

Hydrogen Production Performances via Steam Reforming over Hydrotalcite Derived Catalyst: A Sustainable Energy Production Review

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Abstract

The review outcome represents the optimum catalytic conditions for the production of hydrogen using hydrotalcite derived catalysts. It covers dry and steam reforming of methane, steam reforming of methanol and ethanol to hydrogen. The review also revealed the specific properties of hydrotalcite derived catalysts for the reactions. Among catalyst investigated, Ni & Fe promoted Al-Mg containing hydrotalcite catalyst perform best (99%) for dry reforming of methane at 250°C. For steam methane reforming, Ni containing ca-aluminates hydrotalcite catalyst act as the best (99%) at 550°C. Cu-supported Zn-Al-containing catalyst performs the best (99.98%) for steam reforming of methanol at 300°C whereas Cu impregnated Mg-Al containing hydrotalcite is the best (99%) for steam reforming of ethanol at 200°C - 600°C. It's (HT) tunable and versatile textural and morphological properties showed excellent catalytic performances for different industrial processes and in sustainable hydrogen production.

Keywords

Hydrogen, Hydrotalcite-Derived Catalyst, Catalytic Performance, Promoters

1. Introduction

The demand for fuel is an ever-increasing phenomenon. Energy production in a cleaner way is a global trend. For long, fossil fuels are responsible to meet the 80% of world energy demand [1]. But, the world is going to face a great problem

with the energy crisis because of the depletion of fossil resources [2] [3]. Besides this, global warming due to greenhouse gas emission via burning fossils becomes the alarming concern of the international community [4]. As a result, the substitution of fossil fuels with sustainable and environmentally friendly energy sources is growing up with great interest. Fuels like H₂ and biodiesel can be the alternative fuel from renewable sources [5] [6]. Low cost and environment benign processes or the preparation techniques of these promising fuels draw much attention to the researchers throughout the world. The process involves the selection of proper feed materials, good catalysts, optimum reaction conditions, etc. Here a suitable catalyst choice for effective fuel processing through thermo-catalytic reforming techniques or reactions from different hydrocarbons or biomass is must [7] [8]. Reaction conditions of these thermo-catalytic methods play a vital role in the final product. Catalyst is the most important controller or key to control the reaction conditions [9]-[13]. HT derived materials or mixed oxides are well established as catalysts because of their unique properties. Different factors are strongly related to the catalytic performance of HT derived materials. The performance of HT derived catalyst mostly depends on its preparation procedure [14] [15] [16] [17] [18], pore size [19], total surface area [20] [21] [22], modification [23] [24] [25] [26], types of metal constituents [18] [27] [28], composition [1] [29] [30] [31], promoters [32] [33] [34] [35], operating temperature [36]. Different metallic oxides prepared by HT precursors have shown super catalytic performance during fuel processing [5] [6] [14] [28] [36] [37] [38] [39] [40]. Sometimes, it is necessary to design or tune the HT derived catalyst for superior performance [41] [42]. This redesign can be done by being adjusted the M_i and M_{ii} metal ions as well as their ratio [41] [43] [44] [45] [46] [47]. Basag *et al.*, [18] reported that the performance of HT derived catalyst obtained at higher temperatures. In the last decades, a number of efforts have been taken where the focuses on highly stable and active catalysts. Catalyst deactivation through: 1) coke deposition, 2) sintering and 3) active site oxidation are the common phenomena that occurred during the thermochemical reaction to produce hydrogen or bio-fuel. These drawbacks are mostly removed by using various types of promoters, catalyst supports, and methods of preparation of catalysts. Ali Awad *et al.*, [48] and Gennequin C. *et al.*, [49] took a successful attempt to increase the lifetime of HT derived catalysts that showed longer deactivation time due to carbon deposition. The development of a bimetallic catalyst was one of the effective solutions to this of type of process [50]. Some scholars studied tri-metallic catalysts that exhibited outstanding performances over mono or bi-metallic catalyst [51] [52] [53].

Hydrotalcite has a significant number of effective usages such as anion exchangers, polymer stabilizers, neutralizers (antacids), catalysts and catalyst supports, anion scavengers, electro-active, filtration, adsorbents, pharmaceuticals and photoactive materials [54]-[60]. HT derived catalysts contain some unique properties over other materials due to its easier tunable properties, versatility,

cost-effective materials, and simplicity. Hydrotalcite is considered a better precursor for developing user-friendly catalysts [61]. The catalysts obtained from HT precursors are widely used in fuel processing. Awad *et al.*, observed 75% of CH₄ conversion using Ni based catalyst [48]. In spite of having superior performance (90% conversion yield) of Co-based catalysts, high cost, toxicity and the catalyst lifetime limit its application. Most of the cases 87% and 85% methane conversion were reported using tri-metallic (10%Zn-10%Cu-50%Ni) catalysts at 1023°K temperature and bimetallic catalyst (40%Co-10%W) at 973°K respectively. Lower carbon deposition for tri-metallic catalysts was reported [62]. Reyna-villanueva *et al.*, [53] obtained 98.59% conversion of an ester using HT derived Mg-Al catalyst at 65°C. The modification of HT derived catalyst is performing day by day to maximize its performance. The transesterification reactions are catalyzed by both heterogeneous and homogeneous catalysts, like alkoxides of various natures [63] [64] [65]. These catalysts can fasten the reaction remarkably. But some limitations like reactants purity, sensitive to fatty acid, toxicity and additional cost associated with purifying the final product decreases its applications [64] [66] [67]. Very recently, researchers are focusing on heterogeneous catalysts because of reusability, easy to recover, low purifying cost and simple process of final product separation, etc. [63] [68]. Li *et al.*, [69] prepared HT derived Mg-Co-Al-La catalysts by co-precipitation method followed by calcination of 600°C for six hours. The application of 2% of this catalyst showed 96% - 97% product yields at 200°C. Zeng *et al.*, [70] found 90.5% ester conversion from 1.5% Mg/Al catalyst containing molar ratio 3 at 65°C for four hours while Liu *et al.*, [19] achieved 93% conversion at 120°C for eight(8) hours using Mg/Al catalyst having molar ratio 2.3 but found no leaching. Sikander U. *et al.*, [71] successfully tailored Mg-Ni-Al catalyst to understand the effect of Ni metal to produce hydrogen through thermal decomposition of CH₄. They reported more than 80% of methane conversion using Mg-Ni-Al catalyst doped 40% Ni because of forming the spinel-like structure of carbon nanofiber formed during the course of a thermal decomposition reaction. Improved performance of HT derived catalysts in fuel processing was reported by various scholars [34] [72] [73].

Hydrotalcite derived materials have been investigated as catalyst widely for different reactions or processes. The phases or structure of the hydrotalcite derived catalyst, reaction or process conditions and its performances for hydrogen production is a vital factor for better applications or industrialization of the processes and further improvement. An updated collective summary for hydrogen production via reforming of methane/methanol/ethanol, their efficiency, catalytic conditions of those processes using hydrotalcite derived catalyst is rarely found [74]. This review highlights/finds the superior performance of the reforming or conversion reaction using hydrotalcite derived catalyst, catalytic conditions and how and why the catalyst performs best for hydrogen production.

2. Hydrotalcite Precursor to Final Fuel Processing Catalyst

HT like materials is the best choice as a catalyst due to several properties like large surface area, memory effect, basicity, etc. [75] [76]. However, different techniques used to increase the catalytic activity and stability of HT before utilizing it in catalytic systems. Generally, the calcination treatment of HT was performed in air at a temperature ranging from 400°C to 800°C and time span between 4 and 6 hours [49] [77].

Impregnation of HT with promoter species was also found to enhance the performance of the HT catalyst very effectively. According to the literature reviewed here HT based catalysts impregnated with metal species like Ni, Ce, Zr, Co, etc. exhibited higher activity, stability, and product yield during different fuel processing reactions [78] [79].

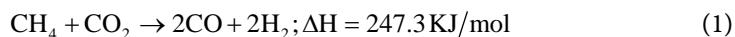
Other than calcination and metal impregnation, reduction pretreatment of HT in hydrogen and/or nitrogen environment at elevated temperatures (between 400°C and 800°C) was also utilized by several researchers to achieve better performance from HT derived fuel processing catalysts [80].

3. Hydrotalcite (HT) Based Catalysts for Hydrogen Production Reactions

Hydrotalcite compound and its derivatives have been reported as active catalysts for various chemical processes like dry reforming of hydrocarbon, steam reforming of hydrocarbon, transesterification reaction, NO_x & CO₂ capture, etc. [81] [82] [83] [84]. Properties like large surface area, porosity, memory effect, small crystal size, thermal stability, and basic properties make HT and their derivatives are promising catalyst precursors for sustainable and eco-friendly fuel production. Results achieved by researchers reveal that catalysts derived from hydrotalcite precursors are potential candidates for application in industrial fuel processing systems [81] [82]. Effective utilization of mixed oxide catalyst synthesized from HT precursor for environmentally friendly fuel (hydrogen, alcohol, and bio-diesel) has been discussed below:

3.1. HT Based Catalysts for CO₂ or Dry Reforming of Methane (DRM)

CO₂ or dry reforming of methane (DRM) is an influential process for hydrogen (H₂) production and an effective way of the utilization of carbon dioxide (CO₂) and methane (CH₄) for environmentally friendly fuel production. DRM process has the potentiality of decreasing greenhouse gases like CH₄ and CO₂. The reaction for dry reforming of CH₄ is given below [85]:



According to Equation (1): strong C-H (439 kJ·mol⁻¹) bonds present in CH₄ leads to an endothermic change in the DRM process that requires high temperature [86]. Researchers have investigated the DRM reaction mechanism, but some issues remained unsolved. For example, there are different views about

rate-determining steps (RDS) [87] [88]. DRM process is mainly affected by temperature, activity, H₂/CO ratio and carbon deposition [89]. Where higher temperatures ensure better productivity but make the DRM method less feasible for industrial applications. The introduction of the catalyst has the potentiality to solve the problem as catalysts make higher activities achievable at lower temperatures. For 50% CO₂ conversion in the DRM process temperature as high as 1035 °C is needed if no catalyst was used [89]. According to recent literature reviews and experiments where catalysts used, especially hydrotalcite based catalysts ensure higher CO₂ and CH₄ conversions at temperatures lower than 800 °C. It is investigated that, methane can be activated and absorbed by the active sites of transition metals present in group 9 and 10 of the periodic table, while Carbon dioxide can be activated and absorbed by oxides [90]. This makes transition metal promoted hydrotalcite derived catalysts promising for the DRM process. **Table 1** presents recent works by different researchers on hydrotalcite derived catalysts for DRM.

Accordingly, Oscar *et al.*, [91] synthesized Pr promoted Ni-Mg-Al based hydrotalcite catalyst by the self-combustion method with microwave-assistance. They found that the promotion of Praseodymium (Pr) in Ni-Mg-Al improved catalyst stability and reduced the carbon deposits on the catalyst surface. However, the incorporation of Pr did not increase the performance of the developed catalyst. Then again, Tanios *et al.*, synthesized Co, Ni, Mg, and Al-based catalyst by hydrotalcite route. The synthesized Co₂Ni₂Mg₂Al₂800 catalyst showed better conversions than commercial Ni (50%)/Al₂O₃ catalyst. The difference in catalytic performance between Co₂Ni₂Mg₂Al₂800 and commercial Ni (50%)/Al₂O₃ catalyst was higher in temperatures 500 °C and 700 °C. The developed catalyst contained less Ni than the commercial catalyst. Moreover, the new catalyst showed good stability at 800 °C. Pellet and powder form of the catalyst showed similar methane conversions. The researchers also found that the presence of toluene decreases CH₄ conversion by an average of 15%. Meanwhile, CO₂ conversion remains almost unaffected by toluene. On the other hand, cerium (Ce) and yttrium (Y) promoted double layered hydroxide (hydrotalcite) catalyst was synthesized by Swirk *et al.* [92] to study the effect of Y on DRM. They promoted hydrotalcite (containing Ni²⁺, Mg²⁺ & Al³⁺ ions) with Ce by co-precipitation method and promoted hydrotalcite with Y by impregnation method. Their study revealed that incorporation of Y and Ce decreased Ni reducibility, improved Ni dispersion, reduced Ni crystal size and increased basicity. Ce Promotion increased both CH₄ and CO₂ conversions at the temperature range of 600 °C - 750 °C and 0.2 wt% loading of yttrium increased conversions during isothermal DRM tests. Elsewhere, the catalytic performance of layered double hydroxide (hydrotalcite) containing a certain amount of Ni and promoted with Iron (Fe) was evaluated by Wierzbicki *et al.*, [93] for the DRM process. The tests revealed that, a small amount of Fe incorporation affected CO₂ adsorption, increased moderate basic sites and at a low temperature of 250 °C increased catalytic activity. However, decreased catalytic performance was observed during higher Fe promotions.

Table 1. Review report of HT based catalyst for CO₂ or Dry Reforming of Methane (DRM).

Catalyst Applied	Method of synthesis	Test Conditions	Observations		CH ₄ Conversion %	Ref.
			Achievement	Limitation		
Pr promoted Ni-Mg-Al	Microwave-assisted self-combustion method	600 °C & atmospheric pressure	6 wt% of Pr decreased the formation of carbon deposits and improved the catalytic stability	Pr only increased the thermal stability but did not improve catalytic conversion	58	[91]
Co ₂ Ni ₂ Mg ₂ Al ₂	Co-precipitation, Grinding and finally calcination at 800 °C for 4 h	400 °C to 800 °C	More active and more stable (less deactivated by carbon) than commercial Ni(50%)/Al ₂ O ₃ catalyst	Presence of toluene decreased the methane conversion	97	[49]
Ce- and Y-promoted Htlc of Ni ₂₊ , Mg ₂₊ , Al ₃₊ and/or Ce ₃₊	Co-precipitation followed by Y impregnation and then calcination at 550 °C for 5 h	Range of 850 °C - 600 °C and isothermal test at 700 °C	Promotion of Ce increased both CO ₂ and CH ₄ conversions at the temperature range of 600 °C - 750 °C and 0.2 wt% loading of yttrium increased both CO ₂ and CH ₄ conversions during isothermal DRM tests	Catalyst promoted with Ce and 0.6 wt% of Y showed decreased catalytic performance and highest basicity.	96.2	[92]
Ni & Fe promoted Htlc of Al & Mg	Co-precipitation followed by calcination at 500 °C for 5 h	250 °C	Low amount of Fe activated the catalysts at low temperature (250 °C)	incorporation of higher amounts of Fe decreased catalytic activity	99	[93]
Co supported Mg-Al	Co-precipitation and then calcination for 4 h at 600 °C	700 °C & ambient pressure	Fantastic initial activity, significant long term stability, improvement in coke and sintering resistance	CH ₄ conversion is below 60%	58.6	[95]
Co/Mg(Al)O	Co-precipitation, then calcination and reduction for 5 h at 800 °C	500 °C - 750 °C	Co/Mg(Al)O-Htlc catalyst was found promising for CH ₄ reforming at low-temperature	At higher temperature (~750 °C) Co catalyst was inferior to Ni catalyst	86.7	[96]
CeO ₂ , ZrO ₂ &ZnO promoted NiO/Mg(Al)O	Co-precipitation and then calcination at 600 °C in air for 6 h	750 °C	The work presented kinetic and mechanistic insights into the functions of Ni-Htlc catalysts in DRM	The developed oxide promoted catalysts exhibited slightly lower activity than Ni catalyst	75 - 80	[97]
Y promoted Ni containing Mg/Al	Co-precipitation and then calcination at 550 °C in air for 5 h	600 °C - 850 °C	Y (yttrium) promotion raised the fraction of medium basic sites, reduced Ni crystallite size, and increased specific surface area	The total basicity of catalyst decreased due to Y (yttrium) promotion	88	[98]
CoAl and CoFeHtlc	Co-precipitation followed by calcination at 800 °C in an oven for 6 h	Between 400 °C - 700 °C & atmospheric pressure	CoAl-Htlc catalyst showed better stability and higher catalytic activity during the DRM reaction compared to Co Fe-Htlc catalyst	Fe based catalyst exhibited lower reactivity due to the active phase re-oxidation by the water formed during reverse WGS reaction	66.4 & 54.5	[99]
Zr- and Y-promoted Ni/Mg/Al-Htlc	Co-precipitation and then calcination at 550 °C in air for 5 h	600 °C - 850 °C with a temperature step of 50 °C	Strong interaction between nickel and the promoted Htlc support with low H ₂ consumption was reported	Reducibility decreased	72.7	[100]
Ni-Mg-Al	Co-precipitation & incipient wetness impregnation	750 °C	Good stability against sintering and coking with improved activity was observed during DRM process having industrially relevant reaction conditions	During DRM carbon deposition in the catalyst increased at lower temperatures	53.6	[101]

Continued

Ni ₂ Mg _{6-x} Al _{1.8} La _{0.2}	Co-precipitation and calcined under an airflow at 800°C	600°C - 800°C	Catalyst exhibited increased CH ₄ and CO ₂ conversion then La free catalyst	carbon deposition on the catalyst surface was Significant	75 - 80	[102]
La promoted Ni-Mg-Al	Co-precipitation followed by calcination at 600°C for 6 hours in flowing air	600°C & 750°C	La-promotion enhanced the reducibility of NiO and was beneficial for preparing hydrotalcite based Ni catalysts for DRM	deactivation of the catalyst is severe at low temperatures	82	[103]
Ce promotion Ni/Al and Ni/Mg/Al	Co-precipitation, calcination in the stream of air for 4 h at 550°C and then adsorption of Ce	550°C, 650°C & 750°C	Ce-promotion in Ni/Mg/Al and Ni/Al increased CH ₄ concentrations and affected both activity, selectivity and stability of the developed catalyst	Excess presence of CH ₄ and CO ₂ in the feed decreases both CH ₄ and CO ₂ conversions	87	[104]
Zr promoted Mg(Ni, Al)O	Co-precipitation followed by calcination at 550°C for 4 h	550°C, 650°C & 750°C	The amount of incorporated Zr and its placement in the catalyst system affected activity, basicity, and textural properties of the catalyst	Zr introduction to the catalyst system decreased activity.	83	[105]
Ni containing Mg-Al	Co-precipitation and then calcination for 5 h at 500°C	300°C	Higher Ni incorporation affected both the CO ₂ adsorption capacity and the reducibility of the catalysts	CH ₄ selectivity of the catalyst decreases at higher temperatures (400°C - 450°C)	98.3	[106]
NiMgAl	Co-precipitation followed by calcination in the static air at 500°C for 10 h	800°C	Catalysts with a higher Mg/Al ratio exhibited better resistance to coke formation and catalytic activity. Ni-Mg-Al catalyst with Mg/Al ratio of 1 exhibited the best catalytic performance and stability	Low activity and stability was reported for Al-rich catalysts	83	[107]
Ni-Mg-Al	Co-precipitation followed by calcination for 6 hrs at different temperatures of 300°C, 400°C, 500°C, 600°C, 700°C, and 800°C	Temperatures between 400°C and 700°C & atmospheric pressure	High catalytic performance due to the lower size of nickel and better stability of the Htlc (NiAl ₂ O ₄) support	Reduction temperature increases with increasing calcination temperatures	90	[108]
CeZr, Zr, and Ce promoted Ni-Mg-Al	Co-precipitation and then calcination for 4 h at 550°C	550°C	Zr affected both the selectivity and catalytic activity of the catalyst	Conversion of both CO ₂ and CH ₄ was comparatively low	40	[78]
CeO ₂ -modified Ni-Mg-Al	Co-precipitation and then calcination for 4 h at 650°C	0.1 MPa & 750°C	CeO ₂ -modified catalysts presented high activity during pressurized DRM	CeO ₂ addition by both co-precipitation and impregnation method led to a decrease in the pore diameter, total pore volume, and surface area.	58	[109]
Ni-Mg-Al	Co-precipitation followed by calcination at 800°C for 5 h.	400°C to 800°C	Catalysts exhibited increased activity for both the CH ₄ and CO ₂ reforming. Moreover, increasing Ni loadings promoted activity	At low temperature (600°C) catalytic stability decreased with higher Ni loadings	86	[110]

The catalytic activity of cobalt (Co) supported hydrotalcite (Mg, Al) catalyst on DRM was studied by Guo *et al.*, [94]. They synthesized Co/MgAl catalyst having a hydrotalcite-like structure of MgAl. The developed catalyst has a significant amount of medium basic sites, impressive initial activity, comparatively higher stability and better resistance to sintering and coking formation. Co supported hydrotalcite catalyst Co/Mg₃Al was also studied by Li *et al.*, [95] to investigate its performance on low-temperature DRM. They also compared the performance of Co/Mg₃Al with nickel-based catalyst Ni/Mg₃Al. According to their comparative study revealed Co/Mg₃Al demonstrated better catalytic activity than Ni/Mg₃Al at low temperature. Co catalysts showed high coking resistance and stable catalytic activity at both low and high temperatures. Hydrotalcite based nickel (Ni) catalyst containing little amount of CeO₂, ZrO₂ and ZnO oxides as promoters have been studied by Niu *et al.*, [96]. According to their study CeO₂-Ni-Hydrotalcite has better stability, highest H₂/CO₂ ratio and CO₂ activation among the developed catalysts. They also observed that oxide promotion slightly decreased the performance of the Ni-catalyst. Then again, Świrk *et al.*, [97] promoted Ni-based hydrotalcite catalyst with yttrium (Y). The addition of 1.5 wt% of Y increased the catalytic performance of the Ni-(Mg/Al) hydrotalcite catalyst. They also reported increased specific surface area, a higher fraction of medium basic sites and reduced Ni crystallite size. Aider *et al.*, [98] developed Co-Al-hydrotalcite and Co-Fe-hydrotalcite catalysts to enhance the catalyst stability and resistance to carbon deposition during the DRM process. Their study revealed that, Co-Al-hydrotalcite has higher catalytic activity due to higher specific surface area, the smaller size of Co and presence of homogeneous Co particles, but due to the active phase re-oxidation of by water, Co-Fe-hydrotalcite has an inferior catalytic performance. Świrk *et al.*, [99] studied DRM over Zr (zirconium) and (Y) yttrium promoted hydrotalcite (Ni/Mg/Al) catalyst. The Zr and Y impregnated Ni/Mg/Al-HT improved catalytic activity and the modified catalyst was stable in DRM at 700 °C. Kalai *et al.*, [100] developed Ni(Mg)-Al Htlc catalyst by conventional incipient wetness impregnation method for Ni promotion and co-precipitation method for hydrotalcite development. Their synthesized 20Ni-Mg-Al catalyst exhibited high CH₄ conversion and a low deactivation rate during DRM. The stability of the developed catalyst was also remarkable.

Dahdah *et al.*, [101] experimented on the effect of lanthanum (La) doping on hydrotalcite (Ni_xMg_{6-x}Al₂) catalyst for CO₂ reforming of methane. Ni₂Mg₄Al_{1.8}La_{0.2} catalyst synthesized by Dahdah and co-workers [101] exhibited better catalytic performance by means of CH₄ and CO₂ conversions, increment of basic sites and catalyst stability. They also mentioned that La helped to remove deactivating carbon by forming La₂O₂CO₃. Kalai *et al.*, [102] also evaluated La promotion on hydrotalcite derived Ni catalyst for DRM. They concluded that La promotion is beneficial to develop hydrotalcite derived Ni catalyst for DRM. They also mentioned about the formation of lanthanum carbonate hydroxide phase due to La addition. Debek *et al.*, [103], examined the performance of hydrotalcite (Ni/Mg/Al

and Ni/Al) derived catalyst promoted with cerium (Ce) on DRM. They promoted hydrotalcite precursor Ni/Mg/Al and Ni/Al with Ce by adsorption of Ce species from $[\text{Ce}(\text{EDTA})]^-$ solution. The Ce promoted catalyst found to increase CH_4 conversion in DRM, but an increased amount of CH_4 and CO_2 in the feed adversely affected both CH_4 and CO_2 conversions. In another study Debek *et al.*, [104] evaluated zirconia promoted Mg(Ni,Al)O Htlcs catalyst in CO_2 reforming of CH_4 . Here, Zr species was introduced at the co-precipitation stage. Their investigative study revealed that the introduction of Zr strongly enhanced selectivity and stability of the catalyst, but reduced activity. Ni containing hydrotalcite (Mg-Al) catalyst was studied by Wierzbicki *et al.*, [105]. According to the researchers, the presence of Ni increased the reducibility and CO_2 adsorption capacity of the catalyst.

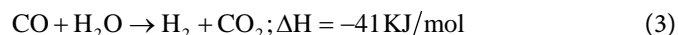
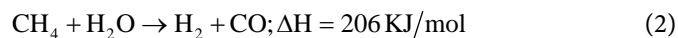
Zhu *et al.*, [106] examined the effect of Mg/Al ratio in Ni-Mg-Al hydrotalcite catalyst during DRM. They found that a higher ratio of Mg and Al in the catalyst leads to higher activity and stability. Where 1 is found to be the best ratio between Mg and Al. Then again, the effect of Ni/Al ratio in the hydrotalcite catalyst for DRM was studied by F. Touahra and co-workers [107]. According to their study, catalytic activity of the Ni-Mg/Al hydrotalcite catalyst was proportional to the molar ratio of $\text{Ni}^{2+}/\text{Al}^{3+}$ in the catalyst and higher calcination temperature during catalyst synthesis was found to enhance activity. Ce-Zr, Zr, and Ce promoted Ni-Mg-Al (hydrotalcite) catalysts were synthesized by Debek *et al.*, to evaluate its performance over low-temperature dry methane reforming. They reported reduced conversion of both CH_4 and CO_2 but the incorporation of Zr in the developed catalyst helped to determine both selectivity and activity of the catalyst. Likewise, CeO_2 to promote hydrotalcite (Ni-Mg/Al) catalyst for pressurized CO_2 reforming of CH_4 was studied by Ren and co-workers [108]. Both the impregnation and co-precipitation method was utilized by the researchers to add CeO_2 in the Ni-Mg-Al precursor. CeO_2 incorporation increased activity but decreased stability and surface area of the catalyst. Finally, the influence of Ni loading on Ni-Mg/Al hydrotalcite catalysts for CO_2 reforming of CH_4 was studied by Lin *et al.*, [109]. According to their work hydrotalcite derived Ni/Mg-Al catalysts were mentioned to be highly active for CO_2 reforming of CH_4 . They also observed that at higher temperatures sintering of Ni particles increases and coke deposition decreases with higher Ni loadings in the catalyst.

Mg(Al)O hydrotalcite type catalysts are promising for CO_2 reforming of CH_4 (DRM). Especially, Ni-based hydrotalcite (Ni-Mg-Al) material promoted with metals like Zr, Y, Ce, Co, and Pr showed potential development in catalytic properties during DRM such as improved activity, stability, coke resistance, and sintering resistance.

3.2. HT Based Catalysts for Steam Reforming of Methane (SRM)

Steam reforming of methane (SRM) or wet reforming of CH_4 is a well-established and industrially applied process for H_2 production. Generally, methane is used

for hydrogen production in steam reforming technology but other light hydrocarbons can also be used. In this process, hydrogen (H₂) and carbon monoxide (CO) is produced by reacting methane (CH₄) and steam (H₂O). CO generation in the reaction is subjected to the WGS (water gas shift) reaction to increasing hydrogen productivity. Equation (2) and (3) illustrates the reactions for the process.



The temperature of the reactions is usually above 700°C and the catalyst is used to enhance H₂ yield. Nickel (Ni) based catalyst is generally used in SRM for their cost-effectiveness and availability. However, Ni as a compound is less activated than other metals and during SRM Ni catalysts become deactivated due to sintering of active phase and coke formation in the surface [110]. Catalytic supports are very effective in reducing coke deposition and sintering [111]. Hydrotalcite catalyst has a large surface area, uniform active metal distribution on the surface and basicity which makes hydrotalcite based catalyst very promising for SRM [112]. This is why hydrotalcite based catalysts are potential for SRM. Hydrotalcite catalysts promoted with metals like Ni, Ce, Zr, Rh, etc. are studied for SRM by researchers and promising results were found. The recent development of hydrotalcite based catalyst for SRM is presented in **Table 2**.

Fasolini *et al.*, synthesized Rh-Mg-Al hydrotalcite catalyst for SRM and they found that a lower Mg/Al ratio and higher rhodium (Rh) amount (from 1% to 2%) in the catalyst increased catalytic activity. Moreover, they developed a thermal treatment method for the catalyst that enhanced catalytic activity by increasing reduced Rh at the surface. They also mentioned that pellet size and amount of catalyst at constant contact time have no influence on catalytic activity. On the other hand, cerium (Ce) promoted catalyst containing nickel, cobalt, and hydrotalcite was developed by Ghungrud *et al.*, for sorption enhanced H₂O reforming of CH₄. Ni and Co containing hydrotalcite were synthesized by the co-precipitation method for HT precursor and then the incipient wetness impregnation technique was applied for Ce promotion. Ce incorporation found to raise thermal stability and basicity. The developed catalyst enhanced H₂ production and inhibited coke formation with good stability. Thus, the researchers concluded that Ce promoted Ni-Co-hydrotalcite is a potential catalyst for high purity H₂ production.

Table 2. Review report of HT derived catalyst for Steam/wet Reforming of Methane (SRM).

Catalyst Applied	Synthesis Method	Test Conditions	Observations		H ₂ %	Ref.
			Achievement	Limitation		
Rh-Mg-Al	Co-precipitation, calcination and then reduction	750°C	lower Mg/Al ratio provides higher activity and doubling Rh amount increases methane conversion	With increasing Rh % in the catalyst, the catalytic stability decreased	77	[80]

Continued

Ce Tailored Co-Ni/Htlc	Co-precipitation, calcination and finally incipient wetness impregnation for Ce promotion	500 °C & 0.1 MPa	Excellent H ₂ productivity, better CO ₂ adsorption capacity, good stability and inhibited coke formation	The activity of the catalyst degrades after a certain regeneration cycle due to metal sintering	90	[79]
Hydrotalcite (Htlc)-based Ni with Ag	Co-precipitation followed by reduction and calcination at 600 °C for 6 h	670 °C & atmospheric pressure	Ni/Ag hydrotalcite catalyst has good surface alloying	Sites surrounding Ag atom found to be inactive to C-H bonds of CH ₄ and Ag blocked the more active sites in Ni nanoparticles	-	[76]
Ce- and Zr-doped Ni/hydrotalcite	Co-precipitation, calcination and then incipient wetness impregnation for Zr & Ce promotions	673 - 873 K & 0.1 MPa pressure	Ce and Zr promoted Ni/hydrotalcite catalyst produced high purity H ₂ with good stability	Zr promoted catalyst has lower stability than Ce promoted one	97.1	[93]
Ni/Mg-Al	Co-precipitation and then calcination at 850 °C for 5 h	650 °C & 0.1 MPa Pressure	Ni/Mg-Al catalyst exhibited better catalytic performance than the conventional Ni/a-Al ₂ O ₃ and Ni/g-Al ₂ O ₃ catalyst	CO ₂ selectivity decreased with rising temperature	-	[94]
Ni-Htlc catalyst and Ni-CaO/Al ₂ O ₃ Sorbent	Co-precipitation & calcination for catalyst and incipient wetness impregnation for sorbent	523 K & 0.1 MPa pressure	Catalysts were viable for high purity H ₂ production and have high stability	Ni-Htlc catalyst showed short breakthrough time and lower adsorption capacity	98.5	[95]
Ni/MgAl + CrFe ₃ O ₄	Dry impregnation followed by drying and calcination at 500 °C for 5 h	500 °C - 700 °C & 1 bar pressure	Ni/MgAl + Cr/Fe ₃ O ₄ mixed catalyst exhibited improved H ₂ selectivity and CH ₄ conversion	Catalysts showed a rapid decrease in H ₂ selectivity and CH ₄ conversion with the decrease of temperature	-	[96]
Ni and/or Rusupported hydrotalcite material	Incipient wetness impregnation, then drying and calcination for 5 h at 400 °C	700 °C & 1 bar pressure	The catalysts showed higher methane conversions that are almost similar to the values predicted by thermodynamic equilibrium and better resistance to carbon deposition	At high space velocities, the product gas seems to have more obstacles in reaching thermodynamic equilibrium	-	[97]
Ru/Ni-Mg/Al	Wet impregnation of co-precipitated Ni-Mg/Al Htlc for Ru incorporation	450 °C - 800 °C	Catalysts with Ru (ruthenium) were active with no need reduction pretreatment before the test and the catalyst showed better catalytic performance	The surface area of the support decreased with Rh impregnation	-	[98]
Ni-Htlc + Calcium Aluminate	Co-precipitation & calcination for Ni-Htlc and pelletization of Ca-based sorbent	550 °C	The catalyst mixture produced high purity H ₂	Only the effect of sorbent addition was studied	99	[99]
Ni/CaO-Hydrotalcite	Incipient wetness impregnation, then drying and calcination at 900 °C for 4 h	400 °C - 600 °C	High H ₂ concentration of 80% was achieved at low temperature (600 °C)	The developed catalyst showed less activity than Ni/Al ₂ O ₃ catalyst	80	[100]
Pt/Htlc (Ni-Mg-Al)	Wet impregnation of calcined Mg/Al-Htlc for Ni and Pt doping	700 °C	Pt-Ni alloying on the surface of the catalyst caused self-regeneration and self-activation via reversible redox between Ni ⁰ and Ni ²⁺ by H ₂ spillover from Pt	CH ₄ conversion over the developed catalyst was not compared precisely	-	[101]

Wang *et al.*, studied the role of bimetallic alloys in SRM reaction. They synthesized hydrotalcite catalyst containing Ni and Ag to study the effect of Ni/Ag alloying on SRM. According to their research, a silver (Ag) atom can influence seven nearby sites and those sites are found to be inactive to C-H bonds of CH₄ and Ag blocked the more active sites in the edges and steps of Ni nano-particles. Though, Ni/Ag hydrotalcite catalyst has better surface alloying than other bimetallic catalysts. Elsewhere cerium (Ce) and zirconium (Zr) was used to promote Ni/hydrotalcite catalyst to evaluate its performance in SRM by Dewoolkar *et al.*, [113]. High basicity and large surface area of the doped catalyst restricted unwanted reactions and coke formation. The developed catalysts, especially Ce doped hydrotalcite catalyst exhibited improved H₂ production and stability. According to their findings, the researchers concluded that Ce and Zr are the potential promoters for Ni/hydrotalcite catalysts to produce pure H₂.

Hydrotalcite type Ni/Mg-Al catalyst for wet reforming of methane was investigated by Qi *et al.*, [114]. Their study revealed that Ni/Mg-Al catalyst has good stability and higher activity than Ni/ γ -Al₂O₃ and Ni/ α -Al₂O₃ catalysts. Where, Ni/Mg-Al catalyst containing Ni/Al/Mg molar ratio of 0.5:1.0:2.5 showed the best activity. They also observed that raising temperature favors CH₄ conversion, but CO₂ selectivity enhanced at low temperatures. Ni-based hydrotalcite catalyst (Ni-HT) was also studied by Dewoolkar *et al.*, [115]. Their hybrid catalytic material comprised of Ni-HT (Ni-hydrotalcite) catalyst and Ni-CaO/Al₂O₃ sorbent. Their developed catalytic mix was able to produce high purity H₂ with good stability. Thus, a conclusion was brought that, the multifunctional hybrid material (Ni-Htlc and Ni-CaO/Al₂O₃) is a viable catalyst for pure hydrogen production from sorption enhanced steam/wet reforming of methane. Kim and co-researchers [116] also studied Ni-hydrotalcite based mixed catalyst containing Ni/MgAl and Cr/Fe₃O₄. By using the catalyst in SRM process high H₂ and CO selectivity coupled with better CH₄ conversion were reported. It was also reported that Cr/Fe₃O₄ as a catalyst enhanced WGS reaction. On the other hand, Hydrotalcite catalyst promoted with nickel (Ni) and ruthenium (Ru) was studied by Velasco and co-workers [117]. According to the study, hydrotalcite derived Ni/Rh bimetallic catalyst was more resistant to carbon deposition than only Ni containing catalysts. They also reported higher CH₄ conversion that was close to values assumed by thermodynamic equilibrium. Ru supported Ni-Mg-Al (hydrotalcite) catalyst for the SRM process was also studied by Nawfal *et al.*, [118]. Ru impregnation was found to increase the reactivity of oxides and CH₄ conversion during SRM. Rh doped Ni-Mg/Al catalyst was reported to exhibit better stability and catalytic activity.

Nickel hydrotalcite coupled with calcium aluminate catalytic system for high purity H₂ production from sorption enhanced SRM was examined by Broda *et al.*, [119]. Ni-hydrotalcite catalyst and calcium aluminate sorbent were able to produce highly pure hydrogen (99 vol %). The calcium aluminate sorbent demonstrated high cyclic CaO conversion and good stability which enhanced H₂ productivity. For high H₂ productivity from sorption enhanced SRM Chanchura-

nasiri *et al.*, [120] also developed hydrotalcite based catalyst containing Ni and CaO. At steam, to methane ratio 3, temperature 600°C and atmospheric pressure the catalytic system offered a high H₂ concentration of 80%. It was also mentioned that CO₂ absorption can improve reaction conditions only if the catalyst is active enough. Finally, commercial hydrotalcite (Mg-Al) promoted with nickel (Ni) and platinum (Pt) as an intelligent catalyst was evaluated by Zhan *et al.*, [121] for SRM. The developed catalyst exhibited self-activation and self-regeneration properties. Well crystallized alloying between Pt-Ni and Mg(Al)O on the catalyst surface enhanced self-activation and self-regeneration. According to the above-mentioned discussion, Ni containing hydrotalcite (Ni-HT) is a promising catalyst for H₂ via steam reforming of methane. It was tried to further enhance the catalytic activity by doping Ni-Htlc with promoters like Rh, Ce, Zr, Ag, Pt, Ru, etc. Among the promoted catalysts: Ce doped Ni-hydrotalcite (Ce/Ni-HT) catalyst excellent better results and the researcher referred that the catalyst has the potentiality to be used in the SRM process for a large scale H₂ production. In conformity with **Table 2** hydrogen productivity from SRM when HT derived catalysts were used is presented below in **Figure 1**.

3.3. HT Derived Catalysts for Methanol Steam Reforming

Methanol is a promising fuel and it is considered as an attractive hydrogen storage medium as the gravimetric hydrogen density of CH₃OH is much higher than that of compressed or liquid hydrogen [122]. The use of methanol for hydrogen storage is advantageous as the necessity of cryogenic or pressurized containers can be avoided. The liberation of hydrogen for methanol can be done by several catalytic reactions such as methanol decomposition, WGS (water gas shift) reaction, methanol steam reforming and partial oxidation of CH₃OH. Among these reactions, methanol steam reforming reaction is more convenient for H₂ production due to low operational temperature (300°C - 400°C), no direct CO production and highest H₂ concentration in the product stream [123]. The reaction for CH₃OH steam reforming is presented in Equation (4) below.

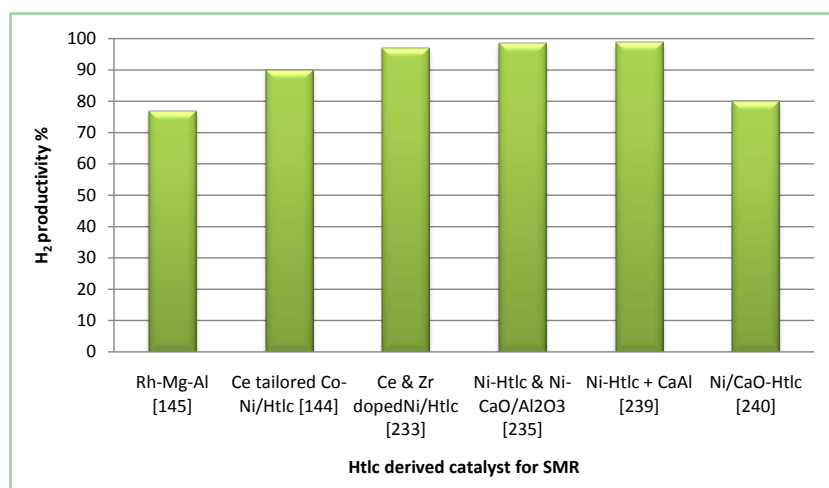


Figure 1. Performance of different HT based catalysts during SMR.



However, obstacles like high endothermicity and rapid speed variation of methanol steam reforming reaction affect H_2 production. To overcome these problems partial oxidation methods and effective catalysts are used [124]. Broadly applied catalysts for CH_3OH steam reforming are zinc oxide, copper, and alumina containing materials which are usually synthesized via co-precipitation method from malachite-boehmite precursor [125]. Hydrotalcite derived materials having copper (Cu), zinc (Zn) and aluminum (Al) are found to have potential applications as a catalyst for methanol steam reforming [126]. In recent years, researchers experimented with hydrotalcite (Htlc) based catalysts containing different Zn, Cu, and Al ratios and metal promoted Zn, Cu, Al-Htlc catalysts for enhancing productivity during methanol steam reforming. **Table 3** presents the catalytic activity and overall performance study of hydrotalcite derived catalysts for CH_3OH steam reforming.

According to **Table 3** Yang *et al.*, [127] studied the influence of rare earth metals (Ce, La, Sm, Y, and Gb) on the performance of Cu/Zn-Al-Htlc catalyst for CH_3OH steam reforming. They utilized the in-situ method on $\gamma\text{-Al}_2\text{O}_3$ for hydrotalcite precursor (Cu/ZnAl-Htlc) synthesis and then modified the precursor with rare earth metals (Ce, La, Sm, Y, and Gb) by wet impregnation technique. The researchers found that the performance of Cu/Zn-Al-Htlc catalyst is dependent on the reducibility and surface area of Cu. Moreover, the addition of Ce, Sm and Gb further enhanced the catalytic activity of Cu/Zn-Al-Htlc catalyst. Among their developed catalysts, Ce-Cu/ZnAl-Htlc exhibited better results with high activity, 100% methanol conversion and very low CO concentration (0.39%) in the product. He *et al.*, [128] also used the in-situ and wet impregnation method to synthesized Cu supported ZnAl-Htlc catalyst for CH_3OH steam reforming. The developed copper supported Zn-Al-Htlc catalyst was able to convert 99.98% CH_4 at 300°C with the H_2 production rate of $981 \text{ cm}^3\text{kg}^{-1}\text{s}^{-1}$. Then again, Kim *et al.*, [129] utilized the co-precipitation process to develop Cu-Al based catalysts from hydrotalcite for utilization in methanol steam reforming. The developed hydrotalcite derived catalyst containing Cu, Ni, Zn, and Al was able to convert 76% CH_3OH . They mentioned that Ni incorporation slightly increased the catalytic performance of the developed catalyst.

The mixed catalyst containing $\text{CuO/ZnO/Al}_2\text{O}_3$ and K-HT (potassium promoted hydrotalcite) was evaluated by Xiang Wu and Sufang Wu [130] for the production of highly pure H_2 from sorption-enhanced methanol steam reforming. It was able to obtain 98.36% H_2 in the product stream. Also found that the introduction of K-HT reduced the Me-OH (methanol) conversion temperature to nearly 50°C and increased the hydrogen concentration over 20% in the product stream. Copper supported zinc-aluminum hydrotalcite (Cu/Zn-Al-Htlc) catalyst for CH_3OH steam reforming was evaluated by Hammoud and co-workers [131]. Co-precipitation (for HT precursor) and wet impregnation (for Cu support) technique was applied for the catalyst development. Among the developed

Table 3. Review report of HT derived catalysts for CH₃OH Steam Reforming.

Catalysts Applied	Synthesis Process	Test Parameter	Observations		CH ₃ OH conversion %	Ref.
			Achievements	Limitations		
Ce, La, Sm, Y, and Gb promoted Cu/Zn-Al-Htlc	In-situ synthesis for catalyst precursor and wet impregnation for doping	250 °C	Ce/Cu/ZnAl hydrotalcite catalyst exhibited high activity, methanol conversion of 100% and low CO concentration	La/Cu/ZnAl and Y/Cu/ZnAl catalysts have inferior performances because of smaller surface area of copper and higher reduction temperatures	100	[127]
Cu supported ZnAl-Htlc/ γ -Al ₂ O ₃	In-situ synthesis for catalyst precursor and wet impregnation for Cu support	300 °C	Cu incorporation enhanced reducibility and catalytic activity	Higher Cu incorporation (>10%) decreased methanol conversion	99.98	[128]
Cu, Ni, Zn, and Al based hydrotalcite	Co-precipitation followed by calcination at 400 °C for 1h	220 °C - 260 °C	The developed Cu _{0.75} Al _{0.25} catalyst showed better activity, active metal dispersion and methanol conversion than the benchmark catalyst	At higher operational temperatures CO concentration increased considerably	76	[129]
CuO/ZnO/Al ₂ O ₃ and K-Htlc	Calcination of parched Htlc at 400 °C for 4 h then dry impregnation for K loading	230 °C	Catalyst with K-Htlc absorbent was able to convert CH ₃ OH at lower temperatures and the product gas contained 99.16 % H ₂ and only 0.39% CO	High regeneration temperature of the absorbent caused sintering of the catalyst	-	[130]
Cu/Zn-Al Hydrotalcite	Co-precipitation for Zn-Al Htlc and wet impregnation for Cu incorporation	200 °C - 350 °C	Catalyst with 10% Cu performed 99.78% methanol conversion	Compromise between reducibility dispersion of Cu species has to be made for good catalytic performance and low CO generation	99.78	[131]
Cu/Zn-Al-Htlc	Co-precipitation inside microemulsion droplets and then calcination in the air for 3 h at 330 °C	260 °C	Catalyst developed by micro-emulsion technique exhibited improved catalytic performances during CH ₃ OH steam reforming	Micro-emulsion produced catalyst with poor intrinsic activity	69	[132]
PdZn-Htlc, Pd ₂ Ga-Htlc, and Pd-Htlc	Co-precipitation for Htlc and reductive decomposition for intermetallic support incorporation	200 °C - 300 °C	Intermetallic nanoparticle supported Htlc catalyst exhibited improved catalytic activity and selectivity. Where Pd ₂ Ga-Htlc catalyst showed the best result	The activity of the intermetallic Htlc catalyst was less than Cu/ZnOHtlc catalyst	9.5	[133]

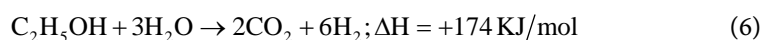
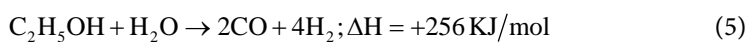
Cu/Zn-Al-HT catalysts, 10% Cu containing HT showed the best result and it exhibited an H₂ yield of 75.44% at 250 °C with 51.87% methanol conversion. Moreover, it was able to convert 99.78% Me-OH at 350 °C. It was also found that catalytic activity and reaction efficiency were dependent on the amount Cu₂O that was present in the enhanced catalyst. Cu, Zn, Al-HT catalyst for CH₃OH steam reforming was also studied by Kuhl *et al.*, [132]. They used the micro-emulsion technique for catalyst synthesis. The researchers were able to reduce the embedding of the copper particles and increase the copper surface area by applying the micro-emulsion technique. Thus, higher catalytic activity was achieved

during CH₃OH steam reforming by the developed catalyst. Finally, Pd₂Ga and PdZn intermetallic nanoparticles supported hydrotalcite catalyst for CH₃OH steam reforming were synthesized by Ota *et al.*, [133]. The researchers found that the Ga presence in the catalyst increased selectivity towards Me-OH and CO₂. However, the intermetallic nano-particles supported hydrotalcite catalyst was less active to Me-OH steam reforming than Cu-ZnO-Hydrotalcite based catalyst.

Hydrotalcite derived catalysts showed high Me-OH conversion and hydrogen productivity in methanol steam reforming. Especially, copper-containing hydrotalcite catalysts showed excellent performance. Methanol conversion by catalysts mentioned in Table 3 is presented in Figure 2.

3.4. HT Based Catalysts for Ethanol Steam Reforming

Nowadays, ethanol (C₂H₅OH/Et-OH) has become a potential source of hydrogen (H₂). Ethanol for hydrogen production is advantageous than natural gas and liquefied petroleum as it is renewable (bio-ethanol), non-toxic, easy to handle and high hydrogen yield [134]. Hydrogen from ethanol can be produced by partial oxidation, steam reforming or oxidative reforming method. Among these methods, ethanol steam reforming has a higher H₂ yield as part of it comes from Steam. Moreover, ethanol steam reforming is easy to apply process. Equations (5) and (6) present the prime reactions of ethanol steam reforming.



However, C₂H₅OH steam reforming is a complicated process, where the number of reactions such as dehydrogenation, dehydration, coking, and decomposition can take place successively or even simultaneously [135]. Temperature management during C₂H₅OH steam reforming is a significant issue due to the endothermic nature of ethanol steam reforming reaction and the necessity of continuous heat supply [136]. Moreover, methane formation during ethanol steam reforming Equation (7) decreases H₂ yield.



To overcome such obstacles, catalysts can play an important role. Catalysts can effectively reduce operating temperature and prevent methane formation [84] [137]. Previous studies revealed that noble metal-derived catalysts exhibited good results for ethanol H₂O reforming [138]. However, noble metal-based catalysts become deactivated over time during ethanol steam reforming due to the carbonaceous material deposition on the surface of the catalyst. The incorporation of catalytic support that can neutralize the acidic sites of the catalyst can solve the problem [84] [136]. Hydrotalcite with basic sites in its structure is a potential catalyst precursor for ethanol steam reforming [139] [140]. Metallic elements (Ni, Co, K, La, Cu, Rh, and Fe, etc.) used in HT to ease the conditions of ethanol steam reforming and enhance product yield that tabulated in Table 4.

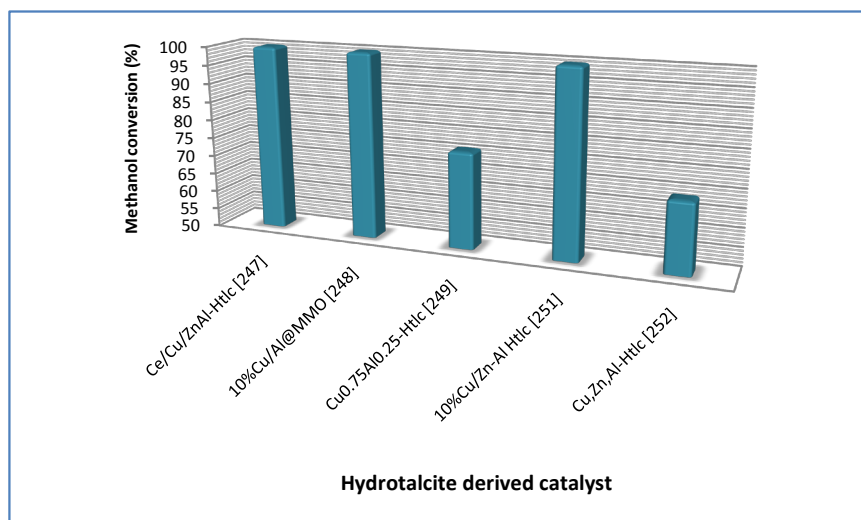


Figure 2. Methanol conversion by HT based catalysts in methanol steam reforming.

Table 4. Review report of HT derived catalyst for Ethanol Steam Reforming.

Catalyst	Synthesis Method	Test Parameters	Observations		H ₂ %	Ref.
			Achievements	Limitations		
Co & La supported Zn, Al-Htlc	Co-precipitation followed by calcination at 600 °C for 3 h	400 °C - 600 °C & atmospheric pressure	Better EtOH conversion, high H ₂ selectivity, and good catalyst stability	EtOH conversion decreased at a lower temperature	75.1	[32]
NiCo-MgAl mixed oxide prepared from Htlc	Ultrasound or microwave radiation assisted co-precipitation followed by thermal decomposition at 500 °C for 16 h	550 °C	Ultrasound or microwave treatment reduced catalyst synthesis time and increased reducibility and basicity of the catalyst	Increase in basicity decreased H ₂ yield due to the formation of unwanted byproducts	77	[141]
Co-Mg-Al	Ultrasound-assisted co-precipitation followed by calcination at 600 °C for 8 h	600 °C & atmospheric pressure	Catalysts with 10% to 15% Co exhibited the best hydrogen yield due to good dispersion of active phase, large surface area and non-agglomeration of the catalyst	Co concentrations less than 10% promotes unwanted product formation and rapid catalyst deactivation	-	[142]
K doped Co/Mg/Al-Htlc	Co-precipitation for Htlc precursor and wet impregnation for K doping followed by calcination at 550 °C for 4 h	400-600 °C & 1 - 18 bar pressure	K doped Co-Htlc catalyst exhibited good stability and no C accumulation happened during the catalytic operation	Staged membrane reactor exhibited lower H ₂ yields because of the H ₂ removal from the reaction medium	80	[143]
Ni-Mg/Al-Htlc	Co-precipitation and then calcination for 4 h at 500 °C in air	200 °C - 650 °C	In dilute condition (3% EtOH) catalyst reduced at 450 °C with H ₂ provided complete EtOH conversion and CO free H ₂ production	At higher temperatures, ethanol conversion decreased and amount of CO in the product stream increased	76	[144]
Shell core La-Ni(Mg-AL)O ₃ at Mg-Al	Co-precipitation followed by calcination at 700 °C - 900 °C for 6 h	700 °C & Atmospheric pressure	The developed shell-core catalyst at temperature ≥ 700 °C showed good stability and high activity during EtOH steam reforming	Catalyst calcined at high temperature (900 °C) caused the spinel phase and coke formation during the reaction	4.0 mol/mo l Et-OH	[145]

Continued

Shell core Ni-Mg/Al	Co-precipitation, then wet impregnation and finally calcination at 700°C for 6 h	700°C	Shell core catalyst exhibited better hydrogen yield for per mol of Ni atoms than the conventional Ni-Mg-Al-Htlc catalyst	Considerable deposition of both encapsulating and filaments C species on the catalyst surface	75	[146]
Ni-Fe-Htlc	Co-precipitation and then calcination in static air at 500 and 800°C for 3 h	500°C	Calcination temperature was found to affect catalytic performance and Fe presence in the Ni-Htlc catalyst found to increase catalytic activity and H ₂ selectivity	High calcination temperature (800°C) of the catalyst caused higher carbon deposition and Ni ^o sintering during ethanol steam reforming	60	[147]
Ni-Fe Htlc	Co-precipitation and then calcination at 500°C for 6 h in static air	400°C - 600°C	Iron in Ni-based Htlc catalyst enhances activity and h ₂ selectivity by promoting ni dispersion and lowering Ni ^o crystal size	Excess iron in the catalyst decreases activity	60	[148]
Cu impregnated Mg-Al(Htlc)	Wet impregnation, grinding and thermal treatment at 275°C for 24 h	200°C - 600°C	Improved H ₂ production and good stability during sorption enhanced ethanol steam reforming	High CO content of around 5000 ppm due to poor catalytic activity for WGS reaction during pre-breakthrough periods	90	[149]
Co-Mg/Al Htlc	Co-precipitation followed by calcination at 550°C for 3 h	250°C - 550°C & atmospheric pressure	Improved activity and selectivity towards H ₂ at moderate temperature and good stability even under higher ethanol loadings	The catalyst showed slow deactivation over time	65	[143]
Htlc based Co-Mg/Al Rh-Mg/Al & RhCo-Mg/Al	Co-precipitation and then wet impregnation for support (Rh & Co) and finally calcination at 800°C for 2 h	500°C & atmospheric pressure	Mg-Al Htlc based catalyst supported with both Rh and Co showed high H ₂ yield from EtOH and low ethane selectivity	Mg containing catalysts generated higher amounts of CH ₄ and CO as compared to magnesium-free catalysts	40	[150]
Htlc derived Co-Zn/Al, Co-Mg/Al, Co-Al, Ni-Mg/Al & Cu-Mg/Al	Urea hydrolysis followed by calcination at 450°C for 7 h	575°C - 675°C	Presence of Zn increased the reducibility of Co in the catalyst. Thus, at 575°C CoZnA was the best catalyst for H ₂ production	CuMgAl exhibited low catalytic activity and selectivity to H ₂	63.7	[151]
Htlc derived Ni/Zn-Mg-Al	Co-precipitation and calcination	700°C & atmospheric pressure	Catalyst containing Mg/Zn ratio of 4 exhibited improved performance and impressive H ₂ yield of 5.15 mol per mol Et-OH at 700°C	Comparatively high coke formation during EtOH steam reforming	5.15 mol/mol Et-OH	[152]
Htlc derived Ni-Co-Zn-Al	Urea hydrolysis followed by calcination at 700°C for 5 h	497°C - 597°C	At temperatures between 447 and 597°C presence of Co increased the selectivity of the catalyst to H ₂ and CO ₂ and decreased selectivity to CH ₄	Catalytic performance decreased at temperatures higher than 550°C	90	[153]
La&Ce promoted hydrotalcite (Ni-Mg/Al)	Co-precipitation followed by La and Ce addition by anion exchange and finally calcination in air at 500°C for 15 h	550°C & 650°C and atmospheric pressure	Incorporation of both Ce and La in the catalyst (Ni/Mg/Al) improved H ₂ yield and at 650°C catalysts achieved near 100% ethanol conversion	Ethanol conversion decreased at low temperature	75	[154]

Cerda-Moreno *et al.*, [32] synthesized Zinc-hydrotalcite (Zn-HT) catalyst containing different amounts of cobalt (Co) via co-precipitation method and subjected the catalysts to ethanol steam reforming. They found that Zn-HT catalyst with 20 wt% Co exhibited the best result in the means of total ethanol conversion and high H₂ yield. A high presence of reduced cobalt and small crystallite size of metallic cobalt in the 20% Co supported Zn-HT was found to be the cause behind the enhanced catalytic activity. Furthermore, 20% Co supported Zn-HT catalyst with 1 wt% of lanthanum (La) improved catalytic stability. Thus, C. Cerda-Moreno and co-workers concluded that Co supported Zn-HT catalyst promoted with La is a potential catalyst for hydrogen production. Developed catalyst offers enhanced Et-OH conversion, good stability and, high H₂ selectivity during Et-OH steam reforming. Munoz *et al.*, [141] synthesized mixed oxide NiCo-MgAl catalyst from HT precursor for oxidative steam reforming of ethanol. They utilized microwave or ultrasound-assisted co-precipitation method for catalyst development and found that microwave or ultrasound assistance reduced catalyst preparation time and improved both reducibility and basicity of the catalyst. However, ultrasound treatment caused surface defects and high basicity of the catalyst favored side reaction that might reduce H₂ yield. Ultrasound-assisted co-precipitation method was also utilized by Espitia-Sibaja and co-workers [142] to prepare the Co-Mg/Al catalyst from HT-like precursor for oxidative ethanol steam reforming. The Co-Mg/Al catalyst with 10% to 15% Co content exhibited the best performance. Whereas, Co content less than 10% promoted the production of undesirable by-products and Co content more than 15% in the catalyst increased particle agglomeration. They also reported that the percentage of active Co phase has an effect on the properties and structure of the catalyst. Cobalt-5HT catalyst (Co/Mg/Al-HtIc) for Et-OH steam reforming was also evaluated by Espinal *et al.*, [143]. They doped the (Co/Mg/Al-HtIc) in catalyst with potassium (K) and used a catalytic membrane reactor for the Et-OH steam reforming and staged membrane reactor. Catalytic membrane reactor at 600°C temperature and 12 bar pressure showed 3 times higher H₂ yield than staged membrane reactor. Thus, the researchers were able to demonstrate long term ethanol steam reforming at moderate temperatures using Co-HT catalyst. Besides, hydrotalcite derived Ni_xMg₂AlO_y catalyst was developed by Fang *et al.*, [144] for the production of hydrogen from bio-ethanol. They studied the influence of Ni content in the performance of the Ni_xMg₂AlO_y catalyst. Ni content and H₂ pretreatment of the catalyst were found to affect the catalytic performances. Their Ni_xMg₂AlO_y catalyst prepared via co-precipitation and thermal treatment method had particle size around 4 nm and showed high H₂ yield with total Et-OH conversion.

Zeng *et al.*, [145] explored a slightly different path, where they synthesized La-Ni(Mg-Al) from perovskite and hydrotalcite precursor for Et-OH steam reforming. The shell core type perovskite at HT catalyst exhibited high H₂ yield, excellent catalytic activity, and improved stabilities during ethanol steam reforming. They mentioned that LaNi(Mg, Al)O₃ perovskite with shell-type con-

figuration present in the catalyst could be linked to the enhanced performance of the catalyst. Zeng and co-workers [146] in another study evaluated the catalytic performance of shell-core Ni-Mg/Al catalyst derived from hydrotalcite type material for ethanol steam reforming. Comparing shell core Ni-Mg/Al catalyst with bulk Ni-Mg/Al catalyst the researchers found that shell core catalysts having lower nickel content exhibited improved H₂ yield at 700 °C. On the other hand, Abelló *et al.*, [147] studied Ni-Fe-HT catalyst for H₂ production by Et-OH steam reforming. They synthesized Ni-Fe catalyst from hydrotalcite-like material (reevesite) and examined the effect of the calcination temperature and Fe content of the catalyst on the catalytic performances. According to their findings, catalyst calcined at 500 °C with nickel/iron ratio of 1 exhibited the best catalytic performances. They concluded that Fe addition positively affects Ni-based HT catalysts by increasing H₂ selectivity, improving Ni dispersion and decreasing carbon deposition. Ni-Fe-HT catalyst was also studied by Bolshak *et al.*, [148] for Et-OH steam reforming. They found a similar result that, the catalyst containing Ni/Fe ratio of 1:1 exhibited higher catalytic activities. However, they also mentioned that increasing temperature during Et-OH steam reforming with Ni-Fe-HT catalyst promoted ethanol dehydrogenation and decreased carbon deposition.

Cunha *et al.*, [149] prepared Cu-Mg/Al HT catalyst for sorption enhanced ethanol steam reforming by impregnating active copper particles to a commercial hydrotalcite compound containing magnesium and aluminum. The developed Cu-Mg-Al catalyst showed good stability and improved hydrogen production during sorption enhanced ethanol steam reforming. But, high CO content in the product stream due to limited catalytic activity for WGS reaction is a drawback of the catalyst. On the other hand, Espinal *et al.*, [134] synthesized cobalt hydrotalcite (Co-Mg/Al-Htlc) catalyst for Et-OH steam reforming and observed that, Co/Mg/Al-Htlc catalyst having Co:Mg:Al molar ratio of 1:2:1 exhibited the best catalytic performance and selectivity towards H₂ at moderate temperatures. In situ experiments conducted by the researchers indicated that Co²⁺ species are beneficial for ethanol steam reforming and spinel Co-Al and CoO particles interact with MgO strongly. Elsewhere, Moura *et al.*, [150] conducted Et-OH steam reforming over Rh (rhodium) and/or Co (cobalt) promoted HT catalyst and examined the effect of the support on the catalytic activity. The catalytic performance evaluation was done in a fixed bed tubular quartz reactor containing 0.150 g catalyst under atmospheric pressure and 500 °C temperature. Among the developed catalysts, Mg-Al HT catalyst containing both Rh and Co exhibited the best performance during Et-OH steam reforming with a H₂ yield of 40% and selectivity of 57%.

Hydrotalcite (Mg-Al) based catalysts containing Co, Ni and Cu were evaluated by Guil-Lo'pez *et al.*, [151] for hydrogen production by oxidative C₂H₅OH steam reforming. They utilized the urea hydrolysis method for catalyst synthesis. Among the developed catalysts CoZnAl-HT showed the best catalytic performance (H₂ selectivity of 85%) and CuMgAl-HT appeared to have the lowest cat-

alytic performance (H_2 selectivity of 21%) at a lower temperature ($575^\circ C$). Their experiment revealed that Co catalysts have better H_2 selectivity and yield during oxidative ethanol steam reforming than Ni catalysts. Ni loaded Mg-Zn-Al catalyst prepared from hydrotalcite precursor via co-precipitation method was investigated by Zeng and co-workers [151] to study the synergy effect of MgO and ZnO during C_2H_5OH steam reforming for hydrogen production [152]. They found that at $700^\circ C$ Ni-Mg-Zn-Al Htlc catalyst with Mg/Zn ratio of 4 showed excellent stability and high hydrogen yield. Busca *et al.*, [153] synthesized a slightly different Ni/Co-Zn-Al catalyst from hydrotalcite precursor via the urea hydrolysis process for C_2H_5OH steam reforming. With the developed Ni-Co-Zn-Al catalyst Guido Busca and co-workers were able to achieve 90% H_2 yield at $540^\circ C$ and water to ethanol feed ratio of 6. They mentioned that the reason behind the high selectivity of the catalyst to H_2 might be related to the stability of partially reduced catalyst surface. Finally, Lucrédio *et al.*, [154] evaluated the influence of lanthanum (La) and cerium (Ce) addition on the catalytic performance of HT type Ni-Mg/Al catalyst during Et-OH steam reforming. Their analysis revealed that, Ni as NiO strongly and La moderately interacts with the Mg-Al support. But, Ce species has almost no interaction with the Mg-Al support. Both La and Ce incorporation resulted in High Et-OH conversion, improved H_2 production, and low carbon deposition. As mentioned by the researchers, the improved catalytic performance of Ce-Ni-Mg-Al catalyst is linked to the less interaction of the support with Ce species, which increased H_2O adsorption on CeO_2 and thus helped ethanol and acetaldehyde conversions.

Hydrotalcite derived materials exhibited impressive catalytic performances in ethanol steam reforming. The hydrogen yield of HT based catalysts during ethanol steam reforming that are discussed in Table 4 is presented in Figure 3 below.

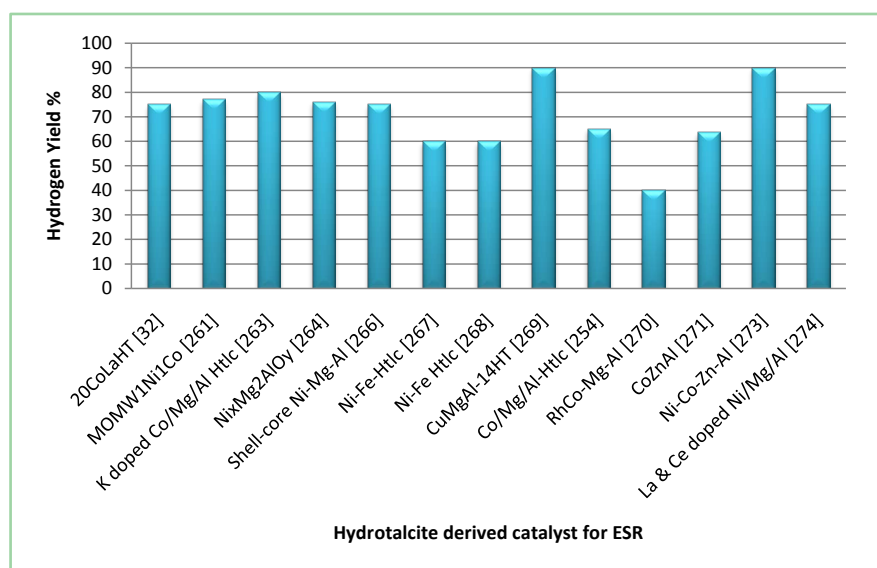


Figure 3. Performance of different Htlc based catalysts during ESR.

4. Discussion (Special Properties of Hydrotalcite Derived Catalyst to Reforming, Transesterification and Hydrogenation Reaction)

Methane reforming to hydrogen depends on a couple of factors that indicate performances of the system. The system requires the presence of steam and high temperature. Due to the interaction between support and catalyst and high temperature causes of catalyst sintering and coke formation. Both cases are fundamental problems of catalyst deactivation. This carbonaceous deactivation of the catalyst is a major limitation of methane reforming to hydrogen. There are couple of studies that have been cited on the pros and cons of DRM and SMR where corresponds to deposition problems and their remedies. Other than catalyst deactivation, the optimum composition of feed gas and steam ratio, operating pressure and temperature are also very important. Catalytic activity, selectivity and stability of a catalyst depends on material structure, active site and surface morphology, molar ratios of the metals, preparation methods, incorporation of promoters and mainly the elements that acts as promoters [155]. As example, MSR has been widely investigated and demonstrated that Cu/ZnO/Al₂O catalyst commonly used at 240 °C - 260 °C [27] [39] [40]. Since, copper leading catalyst are very effective, low cost and it produces significant amount of carbon monoxide but shows less stable and pyrophoric nature. Conant *et al.*, [41] showed catalyst deactivation using water molar fraction above the stoichiometric amount. Hydrotalcite derived Ni/Mg-Al or Fe/Mg-Al catalysts were mentioned to be highly active for CO₂ reforming of CH₄. They also observed that at higher temperature sintering of Ni particles increases and coke deposition decreases with higher Ni loadings in the catalyst. A less activation energy of the reaction is due to the catalyst performances that help to reform methane and prolong the deactivation of the catalyst. Activity, sulfur poisoning, carbon formation, sintering are four challenges of steam methane reforming [156]. Group VIII metals are active selection for the steam reforming of methane. Alkalies' make obstacle the activities of group VIII metals. The support should be able to withstand such conditions without losing strength [157]. For steam methane reforming, Ni containing hydrotalcite and calcium aluminates catalyst work best (99%) at 550 °C that can overcome the limitation of steam methane reforming with the special properties of hydrotalcite derived catalysts.

Superior MSR (Methanol steam reforming) catalyst should more active, stable and cause of producing less CO₂ in the reforming system. Moreover, moderate temperature and pressure also desired. The performance of MSR is significantly dependent on the reforming catalyst. Copper-based and palladium-based catalysts for methanol steam reforming had studied well [158]. Several schemes have been proposed regarding the reaction mechanism of methanol steam reforming. The methanol steam reforming-methanol decomposition-reverse water gas shift reaction scheme is generally accepted for methanol steam reforming reactions occurring over the copper-based or palladium-based catalysts. Three reactions of the methanol decomposition, water gas shift reaction and methanol steam re-

forming are assumed to occur in parallel. since, hydrotalcite derived catalysts are well stable, active surface that prolong the catalyst life and complete the all steps of reaction [159]. Cu (copper) supported Zn, Al-containing catalyst performs best (99.98%) for steam reforming of methanol at 300°C whereas Cu impregnated Mg-Al containing hydrotalcite is best (99%) for steam reforming of ethanol at 200°C - 600°C. Dehydration and dehydrogenation are main two reaction path of steam reforming of ethanol. Carbon deposition occur via the Boudouard reaction that encapsulates carbon and blocks the active sites of the catalysts results in catalyst deactivation. A particular ethanol and water ratio oppose the carbon deposition. Hydrotalcite derived catalyst act as a relatively good carbondioxide sorbent at 400°C.

The performance of transesterification process depends on mode of reaction, molar ratio of alcohol to oil, type of alcohol, reaction time, temperature and amount of catalyst. Catalyst one of the key parameters to influence the whole reforming process. Acid-catalyst transesterification and base catalyst transesterification are two best method of transesterification. Hydrotalcite derived catalyst can be designed into two both such as acid and base nature catalyst. The rate of transesterification is actively correlated with inter-layer electron density of HT. The conversion to methyl esters over the catalysts is in the following order: $KI/Al_2O_3 > KF/Al_2O_3 > KOH/Al_2O_3 > KNO_3/Al_2O_3 > K_2CO_3/Al_2O_3 > KBr/Al_2O_3 \cdot KI/Al_2O_3$ demonstrated superior catalytic activity compared to the other catalysts [160]. The most favorable environment (99.99%) for the transesterification of methanol is at 100°C - 120°C & 4.8 - 5.0 atm over Zr-doped Mg-Al containing hydrotalcite, whereas Ca-Al LDHs best for transesterification of ethanol. The structure of the HT are very suitable to re-structure as required for better catalysis of the system.

Hydrogenation of ethyl acetate to ethanol shows plausible reaction pathway. The most probable cause of higher conversion of ethyl acetate is carbonyl activation that depends on the active sites of the metal in catalysts [161]. The weak acyl structure role is to desorbs resultant products from surface of the catalyst. Ethoxy group are formed through the cleavage of C-O bond of the hemiacetal group and later hydrogenated to ethanol. There are some side products during the hydrogenation reaction. Hydrotalcite derived catalyst could be design considering to prevent the sight reactions, to have enough active sites, formation of the weak acyle structure. Some are very economic metals that ensure those properties in hydrotalcite derived catalyst and happen a better hydrogenation to ethanol. The hydrogenation process can be performed with even small amount of catalyst and in the presence of lower quantities or without solvent. Y_2O_3 -modified Cu/ZnO/ Al_2O_3 hydrotalcite performs best (89.7%) for hydrogenation to different fuels at a temperature of 230°C & 3 - 9 atm.

Multi-component hydrotalcite is an excellent precursor for the preparation of potential mixed oxides with a homogenous distribution of metal [162]. Partial substitution of metal can be used to refine catalytic properties of the material. The anions and water are randomly placed in the interlayer and are loosely

bounded. Suitable anion can be used as per the requirement of the functional system. The strength of the hydrogen bonding between anions and the hydroxyl groups of the layers, size and orientation influence to the thickness of the inter-layer. Calcined hydrotalcite or mixed oxides are highly active and selective, and can play an important role in many catalyzed based reaction. Controlled thermal decomposition of hydrotalcite produced high specific surface area of mixed oxides that have various applications. Hydrotalcite show an important property “memory effect” by which the material recover its original layer structure if they contact with water. Regeneration of these materials can be done efficiently. Another important property of this material is acid-base pairs that can be created and offer active site for many reactions or gas adsorption. Added alkali solution with a fixed pH in such a rate as to maintain the pH at a certain range which help to careful control of charge density of ($M^{(II)}/M^{(III)}$ ratio) of the hydroxide layers to co-precipitate of the two or more metallic salts [162]. These conditions give rise to precipitate higher crystalline particle than those obtained under high super saturation conditions due to the rate of the crystal growth is higher than the rate of nucleation.

Special physical & chemical properties that hydrotalcite shows: 1) Homogenous distribution of metals, 2) Cations exchange materials, 3) High specific surface area and surface energy, 4) Tuneable surface morphology, 5) Cheap, Abundant and environment friendly, 6) High thermal stability make them very active catalyst especially as highly stable, less CO_2 producing nano materials [163]. Due to the multi-layered materials, it can control water ratio and exchange electrons between homogeneously distributed metals on the surface and reforming agent that stipulated kinetics and thermodynamics.

The reaction environment generated by the hydrotalcite derived catalyst is most favorable for steam reforming, transesterification and hydrogenation is because of modification and design flexibility for the desired favorable catalytic activities, large surface area, basic properties, high amount homogeneous dispersion of metals, stability against sintering [164] [165].

5. Conclusions

The aforementioned literature review intends to present an overview of the latest advancement achieved by the researchers to develop hydrotalcite (HT) derived catalyst for hydrogen and bio-fuel production. Hydrotalcite has favorable properties such as memory effect, option to choose between different cations (M^{2+} and M^{3+}) and compositional ratios, basic properties and large surface area with an almost homogeneous distribution of active sites. This is why HT are favorable as catalyst precursors for different chemical processes. The comprehensive survey of literature articles reveals that the selectivity, catalytic performance, and stability of HT derived materials depend on structural property, chemical content, and phase composition. Factors like catalyst synthesis method, calcination, and reduction of catalyst, catalytic test conditions, the addition of promoters and

the molar ratio of cations (M^{3+} , M^{2+} , and/or promoter ions) in the catalyst affect to the catalytic efficiency. Especially, chemical composition (ratio of metallic components) and the interaction of the metal with hydrotalcite precursor have important roles in catalytic performances. Moreover, the promotion of HT precursor with metals like Zr, Ce, Ni, Co, Rh has the potentiality to improve the selectivity, stability, catalytic activity, and product yield as mentioned by various investigations. However, catalyst deactivation due to sintering of active metal ions and coke formation in the catalyst surface after application for a certain period of time has been reported widely. Efforts have been made to overcome the disadvantage by utilizing a modified catalyst synthesis method, pre-treatment and incorporation of metals such as Ru, Pt, Cu, and Ti, etc. But, agreement on a reliable method that may ensure good catalytic stability has not been found.

HT derived materials as fuel processing catalyst has received impressive progress. According to the literature reviewed above researchers were able to synthesize HT based mix oxide catalyst with improved catalytic activity and those catalysts were viable for industrial use. However, to achieve the desired stability with excellent catalytic activity from HT derived catalysts, there are several areas need to provide much attention. Most of the published scholarly articles on the catalytic performance of HT based catalyst deal with one or two active components. But, comprehensive studies about synergic interactions between different active components present in the catalytic system and their effect on activity are hardly found. Generally, HT derived catalysts are used in fixed bed reactors. HT based catalysts might be used in fluidized bed reactors by manipulating the physical properties. This will give the option to add continuous catalyst regeneration to unite in the system. Few conventional metallic promoters to enhance the performance of HT catalysts have been investigated. A wide variety of other inorganic and organic compounds should be studied to evaluate their promotional effect on HT derived catalysts.

Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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