficient energy source to produce hydrogen used in fuel cells [68]. The methane reforming reaction requires a huge amount of energy, 973-1273 K, while the ethanol has been used in various applications such as gasohol and food production. Methane and ethanol have been widely used as energy resources, so there is no need to spend significant amount of energy to convert methane and ethanol to be hydrogen [1].

For producing hydrogen on-board due to the following advantages: mild reforming reaction conditions; no needs for desulfurization; no needs for pre-reforming; no serious carbon formation problem. Under ambient condition, liquid methanol has a high volumetric energy density. Many studies have been conducted on steam reforming of methanol [20].

Hydrogen production from methanol is possible through several process alternatives [20, 69]:

4.1 Methanol decomposition (MD)

$$CH_3OH \rightarrow CO + 2H_2 \quad (\Delta H^\circ = +92.0\ kJ/mol) \quad (5)$$

The decomposition reaction is a strong endothermic reaction The process yields high CO contents [70], Hence, this reaction was unsuitable for the PEM fuel cell application [24], because carbon monoxide produced is Apart from being harmful to health, an atmospheric pollutant and a poison for the fuel cell [71].

4.2 Methanol steam reforming (SRM)

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2\ (\Delta H^\circ = +49.4\ kJ/mol) \quad (6)$$

Steam reforming involves the reaction of steam with the fuel in the presence of a catalyst to produce H_2 and CO. Since steam reforming is endothermic, some of the fuel must be burned and the heat transferred to the reformer via heat exchangers [72]. Yields CO_2 as the major by-product and can produce a high content, up to 75% on a dry basis, which makes it very favorable for fuel cell applications [70]. Unfortunately, a considerable amount of CO (>100 ppm) as a by-product is produced during the reaction [23].

SRM shows the highest hydrogen production efficiencies [5], however a limitation is the endothermicity of the reaction. Moreover, slow heat transfer in the catalytic bed results in slow response at start-up. A promising option that offers good heat transfer characteristics is the combination of endothermic steam reforming with

Table 2. Summary of production hydrogen research using methanol with different method of reaction

Reaction	$T_{reaction}$ (°C)	X_{MeOH} (%)	CO yield (ppm)	CO selectivity (%)	Rate of H_2 production ($cm^3\ g^{-1}\ min^{-1}$)	*S* (H_2) (%)	H_2 yield (%)
SRM [1]	250	-	-	-	-	-	28
MD[3]	275	63	51.6^{b}	81.6	-	91.6	57.9
ATRM [20]	230	98.4	3642	-	-	-	49.4
POM [22]	200	40-60	-	-	-	>90	-
SRM [23]	250	95.5	-	0.14	-	99.9	-
ATRM [43]	250	90	-	3.8	-	-	-
ATRM [45]	270	98	-	0.1-1.2	2.16^{d}	-	-
SRM [46]	250	83^{a}	-	-	-	94^{c}	-
SRM [49]	260	90	-	0.06^{c}	244^{e}	-	-
SRM [51]	250	88.7	-	0.5	-	-	-
SRM [70]	235	-	-	-	-	-	50-74
SRM [73]	300	95.0	-	3.4	32.1	96.6	-
ATRM [74]	230	85	-	-	-	27	-
SRM [77]	160-350	-	-	-	816^{f}	99	-
MD [78]	315	97	-	95	-	-	-
SRM [78]	255	98	-	5	-	-	-
SRM [79]	230	96	-	86	-	-	-
SRM [80]	240	97	<500	-	-	-	>50

^{a} = mol%; ^{b} = %; ^{c} = mol%; ^{d} = l / h; ^{e} = (mmol s^{-1} $kgcat^{-1}$); ^{f} = ($cm^3\ g^{-1}\ h^{-1}$); MD = Methanol Decomposition; SRM = Methanol steam reforming; POM = Partial Oxidation Methanol; ATRM =Autothermal Reforming Methanol

the exothermic combustion of part of methanol feed [73].

4.3 Partial oxidation methanol (POM)

$$CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2 \quad (\Delta H° = -192.2\ kJ/mol) \qquad (7)$$

$$CH_3OH + 0.25O_2 \rightarrow 0.5CO_2 + 0.5CO + 2H_2 \quad (\Delta H° = -50.8\ kJ/mol) \qquad (8)$$

Partial oxidation reaction is a highly exothermic process [73] and needs external cooling in general [5].

Partial oxidation involves the reaction of oxygen with fuel to produce H_2 and CO [72]. The system can only deliver 66% hydrogen when pure oxygen and 41% when air is use to supply the oxygen [70].

Partial oxidation can be conduct with a catalyst (catalytic partial oxidation) or without a catalyst (non-catalytic partial oxidation). The reaction rates are much higher for partial oxidation than for steam reforming, but the H_2 yield per carbon in the fuel is lower. Non-catalytic partial oxidation requires reaction temperatures above 1000 °C to achieve rapid reaction rates, some of the fuel must be combusted because the amount of heat generated by the reaction is not sufficient to preheat the feed to achieve optimal rates [72].

4.4 Autothermal reforming of methanol (ATRM)

$$CH_3OH + (1-\alpha)H_2O + 0.5\alpha O_2 \rightarrow CO_2 + (1-\alpha)H_2 \quad (\Delta H° = 49 - 242.\alpha\ kJ/mol) \qquad (9)$$

Autothermal reforming involves the reaction of oxygen, steam, and fuel to produce H_2 and CO_2, and can be viewed as a combination of partial oxidation and steam reforming [72]. These systems can be very productive, fast starting and compact, since the exothermic partial oxidation reaction can supply heat to steam reforming reaction directly [9].

Autothermal reforming uses the energy produced from partial oxidation to supply the endothermic, steam-reforming reaction, and thus can be run adiabatically. This process has not been extensively studied, but initial results indicate low carbon monoxide yield and high hydrogen concentration in the products [74]. Autothermal reforming promises better dynamic response than both of the before mentioned reforming processes [5].

An ideal method to produce hydrogen with lower amount of CO from steam reforming of methanol greatly requires a high performance catalyst, which must be highly active and selective for hydrogen production and also stable for a long period in a continuous operation. Now the most widely used catalysts for this reaction are copper containing catalysts since copper has been found to be high activity and selectivity for hydrogen production [23]. In order to reduce the CO content in the feed gas obtained from fuel reforming to a tolerable level (less than 10 ppm), it is necessary to find a more active and more effective catalyst [21].

4.5 Water gas shift

Steam and combined reforming are commonly operated with an excess of steam, 20–30%. The excess steam is mainly present in order to reduce the carbon monoxide content [69] and to enrich hydrogen in the reformate stream [75] by inducing the water-gas shift (WGS) reaction in the reformer.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H° = -41.1 \text{ kJ/mol}) \quad (10)$$

The WGS reaction is a reversible, relatively slow and moderately exothermic reaction [75]. WGS is used for ammonia synthesis, to adjust the H_2/CO_2 ratio in the product gas from the steam reforming of hydrocarbons and to detoxify town gas [76].

The Autothermal reforming method is better than the other methods, Based on the reaction temperature is low, high methanol conversion and high yield of hydrogen. However weaknesses in the high yield of CO are produced.

Autothermal reforming also called Oxidative steam reforming (OSR), which is a combination of Methanol steam reforming and Partial Oxidation Methanol [81]. An extremely high rates of hydrogen production were observed in the oxidative steam reforming of methanol [82]. In recent years, the catalytic ATR process has received much research and Development attention as a viable process for hydrogen generation for fuel-cell systems because it offers advantages of simpler design (smaller and lighter unit), lower operating temperature (easier start-up and a wider choice of materials), and flexible load following characteristic as compared to the steam reforming process. It also has higher energy efficiency than the partial oxidation process [44].

In OSR, the exothermic partial oxidation of methanol supplies the heat energy that is required for internal endothermic steam reforming. The overall heat of reaction depends on α (Eq. (9)), which is the molar ratio of oxygen to methanol and affects the hydrogen concentration. Furthermore, the reaction of CO with oxygen in OSR is expected to reduce the amount of CO by-product [83].

In the endothermic steam-reforming process heat is transferred across a heat-conducting boundary to support the reforming reaction between methanol and water. The rate of the process is usually limited by the rate of heat transfer across the boundary. Therefore, improvements to steam reforming are generally sought in designing reactors having low heat resistance and intimate contact between the reforming and the heating zones, such as micro channel technology. On the other hand, in the OSR process heat release is part of the overall reforming process, such that the heat transfer limitation is removed allowing for a many-fold increase in the reaction rate [82].

Methanol autothermal reforming reaction (ATR) has a net reaction enthalpy change of zero which is a combination of the endothermic steam-reforming reaction and the exothermic partial oxidation reaction, thus a reactor for this process does not require any extra external heat after having attained reaction temperature [84].

5. Process Parameter

Process production of H2 on board a vehicle must meet several criteria. For instance, it must be compact and energy efficient, respond to transient behavior, and produce a reformatted with a high H_2 content and extremely low CO level [66]. Maximizing H_2 yield is the goal for increasing the efficiency of the process [82]. An ideal Product of OSR has only H_2 and CO_2. However, in an actual process OSR, CO will be formed in addition to CO_2. Also methanol, oxygen and water may not be fully consumed in the reactor, and methane and other components may form as by-products [82]. Other byproducts such as formaldehyde, formic acid, methyl formate or dimethyl ether often formed by reactions of methanol [73].

Table 3. Effect different preparation method into physicochemical properties of Cu and Zn based catalysts .

Catalyst	composition (wt %)	Preparation method	Pore volume (cm^3 g^{-1})	S_{BET} (m^2 g^{-1})	S_{Cu} (m^2 g^{-1})	Cu dispersion (%)
$Cu/ZnO/Al_2O_3$[4]	-	I	-	-	-	-
Cu/CeO_2 [11]	3.9	CP	-	96	101.6	-
Cu/ZnO [11]	-	AP	-	78	75.3	-
Cu/Zn(Al)O [11]	-	HC	-	114	80.8	-
Cu/Al_2O_3 [11]	-	I	-	157	73.7	-
Cu/CeO_2 [11]	-	I	-	84	61.5	-
$Cu/Zn/Al_2O_3$ [24]	15/15/5	OCP	0.371	70.78	-	7.5
$Cu/Zn/ZrO_2$ [24]	15/15/5	OCP	0.24	40.01	-	7.3
$Cu/Zn/CeO_2$ [24]	15/15/5	OCP	0.2	36.7	-	6.4
$Cu/Zn/Cr_2O_3$ [24]	15/15/5	OCP	0.35	35.8	-	8.0
$Cu/Zn/Al_2O_3/Cr_2O_3$ [24]	15/15/2.5/2.5	OCP	-	-	-	8.5
Cu/Zn/Al [45]	40/50/10	W	0.160	108	-	-
$Cu/CeO_2/Al_2O_3$ [46]	(5.79wt% Cu)	CP	-	-	16.0	39.5
$Cu/CeO_2/Al_2O_3$ [46]	(15,3wt% Cu)	CP	-	-	69.7	29.5
$Cu/CeO_2/Al_2O_3$ [46]	(24.1wt% Cu)	CP	-	-	79.0	25.2
$Cu/CeO_2/Al_2O_3$ [46]	(27.8wt% Cu)	CP	-	-	47.2	13.7
$Cu/ZnO/Al_2O_3$[51]	30/60/10	CP	-	-	88.8	45.8
$Cu/ZnO/Al_2O_3$[51]	40/50/10	CP	-	-	67.0	34.6
$Cu/ZnO/Al_2O_3$[51]	50/40/10	CP	-	-	58.7	30.2
$Cu/ZnO/Al_2O_3$[51]	60/30/10	CP	-	-	54.4	28.1
$Cu/ZnO/Al_2O_3$[51]	30/60/10	CP	-	-	36.3	18.7
$Cu/Zn/Al_2O_3$ [80]	15/15/5	OCP	-	71	17.9	8.25
Cu/Zn/Al [87]	30/30/40	CP	0.26	92	18.3	9.4
Cu/Zn/Al [87]	30/20/50	CP	0.32	106	25.1	12.8
Cu/Zn/Ce/Al [87]	30/25/5/40	CP	0.28	96	20.2	10.2
Cu/Zn/Ce/Al [87]	30/20/10/40	CP	0.34	108	38.6	19.6
Cu/Zn/Ce/Al [87]	30/10/20/40	CP	0.29	101	29.3	14.8
$CuO/ZnO/Al_2O_3$ [83]	30/60/10	CP	-	98.4	54.0	65.5
$CuO/ZnO/Al_2O_3$ [83]	40/50/10	CP	-	-	62.5	79.6
$CuO/ZnO/Al_2O_3$ [83]	50/40/10	CP	-	-	59.8	71.1
$CuO/ZnO/Al_2O_3$ [83]	60/30/10	CP	-	-	55.9	69.8
$CuO/ZnO/Al_2O_3$ [83]	30/50/20	CP	-	73.1	47.6	24.5
$CuO/ZnO/Al_2O_3$ [83]	30/40/30	CP	-	62.0	42.1	22.1
ZnCr/Ti [89]	20% $ZnO–ZnCr_2O_4/TiO_2$	WMP	25.9[b]	4	-	-
ZnCr/Al [89]	20% $ZnO–ZnCr_2O_4/Al_2O_3$	WMP	7.8[b]	126	-	-
ZnCr/Ce [89]	20% $ZnO–ZnCr_2O_4$ /CeO_2	WMP	7.1[b]	15	-	-
ZnCr/Zr [89]	20% $ZnO–ZnCr_2O_4/ZrO_2$	WMP	8.2[b]	4	-	-
ZnCr/CeZr41 [89]	20% $ZnO–ZnCr_2O_4/CO_2–$ ZrO_2 (Ce/Zr=4/1)	WMP	10.5[b]	11	-	-
ZnCr [89]	$ZnO–ZnCr_2O_4$	WMP	9.9[b]	6	-	-

[b] = nm; SBET = BET surface area; SCu = Cu Surface area; CP: Co-precipitation; WMP: Wetness impregnation; I: Impregnation; W = Wash coat; OCP = Oxalic co-precipitation; AP: Aurichalcite precursor; HC: Hydrotalcite precursor

5.1 Catalysts

An ideal method to produce hydrogen with lower amount of CO from steam reforming of methanol greatly requires a high performance catalyst, which must be highly active, selective for hydrogen production, and stable for a long period in a continuous operation. Now the most widely used catalysts for this reaction are copper containing catalysts since copper has found to be high activity and selectivity for hydrogen production [23]. In order to reduce the CO content in the feed gas obtained from fuel reforming to a tolerable level (less than 10 ppm), it is necessary to find a more active and more effective catalyst [21]. Hydrogen produced from methanol via a catalytic reaction. Several catalysts were use to produce hydrogen by autothermal reforming reaction method.

Literature studies of Autothermal Reforming Methanol mainly focus on Cu-ZnO based Catalysts [4,24,45,85,74,80,86,87,81], Another interesting catalyst for the ATRM reaction is Pd/ZnO [19, 88].

Cu-based catalysts deactivate quickly and Pt-based catalyst has poor selectivity. Pd-Zn catalysts are extremely expensive, though they have a high activity and selectivity. Hence, they are not suitable for onboard production of hydrogen [84]. The Cu-Zn based catalysts require a high operation temperature of 523-573 K to produce the effective hydrogen yield [1].

Cu-based catalysts have comparatively low tolerance toward heat because maximum allowable operating temperature (<300 °C) [85]. The rapid deactivation of Cu-ZnO based catalysts by sintering of the metal at temperatures above 300 °C, is a barrier to its practical application in the OMR process [88]. In order to prevent the sintering of the Cu crystallites and improve the activities of the copper catalysts, they are usually modified with Al_2O_3 [24], ZrO_2 [74,86,83], Cr_2O_3 [24], CeO_2 [24,48,50] and TiO_2 [89].

5.2 Support catalysts

In order to operate a hydrogen fuel cell, the hydrogen could be obtained from the process with a high cost of energy expenditure. Number of issues pertaining to the catalyst such as other components (promoters), supports, precursors, and preparation methods have been studied [14]. In order to improve their catalytic activity, several approaches are reported in the literature.

The support materials used in catalyst preparation play a crucial role in determining the physical characteristics and performance of the catalysts as contained in Table 3. Alumina is one of the best known catalyst-support materials frequently used in both research and industrial applications [24]. Cu catalysts deactivated during on-stream experiments. Addition of Al improved the catalyst stability but the methanol conversion rate reduced considerably. To avoid this inconvenience, we have employed CuZnAl ternary oxides obtained from thermal decomposition of CuZnAl hydroxycarbonates containing hydrotalcite as a major phase, since it is known that the nature of precursor and the method of preparation play an important role in the catalytic performance of CuZn based methanol synthesis catalysts [20,25]. CuZnAl mixed oxides derived from hydrotalcite precursors have already been demonstrated to be efficient catalysts for the synthesis of methanol at low pressure [22].

A number of researchers have reported positive effects from incorporating ZrO_2 in copper catalysts as a promoter or support. Zirconium has recently emerged as a particularly interesting support material. ZrO_2 presents special characteristics such as high fracture toughness, ionic conductivity, and stability even under reducing conditions. Moreover, the possession of both amphoteric and redox functions makes it appealing as a more suitable carrier for a number of catalytic applications [90].

CuO-CeO_2 mixed oxide catalysts have been recently proposed as a promising candidate for the selective removal of CO from reformate streams [3,64,65]. These catalysts are able to operate at a temperature range of 100–200 °C with almost ideal selectivity. Their performance is superior to that of Pt-group-based catalysts, since they are more active and remarkably more selective while operating at a lower reaction temperature [91].

CeO_2 promoted catalysts have been rapidly developed in recent years [23]. CeO_2 has the cubic fluorite structure and foreign cations, such as Si^{4+}, Th^{4+}, Zr^{4+}, Y^{3+}, La^{3+}, Sc^{3+}, Mg^{2+}, Ca^{2+} and Cu^{2+} can be introduced into the CeO_2 lattice and can improve the physical properties of the CeO_2. High oxygen mobility, strong interaction with the supported metal (strong metal–support interaction) and the modifiable ability, render the CeO_2-based materials very interesting for catalysis and as a support [11]. The high oxygen mobility, strong interaction with certain metals and the modifying ability make CeO_2 to be a very interesting promoter for catalysts. Table 3 shows physicochemical properties of Cu and Zn based catalysts of some previous studies.

5.3 Preparation methods of catalyst

The method of preparation plays an important role in the structure and performance of methanol reforming catalysts [92]. The preparation method has a stronger influence on the mechanical stability of catalyst [41].

There are several methods for catalyst preparation such as Co-precipitation [11,46,51,87,83], Wetness impregnation [89], Impregnation [4,11], Wash coat [45], Oxalic co-precipitation [24,80], Aurichalcite precursor [11], Hydrotalcite precursor [11], Polyol Method [80].

Wu & Chung [80], reported The sequence of methanol conversion for catalytic preparation method was oxalic co precipitation > polyol method > co precipitation, according to analysis of XRD spectrum, the Cu sizes calculated for oxalic co precipitation, polyol method, co precipitation were 17.5, 36.5 and 65.7 nm, respectively. It is mean that the smaller Cu size resulted made the higher dispersion of Cu on the catalyst so that the methanol conversion was higher [80].

5.4 pH of preparation catalyst

pH has influent into methanol steam reforming, the particle size of catalyst increased with increasing pH value [24]. Kuo & Wu [24], reported effect of pH for life time at reaction temperature of 200 °C on methanol reformation. The sequence of methanol conversion for the life time of $Cu/ZnO/Al_2O_3$ catalyst is pH1> pH5>pH3>pH7>pH9, and concentration of CO was kept between 1000 and 4000 ppm when the reaction temperature was 200 °C. Especially, pH1 has good activity in methanol reforming [24].

5.5 Temperature of preparation catalyst

Precipitation temperature has influence to the size of catalyst particle. Zhang and coworkers [93], reported the stripping-precipitation approach could be explore to control particle agglomeration and size [93].The high dispersion of Cu resulted from the small crystallite size in the precipitate by slow formation at low temperature [94]. Kuo & Wu [24], reported agglomeration of $Cu/ZnO/Al_2O_3$ catalysts apparently decrease from 25 °C to -5 °C when the precipitation temperature of catalyst was gradually decreased. Because the Cu dispersion will be affected by Amount of agglomeration, the dispersion of -5 °C is better [24].

5.6 O_2/CH_3OH molar ratio

Methanol conversion was higher with increasing O_2/CH_3OH molar ratio, However that the hydrogen production rate increases with decreasing O_2/CH_3OH molar ratio [4]. OSR reaction could be from endothermic to exothermic when the oxygen/methanol ratio in the feed increases. Hence it could offer an effective way to regulate the reaction temperature in the reactor and less heat exchange between cold and hot streams is required. This makes the reformer compacter especially important for transportation fuel cell applications [92].

Weidong and coworkers [20], reported when the O_2/CH_3OH ratio increases, the methanol conversion also increases. This increase are apparently relate to oxidative conversion. However, a related fact is that as O_2/CH_3OH ratio was decrease, the carrier (inert N_2 in air) is also reduced [20].

Hyuun and coworkers [85], reported that a reduced copper-based catalyst was testing at different O_2/CH_3OH ratios. They have found that the copper-based catalyst can function significantly below the thermo neutral point of 0.23 O_2/CH_3OH ratios. The change in enthalpy is accounting for by a much reduced exit temperature, which is cause by the highly active catalyst and the endothermic reactions taking place [85].

5.7 H_2O/CH_3OH molar ratio

Methanol conversion and hydrogen production rate increase with increasing H_2O/CH_3OH molar ratio [4]. Wu & Chung [80], reported the methanol conversion was increase with increasing molar ratio of H_2O/CH_3OH up to 1.2, and then decrease. The methanol and water competed simultaneously with the active site of the catalyst. The trend of hydrogen production rate was similar to that of methanol conversion. CO_2 selectivity was increased with increasing molar ratio of H_2O/CH_3OH. It is demonstrated that water-gas shift reaction was enhanced as the molar ratio H_2O/CH_3OH increased [80].

5.8 Weight Hourly Space Velocity (WHSV)

Space velocity is also a crucial factor that can influence the catalyst activity and concentration profiles [95]. The hydrogen production rate is directly proportional to the WHSV of methanol [4]. It was found that lowering the feed rate to the radial flow reactor resulted in lower CO concentration in the reformate stream [82]. The methanol conversion and volumetric percentage of CO decreased when the WHSV increased [80].

Xinrong and coworkers [23] reported the effect of WHSV on the catalytic performance of CeO_2 promoted catalysts. Methanol conversion and the outlet CO concentration decrease with increasing WHSV of methanol, and hydrogen yield have a maximum in the experiment conditions. On the other hand, WHSV of methanol does not affect the selectivity of H2, which remains around 99.9% throughout the experiment.

5.9 Carrier gas

In general, carrier gas was used with inert gas, such as helium and nitrogen, to avoid gas reaction with methanol. However, the cost of carrier gas will increase in industrial application. Hence, if the carrier gas could be replaced with air, the system cost could be reduced, but methanol reformation would become partial oxidation or autothermal reaction [80]. Wu & Chung [80] reported that using air to carry methanol is a good method and increases the reaction reactivity, which could result in a higher

Table 4. Influence of catalyst compositions, temperature of calcinations, temperature of drying, temperature of reaction, S/M, O/M on the performance of different Cu and Zn based catalysts for autotermal reforming reaction of methanol

Catalyst	Composition (wt%)	T_C (°C)	T_D (°C)	T_R (°C)	S/M	O/M	X_{MeOH} (%)	H_2 (%)	CO (ppm)	TOS (h)	S_{CO} (%)	WHSV (h^{-1})
$Cu/ZnO/Al_2O_3$ [4]	-	-	-	300	6.5	0.13	73	-	0	-	0.16	-
$Cu/Zn/Al_2O_3$ [24]	15/15/5	300	100	200	1.2	0.28	80.6	47	1500	35	-	7.27
$Cu/Zn/ZrO_2$ [24]	15/15/5	300	100	200	1.2	0.28	78.8	47.5	1500	35	-	7.27
$Cu/Zn/CeO_2$ [24]	15/15/5	300	100	200	1.2	0.28	56	43	500	35	-	7.27
$Cu/Zn/Cr_2O_3$ [24]	15/15/5	300	100	200	1.2	0.28	67	45	4800	35	-	7.27
Cu/Zn/Al [45]	40/50/10	350	25	270	1.3	-	98	73-75	-	-	0.1-1.2	10
$Cu/ZnO/Al_2O_3$ [80]	15/15/5	300	120	240	1.5	0.15	97.6	57^a	-	-	0.04^a	-
Cu/Zn/Al [87]	30/30/40	400	110	280	1.5	0.15	60	-	9400	-	-	-
Cu/Zn/Al [87]	30/20/50	400	110	280	1.5	0.15	77	-	3400	75	-	-
Cu/Zn/Ce/Al [87]	30/25/5/40	400	110	280	1.5	0.15	69	-	1400	-	-	-
Cu/Zn/Ce/Al [87]	30/20/10/40	400	110	280	1.5	0.15	100	-	995	75	-	-
Cu/Zn/Ce/Al [87]	30/10/20/40	400	110	280	1.5	0.15	90	-	1240	75	-	-
$CuO/ZnO/Al_2O_3$ [83]	30/60/10	350	110	250	1.1	0.1	65.5	-	-	80	0.38	1.4
$CuO/ZnO/Al_2O_3$ [83]	40/50/10	350	110	250	1.1	0.1	79.6	-	-	80	0.37	1.4
$CuO/ZnO/Al_2O_3$ [83]	50/40/10	350	110	250	1.1	0.1	71.1	-	-	80	0.39	1.4
$CuO/ZnO/Al_2O_3$ [83]	60/30/10	350	110	250	1.1	0.1	69.8	-	-	80	0.45	1.4
ZnCr/Ti [89]	20% ZnO–$ZnCr_2O_4/TiO_2$	800	120	240	1.2	0.3	24.8^i / 14.5^s	22.7^i / 24.7^s	-	3	0.9^i / 0.1^s	-
ZnCr/Al [89]	20% ZnO–$ZnCr_2O_4/Al_2O_3$	800	120	240	1.2	0.3	89.2^i / 56.8^s	41.6^i / 35.4^s	-	20	63.4^i / 61.0^s	-
ZnCr/Ce [89]	20% ZnO–$ZnCr_2O_4$ /CeO_2	800	120	240	1.2	0.3	89.1^i / 67.4^s	51.8^i / 48.4^s	-	30	7.8^i / 5.9^s	-
ZnCr/Zr [89]	20% ZnO–$ZnCr_2O_4/ZrO_2$	800	120	240	1.2	0.3	99.2^i / 87.1^s	51.9^i / 49.7^s	-	50	18.2^i / 19.9^s	-
ZnCr/CeZr41 [89]	20% ZnO–$ZnCr_2O_4$/CeO–ZrO_2 (Ce/Zr=4/1)	800	120	240	1.2	0.3	99.9^i / 99.7^s	52.2^i / 52.8^s	-	67	10.7^i / 4.1^s	-
ZnCr [89]	ZnO–$ZnCr_2O_4$	800	120	240	1.2	0.3	99.7^i / 70.7^s	51.8^i / 44.6^s	-	58	18.9^i / 15.0^s	-

T_C = Temperature of Calcinations; T_R = Temperature of reaction; T_D = Temperature of drying; X_{MeOH} = Methanol conversion; TOS =Time on stream; S_{CO} = Carbon dioxide Selectivity; i = Initial; s = Shutdown; a = vol%; H_2 = Yield of hydrogen; CO = Yield of carbon monoxide; S/M = Water per methanol ratio; O/M; Oxygen per methanol ratio; WHSV = Weight hourly space velocity.

volumetric percentage of hydrogen (>50%) and lower volumetric percentage of CO (<500 ppm) [80].

Weidong and oworkers [80], reported during the reaction process, the carrier gas also affects heat transfer, and the heat transfer speed could decrease due to lower flow rate of carrier gas. Heat transfer affects the reaction due to endothermic nature of steam reforming reaction and exothermic nature of partial oxidation [20].

5.10 Temperature of reaction

The long-term activity of catalyst is essential for the automobiles operated by PEM fuel cell to avoid the frequent replacement of reformer catalysts [49] and reaction temperature should be a lower for efficiency of the process.

For all tested catalysts high selectivity to CO_2 could be achieve only at very low catalyst temperatures where methanol conversion and hydrogen production rates were prohibitively low [82].

Udani and coworkers [48], reported the CO selectivity increased with increasing reaction temperature but the CO concentration was always significantly lower than the equilibrium CO concentration [48].

Wu & Chung [80], reported when the temperature is high and methanol retention time is high (The amount of the catalyst is greater), one can readily observe these reactions. Therefore, increasing the amount of the catalyst is not necessary to obtain a good methanol reformation [80].

Xinrong and coworkers [23], reported methanol conversion and hydrogen yield increase with increasing reaction temperature, while methanol is convert almost completely into H_2, CO_2, and CO up to 280 ^oC. In the temperature range of 180–280 ^oC, hydrogen selectivity remains almost unchanged, and the outlet CO concentration is less than 0.4 mol% [23].

Based on some research previously in Table 3, none of the researchers conducted a step precipitation with the same temperature of drying and temperature of calcinations. The effect of drying temperature, calcinations temperature to catalyst activity is interesting to further study.

Table 4 shows that the autothermal reforming methanol influenced by temperature of calcinations and temperature of drying. Therefore, the effect of temperature of calcinations and temperature of drying to catalyst activity is interesting to further study.

6. Conclusions

The results of this resume were to describe autothermal reforming reaction of methanol to hydrogen production using Cu-based catalysts along with the process parameter.

The author gives a conclusion that methanol is very promising as a source of raw material for hydrogen production. Methanol easy to produced from renewable sources, high H/C ratio, more efficient as raw material for hydrogen.

Autothermal methanol reforming reaction method is also quite promising as a composite of partial oxidation methanol and methanol steam reforming. The autothermal reforming method is better than the other methods, Based on the reaction temperature is low, high methanol conversion and high yield of hydrogen. However, weaknesses in the high yield of CO are produce.

Catalyst, promoter catalyst, support catalysts,Preparation catalyst methods, pH on precipitation catalyst, temperature of precipitation catalyst, O_2/CH_3OH molar ratio, WHSV, carrier gas, H_2O/CH_3OH, and temperature of reaction are several factors that influence the success of the hydrogen production process by autothermal reforming methanol method. Cu-based catalyst is better than the other catalysts. Cu has a higher activity and Low in producing CO. The effect of temperature of calcinations and temperature of drying to catalyst activity is interesting to further study.

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