Recent Advances in Cleaner Hydrogen Productions via Thermo-catalytic Decomposition of Methane: Admixture with Hydrocarbon

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Abstract

A continuous increase in the greenhouse gases concentration due to combustion of fossil fuels for energy generation in the recent decades has sparked interest among the researchers to find a quick solution to this problem. One viable solution is to use hydrogen as a clean and effective source of energy. In this paper, an extensive review has been made on the effectiveness of metallic catalyst in hydrocarbon reforming for CO_X free hydrogen production via different techniques. Among all metallic catalyst, Ni-based materials impregnated with various transition metals as promoters exhibited prolonged stability, high methane conversions, better thermal resistance and improved coke resistance. This review also assesses the effect of reaction temperature, gas hour space velocity and metal loading on the sustainability of thermocatalytic decomposition TCD of methane. The practice of co-feeding of methane with other hydrocarbons specifically ethylene, propylene, hydrogen sulphide, and ethanol are classified in this paper with the detailed overview of TCD reaction kinetics over an empirical model based on power law that has been presented. In

33 addition, it is also expected that the outlook of TCD of methane for green hydrogen production

34 will provide researchers with an excellent platform to the future direction of the process over Ni-

35 based catalysts.

36 **Key Words:** Hydrogen production, Methane Conversion, Metallic Catalyst, Process Parameters,

37 Co-Feeding, Reaction Kinetics

38 **Table of Contents**

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1. Introduction

The combustion of fossil fuels such as coal, oil, gasoline and natural gas satisfy the energy demands of industry and domestic users. However, they will run out momentarily due to the rapidly increasing demands [1]. Furthermore, the global warming, greenhouse effect, hole in ozone layer, acid rains and environmental pollution are the drastic effects caused by the fossil fuel combustion [2]. USA, Japan, and Germany are leading the race of CO_2 emissions as they have well stabilized industrial sectors [3]. The concentration of CO_2 in the atmosphere has increased drastically from 396 ppm to 400 ppm in recent few years. Moreover, it is estimated that these emissions will increase from 30 billion metric tons to 43 billion metric tons in 2035 [4]. The average temperature of the earth according to climate forecasts may increase from 274 to 279 K if the increasing greenhouse gas emissions are not critically considered. [5]. Extensive solutions have been reported by the researchers to reduce the hazardous effects of increasing concentration of CO_2 in the atmosphere by establishing various methods of CO_2 capture such as absorption, cryogenic and membrane processes [6]. Another method has been reported by using photocatalytic reactors [7] to convert excessive CO_2 into useful products such as CH_4 and CH_3OH. The invention of few high energy efficient green fuels that reduce the emissions of poisonous gases during combustion is also quoted as an active solution to control greenhouse effect. The search for alternative high energy efficient green fuels has been broadly investigated by many researchers in the past. H_2 has been termed as one of the greenest and lightest fuel that can fill in the energy gap which will be created in the upcoming future. Because of hydrogen's abundance, lightweight, low mass density, high calorific value and non-polluting nature make it a unique source of energy.

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84   Moreover, it has been published that H_2 has the highest heat of combustion, i.e. 142 kJ g^{-1} as

85   compared to petroleum and wood that exhibit 43-35 and 18 kJ g^{-1} respectively [8].

86   The annual H_2 consumption in 2006 was around 50 million tons including industrial and domestic

87   usage. Around 50% of this consumption was attributed to NH_3 industries, 37% in petroleum

88   refineries, 7% in CH_3OH production and 6% in other fields. It has been reported that the H_2

89   produced in existing date has to be multiplied 100 times approximately to meet the world's demand

90   for fossil fuels presently [9]. It is believed that H_2 will play a vital role in fulfilling the extensive

91   energy requirements. However, H_2 cannot be found freely in the atmosphere instead of in the form

92   of bonds with other molecules that indicate its reactivity. Therefore, it must be extracted from other

93   primary energy sources like coal, natural gas, water or other heavy hydrocarbons [10]. Global

94   statistics illustrate that the significant amount of H_2 is being produced by the reforming of natural

95   gas, i.e. 48%, electrolysis of water gives 30%, 18% from burning petroleum products and 4% by

96   coal. The significant contribution to the production of H_2 is from natural gas since there are vast

97   reservoirs of CH_4 in deep seabed especially in industrialized countries like United States [11].

98   Natural gas has been named as the primary energy contributor since early 20's in Malaysia. In

99   2008 alone, approximately over 2.5 trillion m^3 of the natural gas reserve were found in Malaysia

100   specifically in Sarawak (East Malaysia). Moreover, the natural gas reserves in Malaysia are the

101   largest in South East Asia and 12th largest around the globe [12].

102   There are various methods for the H_2 production such as; steam reforming (SRM), partial oxidation

103   (POM), dry reforming (DRM) and thermocatalytic decomposition of CH_4 (TCD) [13-15]. Among

104   these methods, POM, SRM, and DRM are considered as indirect methods of H_2 production. In

105   these methods, CH_4 is treated with O_2, H_2O and CO_2 under given a set of reaction conditions to

106   produce synthesis gas as a mixture of H_2 and CO [16]. However, there is a common shortcoming

107   in all these three processes in the form of emissions of greenhouse gases CO_2 and CO. These gases

108   not only play a major role in global warming but also are very harmful when their mixed feedstock

109   with H_2 is used in low-temperature fuel cells like proton exchange membrane fuel cells (PEMFC)

110   [17].

111   Keeping in view the greenhouse gas emissions and its economic issues, the interest of researchers

112   moved towards exploring a more optimum and green process for H_2 production. Thermocatalytic

113   decomposition (TCD) is a practical approach to decompose CH_4 into H_2 and elemental carbon

114   thermally. This method is considered novel and eco-friendly as there is no emission of greenhouse

115   gases during the reaction [18].

116   Various review papers have been published in the past decades on this topic for example Jose et

117   al. [19], Abbas et al. [9], Ashik et al. [20], Srilatha et al. [21], Sikander et al. [15] and Yongsan et

118   al. [8-10]. Nonetheless, these reviews were limited on the TCD of CH_4 which heavily focussed on

119   catalysts to reactor's type. In recent years, there are distinct works that are focussed on the

120   feedstock combination with CH_4 [22, 23] which provide better conversions and improved the

121   activity and stability of the catalysts. Thus, in this review, an attempt has been made to review on

122   admixture feedstocks with CH_4 with other hydrocarbons critically. Moreover, this article also

123   independently reviews on the type of catalysts, i.e. monometallic and multimetallic and their

124   performances in TCD of CH_4. We also highlighted the outlook of TCD in directing the future

125   research in coming years. Fig. 1 shows a complete process that we take for this review article.
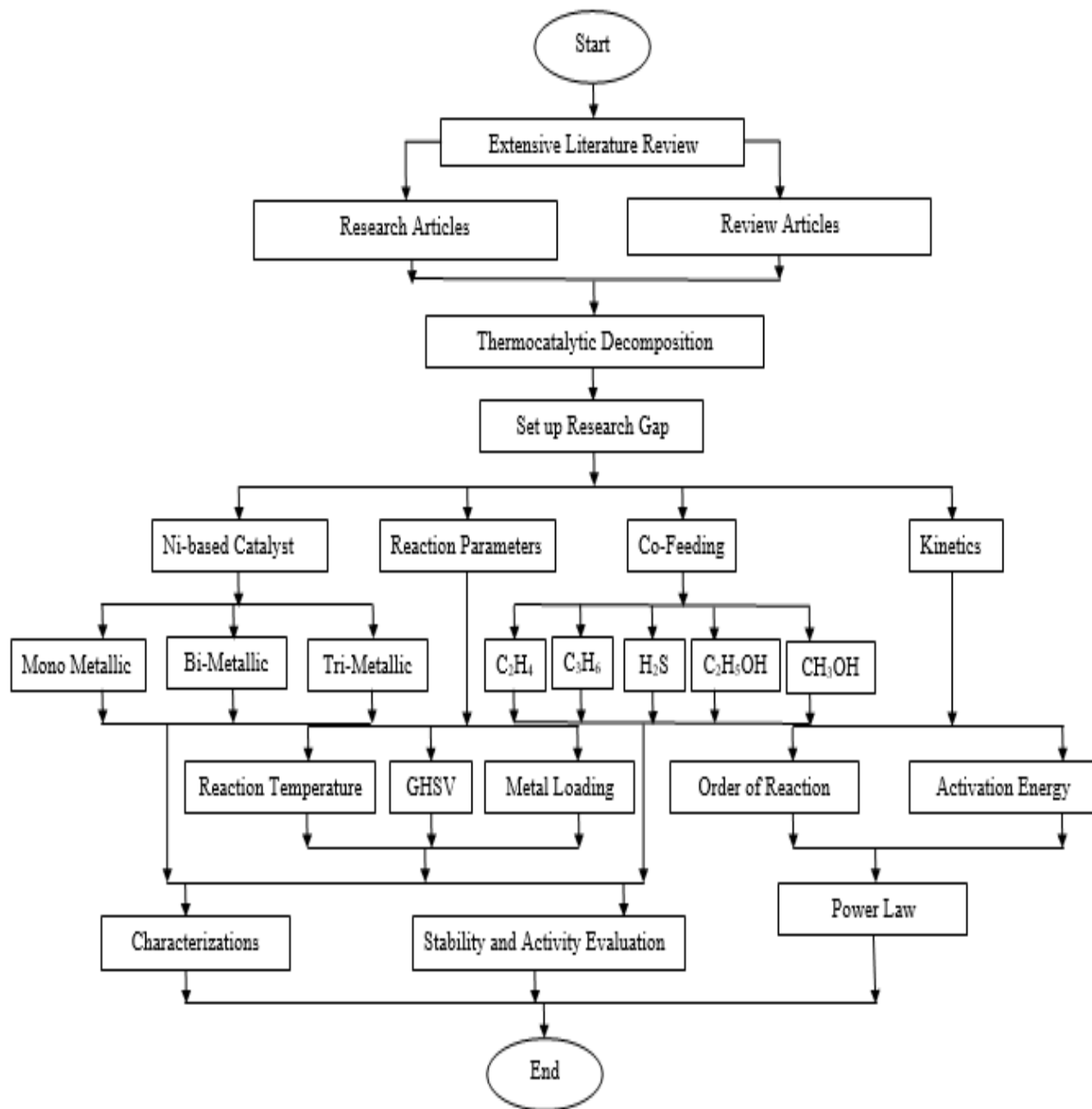
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Fig 1: Process Flow of Review for TCD

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136 **1. Thermo-catalytic Decomposition (TCD) of CH$_4$**

137 TCD of CH$_4$ is a single step process which produces pure H$_2$ and carbon as a by-product [14]. This

138 method is known as an eco-friendly process, and it has been extensively studied by various

139 researchers [24]. The main advantages of TCD include the greenhouse free H$_2$ production that can

140 be directly used in fuel cells and the production of CNF as a by-product [25]. The reaction proceeds

141 as shown in Eqns. (1)−(6) [9].

$$CH_{4\ (gas)} \rightarrow C_{(S)} + 2H_{2\ (gas)} \qquad \Delta H= 74.9 kJmol^{-1} \tag{1}$$
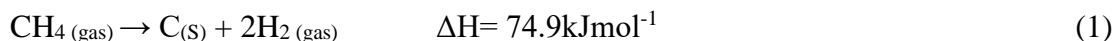
142 The reaction occurs in four stages explained as:

143   (a) In the first step, the CH$_4$ gets itself attached to the surface of the catalyst. The most

144   important part of the catalyst contains the metal impregnated with suitable support and

145   promoters.

$$CH_{4\ (gas)} \rightarrow CH_{3\ (ads)} + H_{(ads)} \tag{2}$$

146   (b) The breaking of sp^3 hybridized C-H bonds occurs. This is the most critical step since

147   high energy is required to break strongly attached bonds.

$$CH_{3\ (ads)} \rightarrow CH_{2\ (ads)} + H_{(ads)} \tag{3}$$

$$CH_{2\ (ads)} \rightarrow CH_{(ads)} + H_{(ads)} \tag{4}$$

148   (c) After the breakage of these bonds, the H converts into the molecular form thus

149   becoming a primary product.

$$H_{(ads)} + H_{(ads)} \rightarrow H_{2\ (Gas)} \tag{5}$$

150   (d) The next step is the attachment of carbon on the surface of active sites. Hence, the

151   active sites blocked, and the surface area of the catalyst is also decreased. Therefore, it

152   is observed that the initial deactivation of the catalyst starts.

$$CH_{(ads)} \rightarrow C_{(Solid)} + H_{(ads)} \tag{6}$$

(e) The last step is the forming of carbon nuclei on the surface of the catalyst. Carbons get the form of MWCNT, CNF or BCNF depending upon nature and the operating conditions.

TCD is an endothermic reaction and occurs at high temperatures, i.e. 1473 K due to the highly stable tetrahedral structure of CH_4 molecule supported by extremely stable C−H bonds with a bond energy of 434 $kJmol^{-1}$. Therefore, the applications of catalyst are mandatory to provide a robust pathway to decrease the activation energy [26]. To improve the reaction kinetics of TCD, Metal-based catalysts, and carbonaceous catalysts were introduced by numerous researchers. These include transition metal having partially filled d-orbital, activated carbon and carbon black [17].

2. Catalysts Involved in TCD

For commercially viable, the development of TCD process requires a low cost synthesized catalyst that results in higher and prolonged activities towards CH_4 decomposition into H_2 and elemental carbon. The literature survey on the study of the single metallic, bi-metallic and tri-metallic catalysts having different ratios in composition and synthesized by distinct techniques have been explained in Sections 2.1-2.3.

2.1. Mono Metallic Catalyst

Over the last few years, countless efforts have been made in the development of the preparation method of a suitable catalyst to optimize TCD of CH_4 for CO_X free H_2. Various monometallic catalysts with different supports have been reported [27]. Apart from production of pure H_2, the invention of highly ordered carbon in the form of carbon nanofiber (CNF), carbon nanotubes (CNT), biwall carbon nanotubes (BWCNT), and multiwall carbon nanotubes (MWCNT) has been reported by researchers using these catalysts [28]. The morphology of the deposited carbon is

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175　mainly dependent upon the metal loadings and reaction parameters. Although the general

176　mechanism of TCD has been proposed to be similar for nearly all metallic materials, the catalytic

177　stability and activity is influenced by catalysis synthesis techniques, pre-treatment of catalyst and

178　most importantly the TCD parameters [24, 29]. Ni, Fe, and Co are the commonly used transition

179　metals impregnated on Al_2O_3, SiO_2, MgO and La_2O_3 support [20].

180　Several investigators have reported productive work in bringing up the most optimized, reactive

181　and stable catalysts for TCD of CH_4. Ni-based materials are often stated as one of the most active,

182　readily available and cost-effective catalysts for CH_4 reforming processes. It is reported that the

183　performance of Ni-based catalysts is strongly dependent on the type of support it is impregnated

184　on as the structure and electronic state of the catalyst changes once the material is successfully

185　prepared. Therefore, it is worth mentioning that the best combination of Ni and apposite support

186　can produce a highly active and stable catalyst for TCD of CH_4 [30]. Bayat et al. [31] studied

187　various Ni loading on $\gamma-Al_2O_3$ support. The results marked the catalysts as highly active and stable

188　in the stated field of study, but they were sensitive to metal loadings and reaction temperatures.

189　Owing to the endothermic nature of the reaction, the conversions of CH_4 increased periodically

190　with reaction temperature. Moreover, it was also observed that at higher metal loadings the

191　conversions were also high due to the presence of ample amounts of NiO on the surface of the

192　support. The study done by Makvandi et al. [32] elaborated that the CH_4 conversions declined with

193　TOS for Ni/Al_2O_3 due to deposition of carbon on the active sites preventing the access of

194　hydrocarbon. Moreover, the conversions increased linearly with metal loadings due to the

195　availability of excessive active sites. The catalytic performance of 60% Ni/Al_2O_3 was inspected by

196　Ahmed et al. [33]. The results revealed that the textural properties play a vital role in the

9

197   performance of the catalyst since nanoparticle (NP) gave the highest yields as compared to the

198   hollow sphere (HS) and bulk catalyst (BC).

199   Apart from Al_2O_3 being the most studied by many researchers, studies on MgO, SiO_2, TiO_2,

200    $MgAl_2O_4$, La_2O_3, SBA−15, and La_2O_3 have also been cited on Ni-based catalyst [34, 35]. The

201   literature survey showed that Ni/SiO_2 catalyst presented notable conversions, but eventually the

202   catalyst deactivated due to the accumulation of carbon in the pores of the catalyst. TPO and TGA

203   analysis supported the formation of MWCNT as a by-product [36]. TiO_2 was also reported to be

204   active support for TCD of CH_4 due to its high surface area and pore volume. This assisted in a fine

205   dispersion of Ni creating vast amounts of NiO for CH_4 breakage [37, 38]. All Ni support TiO_2

206   catalyst was highly active for CH_4 decomposition reaction due to proper metal support interaction

207   that also provided thermal stability to the catalyst.

208   Fe and Co-based materials are also classified as active metals for TCD of CH_4. Besides Ni. Pinilla

209   and co-workers [39] came up with results which showed that high CH_4 conversions are allowed

210   by Fe based catalyst at operating temperatures higher than 1073 K. The researchers also compared

211   the catalytic efficiency of Al_2O_3 and MgO supports and ranked Fe impregnated on prior support as

212   more stable compared to later one. The influence of metal loading and the effects of support on Fe

213   based catalyst was again discussed briefly in [40]. Fe catalyst supported on Al_2O_3 showed high

214   conversions as compared to MgO and TiO_2. The catalytic order w.r.t. support was as $Al_2O_3 >$ MgO

215    $> TiO_2.$ The performance of Fe supported on Al_2O_3 as an active catalyst for TCD of CH_4 was also

216   acknowledged by [41]. The study of Ibrahim et al. [28] also justified that the CH_4 conversions

217   increased with Fe loadings due to the availability of a large number of active sites and because of

218   right interaction in metal and support. The highest conversions were attained by 60%Fe/Al_2O_3.

219 Co-based catalysts are also the area of several studies for optimization of TCD of natural gas into

220 H_2 and elemental carbon. The formation of cobalt oxide, i.e. Co_3O_4 is the main reason for its

221 superior activity and stability of the catalyst [42]. It is also reported that the higher loading of Co

222 produces large CNF having bigger diameter due to the agglomeration of the particles [43]. Besides

223 the excellent performance of Co-based catalysts, its toxicity issues and higher cost as compared to

224 Ni restricts its usage in both industrial and domestic level [31].

225 The detailed performance analysis along with reaction conditions of some of the monometallic

226 catalysts has been summarized in Table 1. Moreover, the catalyst synthesis techniques and carbon

227 yield have also been presented.

Table 1: Catalytic activity and stability of various monometallic catalyst having different supporters and reaction conditions in fixed bed reactor (FBR) for TCD

S. No	Metal	Support	[a]Wc (g)	Preparation	S.A $m^2 g^{-1}$	[d]T_R (K)	[e]R_T (h)	Conversion/Yield (%)	Carbon	Ref
1.	10%Ni	Al_2O_3	0.05	I.M[c]	141	853	1	[g]21	-	[34]
2.	10%Ni	$MgAl_2O_4$	0.05	I.M[c]	134	853	1	[g]12	-	[34]
3.	10%Ni	MgO	0.05	I.M[c]	90	853	1	[g]13	-	[34]
4.	14%Fe	CeO_2	0.15	C.P [N]	11.7	1023	4	[g]03	-	[44]
5.	28%Fe	CeO_2	0.15	C.P [N]	22.2	1023	4	[g]05	-	[44]
6.	42%Fe	CeO_2	0.15	C.P [N]	51.3	1023	4	[g]26	-	[44]
7.	56%Fe	CeO_2	0.15	C.P [N]	60.3	1023	4	[g]25	-	[44]
8.	70%Fe	CeO_2	0.15	C.P [N]	69.5	1023	4	[g]10	-	[44]
9.	00%Fe	CeO_2	0.15	C.P [N]	100.2	1023	4	[g]01	-	[44]
10.	67%Fe	Al_2O_3	0.15	I.M[c]	141.6	1073	3	[f]28	-	[39]
11.	67%Fe	MgO	0.15	I.M[c]	14.7	1073	3	[f]20	-	[39]
12.	05%Ni	Al_2O_3	0.15	I.M[c]	249	973	4	[g]10	-	[32]
13.	7.5%Ni	Al_2O_3	0.15	I.M[c]	248	973	4	[g]18	-	[32]
14.	10%Ni	Al_2O_3	0.15	I.M[c]	245	973	4	[g]29	-	[32]
15.	50%Co	MgO	0.5	I.M[c]	20.4	973	7	[g]83	[i]261	[45]
16.	50%Fe	MgO	0.5	I.M[c]	18.68	973	8	[f]40	[i]599	[46]
17.	50%Ni	MgO	0.5	I.M[c]	28.12	973	8	[f]15	[i]139	[46]
18.	50%Co	MgO	0.5	I.M[c]	28.25	973	8	[f]90	[i]1121	[46]

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S. No	Metal	Support	(a)Wc (g)	Preparation	S.A $m^2 g^{-1}$	(d)T_R (K)	(e)R_T (h)	Conversion/Yield (%)	Carbon	Ref
20.	Ni	SiO_2	3	S.G (O)	-	1073	5	(f)50	(i)215	[47]
19.	Co	SiO_2	3	S.G (O)	-	1073	5	(f)47	(i)156	[47]
21.	Fe	SiO_2	3	S.G (O)	-	1073	5	(f)48	(i)177	[47]
22.	15%Fe	SiO_2	0.3	I.M(c)	179.3	973	4	(f)4	-	[28]
23.	25%Fe	SiO_2	0.3	I.M(c)	141	973	4	(f)12	-	[28]
24.	35%Fe	SiO_2	0.3	I.M(c)	135	973	4	(f)15	-	[28]
25.	40%Fe	SiO_2	0.3	I.M(c)	129.5	973	4	(f)54	-	[28]
26.	60%Fe	SiO_2	0.3	I.M(c)	112.6	973	4	(f)71	-	[28]
						973				
27.	80%Fe	SiO_2	0.3	I.M(c)	51.9	973	4	(f)74	-	[28]
28.	100%Fe	SiO_2	0.3	I.M(c)	5.4	973	4	(f)78	-	[28]
29.	50%Ni	MgO	0.5	I.M(c)	-	973	7	(f)14	-	[48]
30.	10%Fe	Al_2O_3	0.3	I.M(c)	222.5	973	3	(g)9	-	[40]
31.	20%Fe	Al_2O_3	0.3	I.M(c)	237	973	3	(g)35	-	[40]
32.	30%Fe	Al_2O_3	0.3	I.M(c)	203	973	3	(g)42	-	[40]
33.	40%Fe	Al_2O_3	0.3	I.M(c)	184.8	973	3	(g)43	-	[40]
34.	50%Fe	Al_2O_3	0.3	I.M(c)	176.2	973	3	(g)45	-	[40]
35.	10%Fe	MgO	0.3	I.M(c)	125.1	973	3	(g)44	-	[40]
36.	15%Fe	MgO	0.3	I.M(c)	120.8	973	3	(g)47	-	[40]
37.	20%Fe	MgO	0.3	I.M(c)	105.8	973	3	(g)46	-	[40]

S. No	Metal	Support	(a)Wc (g)	Preparation	S.A m^2 g^{-1}	(d)T_R (K)	(e)R_T (h)	Conversion/Yield (%)	Carbon	Ref
38.	30%Fe	MgO	0.3	I.M(c)	97.2	973	3	(g)45	-	[40]
39.	40%Fe	MgO	0.3	I.M(c)	46.9	973	3	(g)40	-	[40]
40.	20%Fe	TiO$_2$	0.3	I.M(c)	96.2	973	3	(g)14	-	[40]
41.	30%Fe	TiO$_2$	0.3	I.M(c)	92	973	3	(g)15	-	[40]
42.	40%Fe	TiO$_2$	0.3	I.M(c)	76	973	3	(g)16	-	[40]
43.	50%Fe	TiO$_2$	0.3	I.M(c)	75.9	973	3	(g)17	-	[40]
44.	50%Ni	SBA−15	1	I.M(c)	182.6	973	7	(f)40	-	[49]
45.	Ni	MgAl$_2$O$_4$	1	-	22.63	973	7	(f)34	-	[50]
46.	50%Co	Al$_2$O$_3$	0.5	I.M(c)	24.2	973	7	(f)88	(i)298	[51]
47.	50%Co	SiO$_2$	0.5	I.M(c)	93.2	973	7	(f)48	(i)172	[51]
48.	50%Co	MgO	0.5	I.M(c)	20.1	973	7	(f)73	(i)1121	[51]
49.	30%Ni	Al$_2$O$_3$	0.05	I.M(c)	121.3	973	5	-	-	[31]
50.	40%Ni	Al$_2$O$_3$	0.05	I.M(c)	105.6	973	5	-	-	[31]
51.	50%Ni	Al$_2$O$_3$	0.05	I.M(c)	89.2	973	5	-	-	[31]
52.	60%Ni	Al$_2$O$_3$	0.05	I.M(c)	66.1	973	5	-	-	[31]
53.	60%Ni (N.P) (K)	Al$_2$O$_3$	0.5	-	58.7	973	6	(f)60	-	[33]
54.	60%Ni (B) (L)	Al$_2$O$_3$	0.5	-	22.8	973	6	(f)50	-	[33]
55.	60%Ni (H.S) (M)	Al$_2$O$_3$	0.5	-	22.0	973	6	(f)19	-	[33]
56.	5%Co	SiO$_2$	-	I.M(c)	382	-	3	-	-	[52]
57.	10%Co	SiO$_2$	-	I.M(c)	351	-	3	-	-	[52]

S. No	Metal	Support	[a]Wc (g)	Preparation	S.A m^2 g^{-1}	[d]T_R (K)	[e]R_T (h)	Conversion/Yield (%)	Carbon	Ref
58.	20%Co	SiO_2	-	I.M[c]	292	-	3	-	-	[52]
59.	5%Co	Al_2O_3	-	I.M[c]	227	-	3	-	-	[52]
60.	10%Co	Al_2O_3	-	I.M[c]	27.4	-	3	-	-	[52]
61.	30%Fe	Al_2O_3	0.3	I.M[c]	150.1	973	3	[g]68	-	[53]
62.	-	NiO	2	-	25.4	1073	6	[f]62	[i]263	[54]
63.	-	Fe_2O_3	2	-	13.8	1073	6	[f]50	[i]147	[54]
64.	20%Ni	CeO_2	2	-	42.1	973	6	[f]62	[i]1360	[35]
65.	20%Ni	ZrO_2	2	-	23.8	973	6	[f]61	[i]1159	[35]
66.	20%Ni	La_2O_3	2	-	10.6	973	6	[f]68	[i]1576	[35]
67.	Ni	Al_2O_3	-	I.M[c]	201.03	1073	4	[g]15.33	-	[55]
68.	Pd	Al_2O_3	-	I.M[c]	195.31	1073	4	[g]15.68	-	[55]
69.	10%Ni	TiO_2	1	I.M[c]	23.68	973	6	[f]27	[i]1399	[37]
70.	20%Ni	TiO_2	1	I.M[c]	18.49	973	6	[f]30	[i]1180	[37]
71.	30%Ni	TiO_2	1	I.M[c]	12.31	973	6	[f]33	[i]1380	[37]
72.	40%Ni	TiO_2	1	I.M[c]	-	973	6	[f]37	[i]1522	[37]
73.	50%Ni	TiO_2	1	I.M[c]	-	973	6	[f]42	[i]1544	[37]
74.	Ni	MgO	1	I.M[c]	24.20	1073	6	[f]37	[i]850	[56]
75.	5%Fe	MgO	0.5	I.M[c]	79	1173	-	-	[i]4.7	[57]

(a)Weight of catalyst (b) Fusion method (c) Impregnation method (d) Reaction temperature (e) Reaction Time (f) H_2 yield (g) Methane (h) g c/ g ni
(i) % (J) mg (K) Nano particle (L) Bulk (M) Hollow Sphere (N) Co Precipitation (O) Sol Gel

2.2.Bi-Metallic Catalyst

The transition metals such as Ni, Fe, and Co as explained in <mark>Section 2.1</mark> have shown better performance as active metal precursors for TCD of CH_4 into CO_X free H_2 and CNF [58]. The deactivation of this catalyst at high temperatures is due to the encapsulation of nearly in active carbon. This has opened new horizons of research in this field (c.f. Table 1). The modification of Ni-based catalyst with other transition metals is reported to be a viable solution to this problem [59]. The impregnation of a second metal on Ni provides significant changes in its activity and stability due to alloying effect [45] (c.f. Tables 2 and 3).

To optimize the TCD of CH_4, innumerable Ni-based bimetallic catalysts supported on $\gamma-Al_2O_3$ were employed. It was reported that Ni acts as an active phase and Al_2O_3 being inactive, which aids the dispersion of Ni-containing phases. Interestingly, inactive Al_2O_3 proved to be responsible for most of the mechanical properties exhibited by the catalyst [60]. Echegoyen et al. [61] reported that the addition of textural promoter in Ni-based catalyst prevent from sintering. The group synthesized Cu promoted catalyst supported on MgO. The presence of Cu enhanced the catalytic stability of the catalyst for 8 h. Cu itself is inactive for TCD of CH_4. The basic function is to aid CNF formation and increase the carbon diffusion rate, thus keeping the surface of Ni fresh for CH_4 adsorption. Moreover, Cu promoted catalyst results in the formation of broader and lengthier CNF as a by-product [62]. A further study from [63] concluded that TiO_2 could also use as textural support on high loading bimetallic catalyst and presence of Cu as promoter either in the form of oxide or nitrate enhance conversions of CH_4 and carbon formations.

The influence of Mo on the catalytic efficiency of Ni/Al_2O_3 was investigated in [64]. The results showed that addition of Mo with other transition metals improves CH_4 conversions and CNT production as carbon bundles. Another critical aspect of Mo is its reduction to molybdenum

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carbides at the initial stages of the reaction. Ni and Mo both serve TCD of CH_4 and CNT formation in different ways. The former is responsible for the dissociation of CH_4 into H_2 and elemental carbon while the latter serves as a reservoir for carbon diffusion. The presence of Mo as a promoter impregnated on Al_2O_3 in Ni-based catalysts provided strong MSI and minimized sintering of material and ultimately increase the catalytic stability [65]. It was also observed in the above study that TCD of CH_4 is not affected by the surface measurements of the catalyst [65].

Awadallah et al. [43] studied the effects of Co loadings on Mo/Al_2O_3. The results summarized that CH_4 conversions and diameter of CNF increased intermittently with higher metal loadings despite the decline in surface area which confirmed that TCD is a metal-catalyzed reaction. The presence of ample amount of Co_3O_4 on the surface of the catalyst boosted the catalyst stability. The transition metals of group Ⅵ (Mo, Cr, W) were impregnated with Co/MgO [45]. The results revealed that the CH_4 decompositions were stable for longer runs due to the formation of mixed oxides, i.e. $CoMO_4$ and $CoWO_4$ which increased the dispersion and stabilization of Co particles. The carbon yield exhibited was in the order of Mo > W > Cr. Bimetallic metals of group VIII Ni, Fe and Co supported on MgO with a total metal content of 50%. They were tested for non-oxidative decomposition of CH_4 [48]. Fe−Co/MgO achieved the highest catalytic stability due to the presence of Fe_2O_3 and Co_3O_4 on the surface of MgO resulting in higher adsorption and solubility of CH_4. Besides these results, the CH_4 decompositions declined for Ni−Fe and Ni−Co based catalyst due to the formation on stable, robust solution $Mg_x Ni_{(1-x)} O$. The authors believed that it was difficult to remove Ni species from inactive $Mg_x Ni_{(1-x)} O$ because of powerful MSI. Additionally, RAMAN revealed that the degree of graphitization and crystallinity was high in Fe−Co/MgO as compared to the Ni-based catalyst.

Reasonable results were reported elsewhere [42] as CH_4 conversions increased with higher loadings of cobalt in Co−W/MgO. Presence of large quantities of Co on the surface of the MgO was the primary reason for substantial diffusion of feedstock. Ahmad et al. [66] highlighted the effects of varying the composition of catalyst support on 50% Ni-based catalyst. Different compositions of CeO_2 and Al_2O_3 as catalyst supporters were synthesized by co-precipitation method and later were impregnated with 50%Ni. The conversions of CH_4 are strongly dependent on the amount of CeO_2 in the catalyst while it also affected the surface properties. The addition of CeO_2 to Al_2O_3 avoided the formation of inactive $NiAl_2O_4$ as confirmed by TPR analysis.

Apart from Ni, numerous works have been done on investigating the stability and activity of the Fe-based catalyst. Al-Fatesh et al. [67] studied the effects of modifying Fe/MgO catalyst by Ni, Co and Mn additives. Both CH_4 conversions and H_2 yields were enhanced in the presence of metal additives in the order of Ni> Co> Mn. It is believed that the catalytic activity is rational to the surface area of the catalyst. However, the authors observed that the activities are dependent on the interaction between metal additives and the availability of active sites. Some other similar studies were also given elsewhere [65].

Ahmad et al. [68] worked on Ce and Co-based Fe/Al_2O_3. It was concluded that the catalyst reduced at higher temperature showed a decline in performance due to the sintering of the active sites. Furthermore, the addition of Co and Ce in the bimetallic catalyst provides two types of active sites thus favoring the reaction yields. Additionally, the conversions increased with higher Co loadings [29]. So, it was found that 15% Co coupled with 30%Fe/Al_2O_3 holds appropriate MSI and metal dispersion that leads to the excellent performance of the catalyst [53]. In another different study compositions of Ni, Co over Al_2O_3 was studied for TCD of CH_4. The best results were produced

by using 25% each of Ni and Co (25%NiCoAl). The presence of Co-leads in the formation of thick wall highly stable MWCNT [69].

The same group of scholars [70] studied the effect of preparation method and calcination temperature on the catalytic stability of Ni−Fe/Al$_2$O$_3$. The results depicted that the CH$_4$ conversions and carbon morphology is dependent on metal additives, synthesis procedure, and calcination temperatures. The impregnation method gave the highest yields as compared to co-precipitation and sol-gel method irrespective of the calcination temperatures. It was also noticeable that XRD analysis at higher calcination temperatures detected additional peaks of metal aluminates. Wasim et al. [71, 72] employed La$_2$O$_3$ as catalyst support for Ni−Co catalyst. 12.5% of Ni and Co were found to be the optimum composition of the catalyst. The conversions were directly proportional to the reaction temperature owing to the endothermic nature of the reaction while declined with the rise in GHSV. The authors reported CDM as a four-step mechanism which included breakage of CH$_4$ bonds, the release of H$_2$, carbon diffusion and formation and accumulation of CNF over the surface of the catalyst. Moreover, the rise in calcination temperatures also affected the catalytic performance due to the destruction of active sites of the catalyst.

The study on optimizing TCD of CH$_4$ over bimetallic catalyst was carried on by Bayat et al. [73] with different catalyst compositions and metal additives. The authors impregnated Cu with Ni/Al$_2$O$_3$. The study revealed that the addition of Cu as promoter enhance TCD in several ways including high metal dispersion, reducibility, and rates of CH$_4$ adsorption. Moreover, the high affinity of Cu with graphene inhibits the formation of encapsulating carbon and keeps the Ni surface fresh for CH$_4$ diffusions [74]. This observation was also seen in the study made by Kumar et al. [75]. The successful impregnation of Ni and Cu on Al$_2$O$_3$ synthesized formerly by sol-gel

method resulted in the formation of mixed oxides $Ni_x Cu_{(1-x)} O$ species and Ni−Cu alloy in the calcined and reduced catalyst. Along with Cu, Pd is also regarded as a strong promoter in catalytic decomposition of CH_4 into CO_X free H_2 and CNF. Improved catalytic activity and thermal stability are the results of impregnating Pd on Ni-based catalysts [55]. Bayat et al. [76] suggested that the rate of carbon diffusion in Pd is faster as compared to Ni. This aspect results in increasing the diffusion rate of carbon inhibits the formation of encapsulating carbon over Ni. Additionally, during CDM reaction carbon grows from several facets of Ni−Pd alloy forming branched carbon that boosts up catalyst stability and activity. Supportive results were elaborated by the same group in which the authors impregnated Fe on Ni/Al_2O_3 [77]. The addition of Fe improved the conversions at higher temperatures due to its high ability to diffuse carbon thus avoiding the formation of encapsulating carbon. It is also reported that though Fe based catalyst results in fewer conversions as compared to Ni-based. Since the diffusion rate of carbon in the former catalyst is much higher compared to the later one [78]. Many studies have been devoted to modifying the supports by co-precipitating a couple of oxides together. Ahmad et al. [66] synthesized $CeO_2−Al_2O_3$ as a catalyst support and demonstrated that the conversion of CH_4 was mostly dependent on CeO_2 content. In another work by Rastegarpanah et al. [79, 80], it was concluded that $MgO−Al_2O_3$ performed well under a specified set of conditions. The effects of $TiO_2−Al_2O_3$ were also reported by [38]. The catalytic activity and stability of various catalyst having different supporters and reaction conditions in FBR in TCD for bimetallic catalyst have been furnished in Table 2.

Table 2: Catalytic activity and stability of various catalysts having different supporters and reaction conditions in FBR in TCD

S. No	Metal	Support	[a]Wc (g)	Preparation	S.A $m^2\,g^{-1}$	[d]T_R (K)	[e]R_T (h)	Conversion/Yield (%)	Carbon	Ref
1.	Ni-Cu	Al	0.3	F.M[b]	-	973	8	[f]75	-	[60]
2.	Ni-Cu	Mg	0.3	F.M[b]	-	1073	8	[f]79	-	[61]
3.	Ni-Cu	SiO$_2$	0.3	F.M[b]	-	1073	8	[f]79	-	[62]
4.	Ni-Cu	TiO$_2$	0.3	F.M[b]	-	1073	8	[f]80	-	[63]
5.	50%Fe-5%Mo	Al$_2$O$_3$	0.15	I.M[c]	193	1073	3	[f]16	[h]5.9	[39]
6.	50%Fe-7.5%Mo	MgO	0.15	I.M[c]	15.3	1073	3	[f]28	[h]4.75	[39]
7.	Ni−Cu	MgO	0.2	I.M[c]	-	843	4	[f]58	[h]5.85	[81]
8.	Ni−Mo	MgO	0.2	I.M[c]	-	843	4	[f]15	[h]3.90	[81]
9.	Ni−Co	MgO	0.2	I.M[c]	-	843	4	[f]14	-	[81]
10.	Ni−Mo	Al$_2$O$_3$	0.5	I.M[c]	-	1073	8	-	[i]669	[64]
11.	5.2%Ni−10.96%Mo	Al$_2$O$_3$	0.5	I.M[c]	127.9	973	8	[f]70	[i]341	[65]
12.	10%Ni−9.5%Mo	Al$_2$O$_3$	0.5	I.M[c]	101.2	973	8	[f]80	[i]612	[65]
13.	20%Ni−8.5%Mo	Al$_2$O$_3$	0.5	I.M[c]	89.2	973	8	[f]81	[i]834	[65]
14.	30%Ni−7.5%Mo	Al$_2$O$_3$	0.5	I.M[c]	91.3	973	8	[f]82	[i]1009	[65]
15.	40%Ni−6.5%Mo	Al$_2$O$_3$	0.5	I.M[c]	71.4	973	8	[f]82	[i]1379	[65]
16.	3.1%Co−10.5%Mo	Al$_2$O$_3$	0.5	I.M[c]	190.9	973	8	[f]15	[i]55	[43]
17.	10%Co−9.3%Mo	Al$_2$O$_3$	0.5	I.M[c]	177.4	973	8	[f]65	[i]762	[43]

S. No	Metal	Support	(a)Wc (g)	Preparation	S.A $m^2 g^{-1}$	(d)T_R (K)	(e)R_T (h)	Conversion/Yield (%)	Carbon	Ref
18.	20%Co−8.3%Mo	Al_2O_3	0.5	I.M(c)	143.9	973	8	(f)82	(i)456	[43]
19.	30%Co−7.3%Mo	Al_2O_3	0.5	I.M(c)	124.8	973	8	(f)83	(i)517	[43]
20.	40%Co−6.3%Mo	Al_2O_3	0.5	I.M(c)	107.6	973	8	(f)84	(i)568	[43]
21.	20%Ni−20%Co	Al_2O_3	0.3	I.M(c)	151	973	5	(g)70	(i)600	[69]
22.	22%Ni−22%Co	Al_2O_3	0.3	I.M(c)	150	973	5	(g)72	(i)700	[69]
23.	25%Ni−25%Co	Al_2O_3	0.3	I.M(c)	120	973	5	(g)74	(i)850	[69]
24.	27%Ni−27%Co	Al_2O_3	0.3	I.M(c)	123	973	5	(g)73	(i)720	[69]
25.	30%Ni−30%Co	Al_2O_3	0.3	I.M(c)	127	973	5	(g)70	(i)650	[69]
26.	25%Co−25%Cr	MgO	0.5	I.M(c)	39.8	973	7	(g)73	(h)1.6	[45]
27.	25%Co−25%Mo	MgO	0.5	I.M(c)	50.7	973	7	(g)81	(h)2.38	[45]
28.	25%Co−25%W	MgO	0.5	I.M(c)	34.5	973	7	(g)76	(h)2.04	[45]
29.	40%Co−10%W	MgO	0.5	I.M(c)	38.1	973	7	(g)85	(i)280	[42]
30.	30%Co−20%W	MgO	0.5	I.M(c)	36.8	973	7	(g)73	(i)237	[42]
31.	20%Co−30%W	MgO	0.5	I.M(c)	29.5	973	7	(g)69	(i)229	[42]
32.	10%Co−40%W	MgO	0.5	I.M(c)	16.7	973	7	(g)20	(i)51	[42]
33.	25%Fe−25%Co	MgO	0.5	I.M(c)	52.7	973	7	(f)82	(i)340	[48]
34.	25%Ni−25%Fe	MgO	0.5	I.M(c)	68.2	973	7	(f)16	(i)411	[48]
35.	25%Ni−25%Co	MgO	0.5	I.M(c)	24.1	973	7	(f)13	(i)766	[48]

S. No	Metal	Support	(a)Wc (g)	Preparation	S.A $m^2\,g^{-1}$	(d)T_R (K)	(e)R_T (h)	Conversion/Yield (%)	Carbon	Ref
36.	60%Ni	15%TiO_2−Al_2O_3	0.5	I.M(c)	94	973	7	(f)25	(i)126	[38]
37.	60%Ni	25%TiO_2−Al_2O_3	0.5	I.M(c)	135	973	7	(f)60	(i)504	[38]
38.	60%Ni	50%TiO_2−Al_2O_3	0.5	I.M(c)	70	973	7	(f)65	(i)413	[38]
39.	Ni−Pd	$MgAl_2O_4$	1	-	29.38	973	5	(f)43	-	[50]
40.	Ni−Co	SBA−15	3	I.M(c)	312.0	973	5	(f)44	(i)257	[47]
41.	Ni−Fe	SBA−15	3	I.M(c)	294.0	973	5	(f)41	(i)233	[47]
42.	Co−Fe	SBA−15	3	I.M(c)	286.0	973	5	(f)46	(i)233	[47]
43.	50%Ni−0.2%Pd	SBA−15	1	I.M(c)	198.2	973	7	(f)45	(i)489	[49]
44.	50%Ni−0.4%Pd	SBA−15	1	I.M(c)	201.8	973	7	(f)50	(i)489	[49]
45.	12.5%Ni−12.5%Co	La_2O_3	0.3	I.M(c)	63.3	973	5	(f)77	-	[72]
46.	50%Ni-5%Fe	Al_2O_3	0.05	I.M(c)	83.7	948	11	(g)35	-	[77]
47.	50%Ni-10%Fe	Al_2O_3	0.05	I.M(c)	78.8	948	11	(g)70	-	[77]
48.	50%Ni-15%Fe	Al_2O_3	0.05	I.M(c)	74.8	948	11	(g)68	-	[77]
49.	7.39%Ni−7.28%Co	La_2O_3	0.3	I.M(c)	30.19	973	5	(g)70	(i)20	[71]
50.	9.81%Ni−9.72%Co	La_2O_3	0.3	I.M(c)	61.64	973	5	(g)79	(i)50	[71]
51.	11.32%Ni−12.11%Co	La_2O_3	0.3	I.M(c)	63.32	973	5	(g)80	(i)90	[71]
52.	14.75%Ni−13.92%Co	La_2O_3	0.3	I.M(c)	56.02	973	5	(g)79	(i)60	[71]
53.	18.85%Ni−19.63%Co	La_2O_3	0.3	I.M(c)	48.45	973	5	(g)78	(i)35	[71]
54.	Ni−Pd	Al_2O_3	-	I.M(c)	212.80	1073	4	(g)40	-	[55]
55.	65%Ni−10%Cu	SiO_2	-	-	37.70	923	6	(g)43	-	[82]

S. No	Metal	Support	$^{(a)}$Wc (g)	Preparation	S.A m^2 g^{-1}	$^{(d)}T_R$ (K)	$^{(e)}R_T$ (h)	Conversion/Yield (%)	Carbon	Ref
56.	50%Ni−20%Cu	SiO$_2$	-	-	27.83	923	6	$^{(g)}$27	-	[82]
57.	5%Ni−Cu	Al$_2$O$_3$	2.5	I.M$^{(c)}$	63.80	1123	4	$^{(f)}$40	-	[83]
58.	10%Ni−Cu	Al$_2$O$_3$	2.5	I.M$^{(c)}$	84.10	1123	4	$^{(f)}$58	-	[83]
59.	15%Ni−Cu	Al$_2$O$_3$	2.5	I.M$^{(c)}$	42.60	1123	4	$^{(f)}$52	-	[83]
60.	20%Ni−Cu	Al$_2$O$_3$	2.5	I.M$^{(c)}$	34.30	1123	4	$^{(f)}$37	-	[83]
61.	50%Ni-5%Pd	Al$_2$O$_3$	0.05	I.M$^{(c)}$	72.75	1023	10	$^{(g)}$65	$^{(j)}$360	[76]
62.	50%Ni-10%Pd	Al$_2$O$_3$	0.05	I.M$^{(c)}$	45.81	1023	10	$^{(g)}$72	$^{(j)}$380	[76]
63.	50%Ni-15%Pd	Al$_2$O$_3$	0.05	I.M$^{(c)}$	26.91	1023	10	$^{(g)}$81	$^{(j)}$400	[76]
64.	50%Ni-20%Pd	Al$_2$O$_3$	0.05	I.M$^{(c)}$	12.36	1023	10	$^{(g)}$76	$^{(j}$410	[76]
65.	30%Fe−6%Ce	Al$_2$O$_3$	-	I.M$^{(c)}$	56.25	973	3	$^{(f)}$66	-	[68]
66.	30%Fe−15%Ce	Al$_2$O$_3$	-	I.M$^{(c)}$	52.1	973	3	$^{(f)}$62	-	[68]
67.	30%Fe−30%Ce	Al$_2$O$_3$	-	I.M$^{(c)}$	95.3	973	3	$^{(f)}$54	-	[68]
68.	50%Ni-5%Cu	Al$_2$O$_3$	0.05	I.M$^{(c)}$	72.25	1023	11	$^{(g)}$20	-	[73]
69.	50%Ni-10%Cu	Al$_2$O$_3$	0.05	I.M$^{(c)}$	70.34	1023	11	$^{(g)}$79	-	[73]
70.	50%Ni-15%Cu	Al$_2$O$_3$	0.05	I.M$^{(c)}$	51.89	1023	11	$^{(g)}$84	-	[73]
71.	30%Fe−15%Ni	Al$_2$O$_3$	0.3	I.M$^{(c)}$	132.5	973	3	$^{(g)}$73	-	[53]
72.	30%Fe−15%Co	Al$_2$O$_3$	0.3	I.M$^{(c)}$	133.6	973	3	$^{(g)}$74	$^{(h)}$15	[53]
73.	5%Ni−20%Fe	Al$_2$O$_3$	0.3	I.M$^{(c)}$	147.7	973	3	$^{(g)}$65	-	[70]
74.	10%Ni−20%Fe	Al$_2$O$_3$	0.3	I.M$^{(c)}$	140.6	973	3	$^{(g)}$66	-	[70]
75.	30%Fe−6%Co	Al$_2$O$_3$	0.3	I.M$^{(c)}$	43.4	973	3	$^{(g)}$66	-	[29]

S. No	Metal	Support	$^{(a)}$Wc (g)	Preparation	S.A $m^2\ g^{-1}$	$^{(d)}T_R$ (K)	$^{(e)}R_T$ (h)	Conversion/Yield (%)	Carbon	Ref
76.	30%Fe−15%Co	Al_2O_3	0.3	I.M$^{(c)}$	52.4	973	3	$^{(g)}$74	-	[29]
77.	30%Fe−30%Co	Al_2O_3	0.3	I.M$^{(c)}$	72	973	3	$^{(g)}$71	-	[29]
78.	50%Ni	25%CeO$_2$−75% Al$_2$O$_3$	0.5	I.M$^{(c)}$	34	973	6	$^{(f)}$52	-	[66]
79.	50%Ni	50%CeO$_2$−50% Al$_2$O$_3$	0.5	I.M$^{(c)}$	51	973	6	$^{(f)}$40	-	[66]
80.	50%Ni	75%CeO$_2$−25% Al$_2$O$_3$	0.5	I.M$^{(c)}$	69	973	6	$^{(f)}$42	-	[66]
81.	15%Fe−6%Ni	MgO	0.3	I.M$^{(c)}$	100	973	3	$^{(g)}$66	$^{(h)}$16.26	[67]
82.	15%Fe−6%Co	MgO	0.3	I.M$^{(c)}$	86	973	3	$^{(g)}$69	$^{(h)}$15.06	[67]
83.	15%Fe−6%Mn	MgO	0.3	I.M$^{(c)}$	122	973	3	$^{(g)}$68	$^{(h)}$15.49	[67]
84.	5%Fe−1%Mo	MgO	0.5	I.M$^{(c)}$	90	1173	-	-	$^{(i)}$32.3	[57]
85.	5%Fe−1%Cu	MgO	0.5	I.M$^{(c)}$	54	1173	-	-	$^{(i)}$5.8	[57]
86.	50%Ni	SiO$_2$− Al$_2$O$_3$	0.5	I.M$^{(c)}$	107	973	3	$^{(f)}$60	-	[84]
87.	50%Ni	SiO$_2$−CeO$_2$	0.5	I.M$^{(c)}$	37	973	3	$^{(f)}$55	-	[84]
88.	50%Ni	SiO$_2$−La$_2$O$_3$	0.5	I.M$^{(c)}$	44	973	3	$^{(f)}$58	-	[84]
89.	50%Ni	SiO$_2$− MgO	0.5	I.M$^{(c)}$	54	973	3	$^{(f)}$13	-	[84]
90.	55%Ni	MgO−Al$_2$O$_3$	0.025	-	66.31	948	5	$^{(g)}$8	$^{(j)}$140	[80]
91.	55%Ni−10%Ce	MgO−Al$_2$O$_3$	0.025	-	55.06	948	5	$^{(g)}$12	$^{(j)}$150	[80]
92.	55%Ni−10%Co	MgO−Al$_2$O$_3$	0.025	-	46.84	948	5	$^{(g)}$12	$^{(j)}$120	[80]
93.	55%Ni−10%Cu	MgO−Al$_2$O$_3$	0.025	-	43.57	948	5	$^{(g)}$10	$^{(j)}$280	[80]
94.	55%Ni−10%Fe	MgO−Al$_2$O$_3$	0.025	-	66.18	948	5	$^{(g)}$13	$^{(j)}$100	[80]
95.	55%Ni−10%La	MgO−Al$_2$O$_3$	0.025	-	41.86	948	5	$^{(g)}$11	$^{(j)}$120	[80]

S. No	Metal	Support	[a]Wc (g)	Preparation	S.A $m^2 g^{-1}$	[d]T_R (K)	[e]R_T (h)	Conversion/Yield (%)	Carbon	Ref
96.	10%Ni	0.5%MgO−Al$_2$O$_3$	0.025	-	236.0	973	5	[f]05	-	[79]
97.	10%Ni	1.0%MgO−Al$_2$O$_3$	0.025	-	224.0	973	5	[f]06	-	[79]
98.	10%Ni	1.5%MgO−Al$_2$O$_3$	0.025	-	216.0	973	5	[f]08	-	[79]
99.	10%Ni	2.0%MgO−Al$_2$O$_3$	0.025	-	220.0	898	5	[g]04	-	[79]
100.	25%Ni	2.0%MgO−Al$_2$O$_3$	0.025	-	149	898	5	[g]05	-	[79]
101.	40%Ni	2.0%MgO−Al$_2$O$_3$	0.025	-	105	898	5	[g]13	-	[79]
102.	55%Ni	2.0%MgO−Al$_2$O$_3$	0.025	-	66	898	5	[g]20	-	[79]
103.	6%Ni-30%Fe	Al$_2$O$_3$	0.3	I.M[c]	135.5	973	3	[g]61	-	[85]
104.	15%Ni-30%Fe	Al$_2$O$_3$	0.3	I.M[c]	132.5	973	3	[g]62	-	[85]
105.	30%Ni-30%Fe	Al$_2$O$_3$	0.3	I.M[c]	130.0	973	3	[g]56	-	[85]
106.	6%Mn-30%Fe	Al$_2$O$_3$	0.3	I.M[c]	143.9	973	3	[g]11	-	[85]
107.	15%Mn-30%Fe	Al$_2$O$_3$	0.3	I.M[c]	131.1	973	3	[g]10	-	[85]
108.	30%Mn-30%Fe	Al$_2$O$_3$	0.3	I.M[c]	123.8	973	3	[g]13	-	[85]

2.3. Tri-metallic Catalyst

summarized various contributions relevant to this study. Moreover, the effects of monometallic and bimetallic have been explained in Tables 1 and 2 respectively. Although the CH_4 yields were improved with higher metal loadings and shifting from mono metallic to bimetallic due to alloying effect, some of the scholars tried to further optimize the process by taking into account the effectiveness of commissioning trimetallic catalyst for CO_X free H_2 production [86, 87].

Kumar et al. [88, 89] synthesized different compositions of Ni−Cu−Zn/MCM 22. The catalytic stability was widely explored over reaction temperature, metal loadings, and GHSV. It was depicted that the combination of Cu and Zn enhanced the CH_4 conversions and H_2 yields. Interestingly, the carbon yield also increased by incrementing the loadings of Cu and Zn which proved that the carbon diffusion rate of the promoted catalyst was improved as compared to the un-promoted Ni-based catalyst. This suggests that bimetallic promoters are more active catalysts as compared to monometallic promoters. Pure H_2 and unreacted CH_4 were the only gaseous products detected by gas chromatography, whereas TEM analysis confirmed the formation of MWCNT as by-product deposited on the surface of the catalyst.

Bayat et al. [90] worked on Fe−Cu promoted Ni/Al_2O_3 catalyst. The addition of Fe and Cu in the metallic catalyst amended the catalytic stability. The promoting effect enhanced the carbon diffusion rates and hindered the formation of encapsulated carbon over the active sites. Moreover, the degree of reducibility and the dispersion of NiO on the support was also improved. The performance evaluation of the catalyst revealed that bi-promoted catalyst performed well at higher reaction temperatures. Similar results were also reported in [91] where the authors mentioned that the modification of Ni-based catalyst with Fe and Cu made it possible to carry the TCD reactions

above 973 K without affecting the physiochemical properties and stability of the materials. The effects of impregnating Ni and Co on Fe based catalyst was also studied [53] in detail, and both CH_4 conversions and stability of the catalyst were increased. Catalytic activity and stability of various trimetallic catalyst having different supporters and reaction conditions in FBR in TCD have been summarized in Table 3.

It can be concluded from the forementioned discussion that Ni-based catalysts are frequently used in reforming reactions due to their low cost, easy availability and highly reactive nature. The applications of these catalysts are also evident in the thermocatalytic decomposition of methane, but the only limitation that restricts industrial usage is its fast deactivation due to encapsulation of low active carbon produced as a by-product. The reaction rate of TCD is very high due to highly active nature of Ni, and hence ample amount of carbon is produced but the low diffusion rate of carbon in Ni forces the material to lose its catalytic stability and activity shortly. Hence, the impregnation of monometallic and bimetallic promoters on the Ni-based catalyst is proposed to be an active solution to this issue as explained in Sections 2.2 and 2.3 respectively.

Table 3: Catalytic activity and stability of various trimetallic catalysts having different supporters and reaction conditions in FBR in TCD

S. No	Metal	Support	[a]Wc (g)	Preparation	S.A $m^2\ g^{-1}$	[d]T_R (K)	[e]R_T (h)	Conversion/Yield (%)	Carbon	Ref
1.	50%Ni−5%Cu−5%Zn	MCM−22	1	I.M[c]	19	1023	-	[g]84	[i]900	[88]
2.	50%Ni−10%Cu−10%Zn	MCM−22	1	-	19	1023	-	[g]87	-	[89]
3.	50%Ni−15%Cu−5%Zn	MCM−22	1	-	14	1023	-	[g]80	-	[89]
4.	50%Ni−5%Cu−15%Zn	MCM−22	1	-	12	1023	-	[g]70	-	[89]
5.	50%Ni−15%Cu−15%Zn	MCM−22	1	-	07	1023	-	[g]74	-	[89]
6.	30%Fe−5%Ni−10%Co	Al_2O_3	0.3	I.M[c]	131.1	973	3	[g]67	-	[53]
7.	30%Fe−7.5%Ni−7.5%Co	Al_2O_3	0.3	I.M[c]	142.2	973	3	[g]68	-	[53]
8.	30%Fe−10%Ni−5%Co	Al_2O_3	0.3	I.M[c]	138.4	973	3	[g]70	-	[53]
9.	50%Ni−10%Fe−5%Cu	Al_2O_3	0.05	I.M[c]	73.3	1023	10	[g]70	-	[90]
10.	50%Ni−10%Fe−10%Cu	Al_2O_3	0.05	I.M[c]	59.7	1023	10	[g]81	-	[90]
11.	50%Ni−10%Fe−15%Cu	Al_2O_3	0.05	I.M[c]	51.0	1023	10	[g]82	-	[90]
12.	Fe−Mo−Cu	MgO	0.5	I.M[c]	67	1173	-	-	[i]14.2	[57]

3. TCD Parameters

TCD of CH_4 is an endothermic process that is strongly affected by the reaction parameters, i.e. reaction temperature, GHSV, and metal loadings. It is also proposed that the morphology of the carbon deposited on the surface of the catalyst also depend upon the reaction parameters [24]. Therefore, to obtain higher CH_4 conversions and increase the catalyst deactivation time, it is mandatory to have an optimum set of conditions. The individual impact of independent factors of CH_4 decomposition has been discussed in subsequent sections.

3.1. Reaction Temperature

The reaction temperature has a very significant role in the CH_4 conversions and catalyst stability. It is well understood that the product formation increases with the reaction temperatures due to the endothermic nature of the reaction, but the catalyst stability is affected due to the deposition of high amounts of carbon produced as a result of fast reaction rates [92].

The CH_4 cracking reaction by using Ni supported on SiO_2, Al_2O_3, MgO, and ZrO_2 was studied by Ermakova et al. [93]. The high catalytic stability was attained at temperatures ranges of 773−823 K, but at a higher temperature (873 K), the conversions dropped rapidly. It was reported that at 873 K the rate of carbon formation as a by-product was higher than the rate of carbon diffusion. Therefore, it grew on the active sites of the catalyst resulting in their early deactivation. In another work done by Martins et al. [94], the effects of reaction temperature over Ni−Cu/SiO_2 were studied. The catalyst gave uniform conversions at 773 K, but the conversion declined when TCD was carried out at a temperature higher than 873 K. The possible reason for the loss in activity was found to be the sintering and encapsulation of carbon on the active sites. The effect of reaction temperature was also explored by Pinilla et al. [39]. The study was done on Fe−Mo/MgO. The results were consistent with the above discussion as the initial H_2 yields were increased with

reaction temperature, but with time on stream (TOS) the yields dropped. The principal reason attributed to this observation was the high reaction rate at mounted temperatures which produces ample amount of carbon. This carbon is deposited over the surface of the catalyst instead of diffusing. Moreover, at higher reaction temperatures the catalyst loses its morphology due to sintering. The H_2 yield at different reaction temperatures has been depicted in Fig 2.
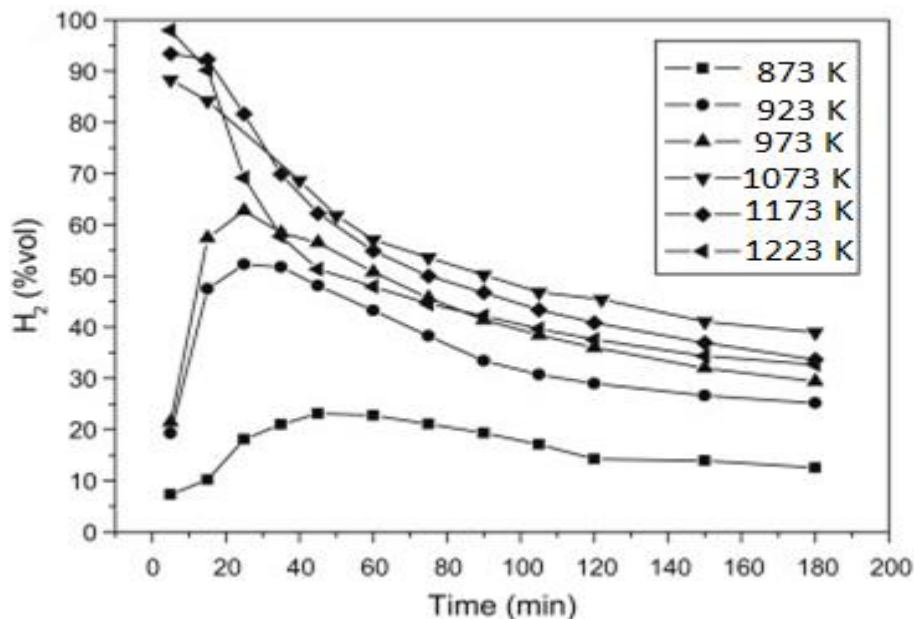
Fig 2: Influence of reaction temperature on H_2 yield over Fe−Mo/MgO; Reproduced with

permission from Pinilla, Copyright 2011 Elsevier [39]

3.2. Gas Hour Space Velocity

The CH_4 conversions are also strongly affected by GHSV. Kumar et al. [75] studied the effect of GHSV over various catalysts. Author conducted a series of experiments to elaborate the effect of GHSV (600−3000 mL $h^{-1}g_{cat}^{-1}$) at 1023 K. The highest activity of the catalyst 50%Ni−xCu/SiO$_2$ (x= 0%, 5%, and 10%) was observed at lowest GHSV, i.e. 600 mL $h^{-1}g_{cat}^{-1}$. As the GHSV was increased, the CH_4 conversions and carbon yields dropped because of relatively less diffusion time available to feedstock on the active sites of the catalyst as shown in Fig 3. It was concluded that sufficient contact time of CH_4 with the catalyst at lower GHSV was the driving factor that resulted

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in better performance. Additionally, at higher flow rates the carbon depositions are high that damage the active sites of the catalyst. To optimize the process, the flow rate should be in optimum range to provide adequate contact time to the feedstocks and to promote equilibrium between the amounts of carbon formed and diffused. Similar results were also published by Bayat et al. [73] over 50%Ni-10%Cu/Al$_2$O$_3$ at GHSV (10,000−50,000 mL h^{-1}g$_{cat}^{-1}$) at 948 K.
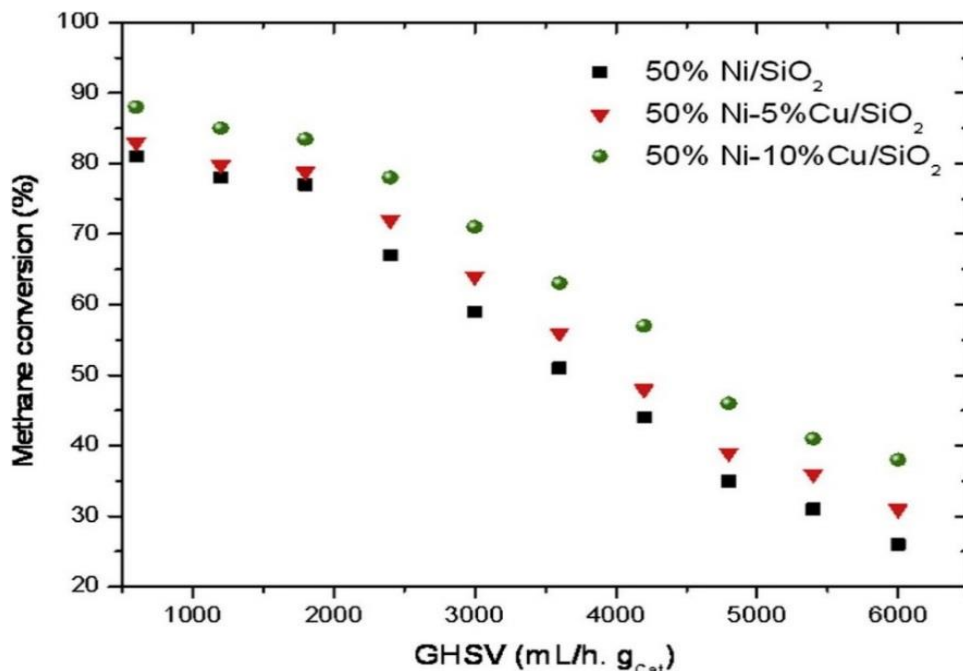
Fig 3: GHSV of reactant vs Catalytic Activity at 1023 K; Reproduced with permission from

Saraswat, Copyright 2013 Elsevier [75]

3.3. Metal loadings

3.3.1. Performance of Catalyst

The effects of metal loadings are highly significant in TCD of CH$_4$. Manoj Pudukudy et al. [37] compared the effects of increasing metal loadings on the catalyst support. The authors impregnated 10−50% Ni on TiO$_2$ and performed TCD at 973 K. The results showed that the CH$_4$ conversions increased periodically with an increase in metal loadings. The high performance of 50%Ni/TiO$_2$ was due to the increased availability of NiO on the surface of the catalyst. The effects of increasing

the amount of Cu impregnated on Ni/Al_2O_3 was also reported in [73]. The addition of higher amounts of Cu drastically increased the CH_4 conversions and catalyst stability by keeping the catalyst surface and active surface clean for CH_4 dissociation. By increasing the amount of Cu to 15%, an increase in CH_4 was observed. However, a further increase in the Cu content reduced the stability due to the quasi-liquid state of the catalyst. Similar discussions were also made by other researchers where the conversions increased linearly with the metal loading to a certain extent and then dropped drastically owing to the agglomeration of the particles [89, 90]. The CH_4 conversions along with metal compositions of some of the catalysts have been presented in Table 4.

Table 4: Effect of Metal Loadings *

Sr. No	Metal Loadings	*Conversion/Yield (%)	Ref
1.	10%Ni/TiO$_2$	[a]27	[37]
2.	20%Ni/TiO$_2$	[a]30	[37]
3.	30%Ni/TiO$_2$	[a]33	[37]
4.	40%Ni/TiO$_2$	[a]37	[37]
5.	50%Ni/TiO$_2$	[a]42	[73]
6.	50%Ni-5%Cu/Al$_2$O$_3$	[b]20	[73]
7.	50%Ni-10%Cu/Al$_2$O$_3$	[b]79	[73]
8.	50%Ni-15%Cu/Al$_2$O$_3$	[b]84	[73]
9.	50%Ni−10%Fe−5%Cu/Al$_2$O$_3$	[b]70	[90]
10.	50%Ni−10%Fe−10%Cu/Al$_2$O$_3$	[b]81	[90]

*Dependent on reaction conditions [a] H_2 Yield [b] CH_4 Conversions

3.3.2. Morphology of Carbon

The effect of metal loadings on the morphology of the carbon deposited on the surface of the catalyst was discussed by Awadallah et al. [43]. The authors reported that wider CNF is formed because of impregnating higher metal loadings on the support. It is reported that the growth mechanism of CNF takes place in the following steps.

- Dissociation of CH_4 over the surface of the catalyst to evolve H_2 and elemental carbon.

- Diffusion of carbon through the metals.

- Formation of CNF on the active sites of the catalyst.

Interestingly, the metal support interaction (MSI) affected the morphology of the carbon. At low metal loadings, the base growth mechanism (BGM) dominates while in higher metal loadings, tip growth mechanism (TGM) plays its role. Therefore, larger and broader CNF and CNT are formed at higher metal loadings due to particle agglomerations and tip growth mechanism. Fig 4 shows the TEM images of carbon formed on 10%Co−Mo/Al_2O_3 and 20%Co−Mo/Al_2O_3 respectively.
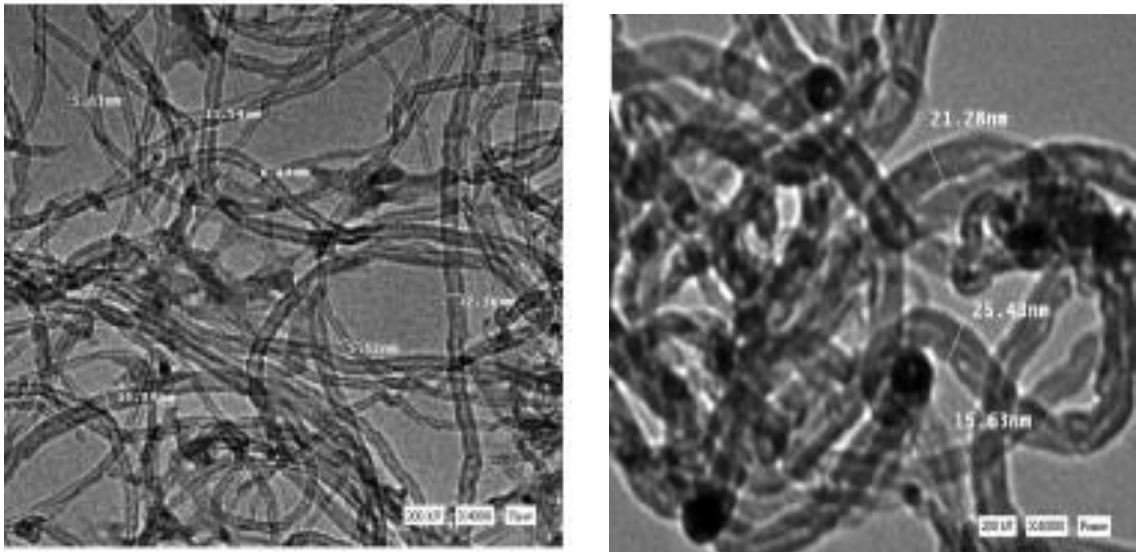
Fig.4: TEM images of carbon formed (a) 10%Co−Mo/Al_2O_3 (b) 20%Co−Mo/Al_2O_3 ;Reproduced with permission from A. E. Awadallah, Copyright 2014 Elsevier [43]

Therefore, to obtain maximum output from the catalyst as of CH_4 conversions, an optimum set of reaction parameters is an essential aspect. It is believed that the increase in reaction temperatures increase the CH_4 conversions but, due to the high rate of reaction, an ample amount of carbon gets accumulated on the catalyst surface and deactivates it. Furthermore, the increase in GHSV restricts the catalytic activity. The low rate of CH_4 diffusion on the surface of the catalyst, due to the

reduced contact time between the catalyst and feedstock, is often cited as a reason behind low yield at higher space velocities. The effect of higher metal loadings and the impregnation of promoters is also worth mentioning. TCD is a catalyst-based reaction, and the overall efficiency of the reaction depends upon the active sites available for CH_4 adsorption. So, better results are obtained at higher metal loadings.

4. TCD over admixtures as Feedstocks

TCD is an environmentally friendly technique to produce pure H_2 and CNF as a by-product. The major drawback of TCD limiting its industrial applications is the catalyst deactivation due to the encapsulation of less reactive carbon on the catalyst surface, which is described in the previous section [95]. The mechanism of catalyst deactivation due to deposition of carbon has been elaborated as [96, 97].

- The formation of CNF which is also called the initial stage of deactivation of the catalyst.

- The rapid deactivation of the catalyst due to the encapsulation of the active phase of the catalyst.

- The complete deactivation of the catalyst due to the detachment of metal from support.

The researchers thoroughly reviewed this problem and came up with two distinct solutions, i.e. co-feeding of CH_4 with other hydrocarbons and regeneration of spent catalyst by treating it with O_2, CO_2, and H_2O at very high temperatures [98, 99]. The co-feeding of CH_4 with other hydrocarbons, either alternatively or collectively, enhances the catalyst deactivation [23]. These hydrocarbons produce carbon which is much more reactive as compared to carbon eliminated from CH_4. The activity of carbon originating from different hydrocarbons is in of the order $C_{benzene} > C_{acetylene} > C_{ethylene} > C_{propane}$ and $C_{methane}$ [100]. Limited work has been done on co−feeding of CH_4 with other hydrocarbons to stabilize the catalyst activity and deactivation time. Most studies are carried

out on ethane [101], C_2H_4 [102, 103], C_3H_6 [100], C_2H_5OH [104, 105], CH_3OH [22, 23] and C_2H_2 [106]. Moreover, CO_2 [107] and H_2S [108] is also used as co-feed with CH_4.

4.1.Ethylene

Anna Malaika et al. [102] explored the effect of ethylene (C_2H_4) on the decomposition of CH_4 by carbon catalyzed catalysts. It was reported that although C_2H_4 also formed a carbonaceous by-product on the surface of the catalyst as compared to CH_4 originated carbon; it has better catalytic properties towards CH_4 in CDM reactions [109]. The preliminary study without catalyst resulted in the negligible conversion of CH_4. In the initial stage of the carbonaceous catalyzed reaction, the high content of H_2 and CH_4 with zero amount of C_2H_4 showed that at initial stages of TCD, activated carbon catalyze the decomposition of C_2H_4 as compared to CH_4. With TOS, the concentrations of both CH_4 and C_2H_4 reached a plateau. TCD of a mixture of CH_4 and C_2H_4 is summarized in Eqs. (7)−(9).

$$C_2H_4 \rightarrow 2C + 2H_2 \tag{7}$$

$$C_2H_4 \rightarrow C + CH_4 \tag{8}$$

$$CH_4 \rightarrow C + 2H_2 \tag{9}$$
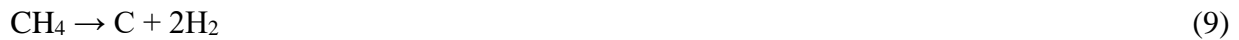
The TCD was carried out at three different reaction temperatures, and concentration of C_2H_4 in the feedstock and their effects on H_2 concentration have been explained in Fig 5. At higher reaction temperatures, the CH_4 conversions were relatively high as equilibrium constant moved towards products formation. For each catalyst and reaction temperature, the addition of C_2H_4 leads to an increase in H_2 yield and the catalyst deactivation time was decreased. C_2H_4 is expensive gas, and its usage in TCD reactions increases the overall operating cost of the process. Anna Malaika et al. [103] produced C_2H_4 in situ by oxidative coupling of CH_4 (OCM) during TCD. The OCM reaction

was carried out over Na/CaO, or Li/MgO synthesized by the impregnation method, while the TCD

catalyst was activated carbon.

The pilot study suggested that at 1123 K reaction temperature, 0.8 g of catalyst and 10% O_2 mixed

with CH_4 gave higher amounts of C_2H_4 during OCM reactions. Therefore, in the first level of

TCD−OCM reaction CH_4 mixed with oxygen was passed over metal oxide catalyst resulting in the

formation of C_2H_4. In the next stage, the unreacted CH_4 with post reaction gases was subjected to

activated carbon. It was reported that although this method can be effective in restricting the

deactivation of the catalyst, the formation of CO_2, water vapors, and unreacted C_2H_6 restricts its

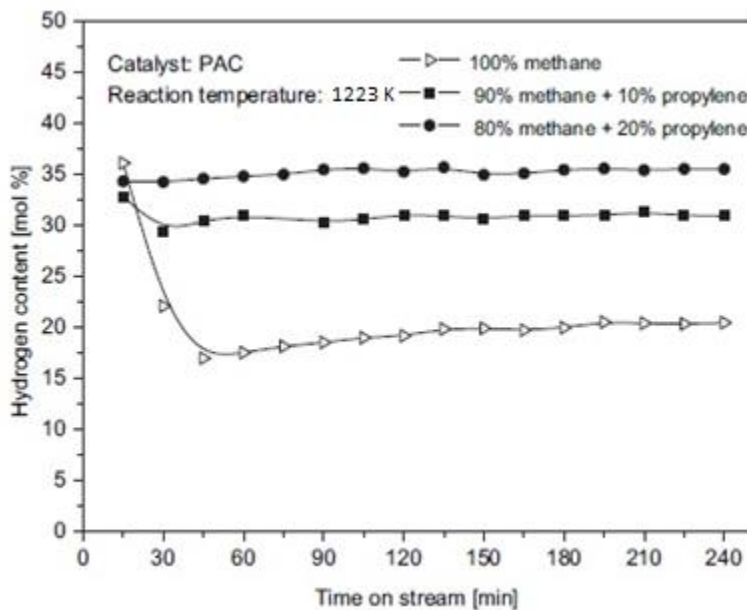applications industrially where pure H_2 is required as feedstock.
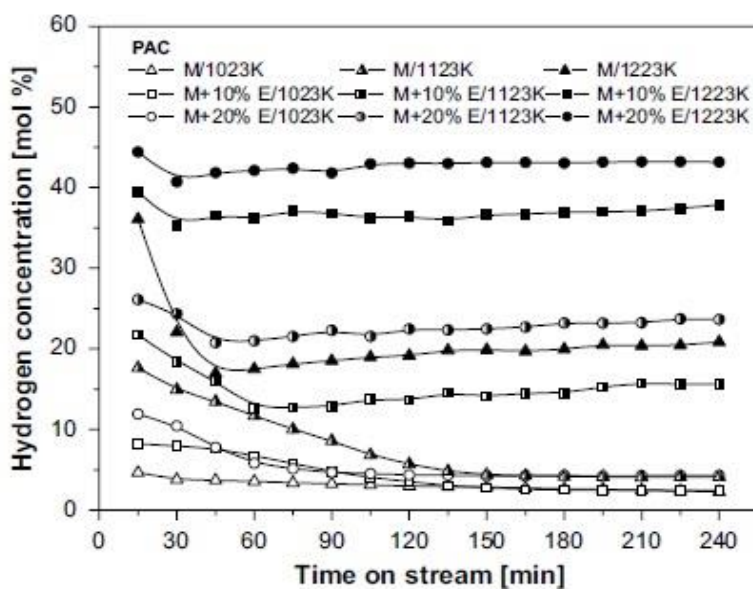
Fig 5: Influence of C_2H_4 on H_2 concentrations at different reaction parameters; Reproduced with

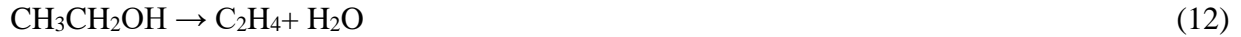permission from A. Malaika, Copyright 2009 Elsevier [102]

4.2.Propylene

The first attempt by employing propylene (C_3H_6) as co−feed with CH_4 for TCD reaction was

reported by Anna Malaika et al. [100] because C_3H_6 is cheaper than C_2H_4 as in Fig 6. It was

reported that the decomposition of C_3H_6 results in the formation of a variety of hydrocarbons

including H_2, CH_4, C_2H_4, C_3H_6, C_2H_6, and C_3H_8 thus making its reaction mechanism difficult to comprehend. Apart from the detection of these gases by chromatographic analysis of post reaction gases, the deposition of active carbon as a by-product on the surface of the catalyst was also confirmed by SEM analysis. The authors have mentioned that though H_2 is produced by the catalytic decomposition of C_3H_6 and CH_4 while also consumed by the hydrogenation of C_3H_6 and C_2H_4 into C_3H_8 and C_2H_6 respectively. Thus, the total amount of H_2 produced as the product also depends on the intake during hydrogenation reactions. The comparative study was made by using three types of activated carbon catalyst, at different reaction temperatures and different amount of C_3H_6 in the feedstock. The catalyst deactivation time improved at higher reaction temperatures due to the formation of filamentous carbon on the surface of the catalyst. Fig 6 shows that the addition of C_3H_6 has improved the H_2 production quite significantly.

Fig 6: Influence of C_3H_6 on H_2 concentrations at different reaction parameters; Reproduced with permission from A. Malaika, Copyright 2010 Elsevier [100]

4.3. Hydrogen Sulphide

The addition of hydrogen sulphide (H_2S) to catalytic decomposition of CH_4 is of great practical significance. The effects of adding a small number of H_2S (0.5−1 vol. %) in feedstock on CH_4 decomposition over activate carbon, Ni-based catalyst and a mixture of both was investigated in [108]. It was reported that the addition of 1% H_2S increased the conversion of CH_4 by 5% in the results without deactivating the carbonaceous catalyst which supports the previous study on tolerance of carbonaceous catalyst to sulphur compounds [101]. This observation makes carbon catalyst superior to the metallic catalyst in this specific area as the latter are poisoned by sulphur compounds [110]. It was also worth noted CH_4 conversions were accelerated due to the formation of HS radicles which can attack CH_4 molecules at higher temperatures resulting in CH_4 radicles and elemental carbon.

4.4. Ethanol

The effect of ethanol (C_2H_5OH) on the catalytic decomposition of CH_4 was explored by Paulina Rechnia et al. [105]. C_2H_5OH was dozed alternately with CH_4 at reaction temperatures of 1023−1223 K by using activated carbon as catalyst synthesized by hazelnut shells. The authors explained that apart from H_2, and unreacted CH_4 in the outflow stream minor concentrations of CO, CO_2, H_2O, and C_2H_6 were detected by gas chromatography. The preliminary study was made on the decomposition of un-diluted CH_4 at different reaction temperatures. The lowest CH_4 conversion was obtained at 1023 K, i.e. 3.4% that increased to 26% at 1223 K. In the next stage of the experiment, C_2H_5OH was introduced into the reactor at three different reaction temperatures. The choice of employing C_2H_5OH as an additive was based on the prior study that apart from CH_4 and H_2 production it also produces C_2H_4 which works against catalyst deactivation [100]. The decomposition of CH_4 and C_2H_5OH was carried out at the same reaction temperatures. The results

obtained at all three reaction temperatures were quite interesting. The most optimum results were obtained at 1123 K in which the cyclic addition of C_2H_5OH leads to an increase in CH_4 conversion as shown in Fig 7. It is worth noting that at 1023 K the CH_4 conversions decreased by the introducing C_2H_5OH since it was not converted completely. At 1223 K total C_2H_5OH and C_2H_4 were decomposed, and a high degree of graphitization of carbon originated from CH_4 and C_2H_5OH inhibited higher CH_4 conversions. As the amount of C_2H_5OH was increased, the concentration of CO also increased. Alternatively, the production of C_2H_4 and water as the concentration of both gases were found the same. Several other side reactions also occurred in TCD of CH_4 and C_2H_5OH. It was reported that these reactions occurred as shown in Eqs (10)−(16). [104, 111].

$$CH_3CH_2OH \rightarrow CO+H_2+CH_4 \qquad (10)$$

$$CH_3CH_2OH \rightarrow C+CO+3H_2 \qquad (11)$$

$$CH_3CH_2OH \rightarrow C_2H_4+ H_2O \qquad (12)$$

$$C_2H_4 \rightarrow 2C+ 2H_2 \qquad (13)$$

$$C_2H_4 \rightarrow C+ CH_4 \qquad (14)$$

$$H_2O+C \rightarrow CO +H_2 \qquad (15)$$

$$2H_2O+C \rightarrow CO_2 +2H_2 \qquad (16)$$
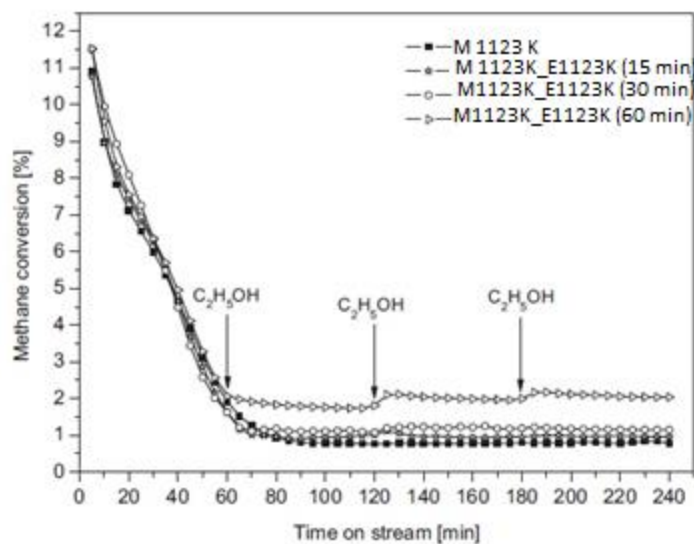
Fig 7: C_2H_5OH Assisted CH_4 decomposition at 1123 K; Reproduced with permission from P.

Rechnia, Copyright 2012 Elsevier [105]

4.5.2%Methanol/Methane

The effect of 2% premixed methanol in methane used as feedstock for TCD has been explored by our group. Different composition of Ni-based catalyst was synthesized by wet impregnation method [142]. The results showed that methane conversions increased proportionally with metal loadings and 50%Ni/Al_2O_3 gave the best results. Additionally, the addition of Pd on Ni-based catalyst having drastic effects on the activity and stability of the catalyst was also reported [149]. Furth more, the activity and stability of Cu promoted Ni-based catalyst was also evaluated in [112]

5. Kinetics and reaction mechanism of TCD

Kinetic studies are often done to find an appropriate reaction rate model that correlates the experimental data, describes the rate of reaction, the order of reaction and activation energies [113]. The proper understanding of kinetics models can further optimize the catalyst design and improves the overall efficiency of the process concerning CH_4 consumption rates and carbon depositions. SRM is often termed as one of the early methods used in industries for H_2 production,

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but the formation of ample amount of greenhouse gases opens the floor for further research in finding an environment for H_2 production [114]. TCD of CH_4 is widely explored by scholars, and a series of catalysts are being synthesized reported in the literature (c.f. Table 1-3) having specific reaction order and activation energies (c.f. Table 5) [115]. Ashik et al. [116] thoroughly studied the reaction mechanism of TCD over Ni/SiO_2 nanocatalyst prepared by co-precipitation cum modified Stober method. The studies were made around the reaction temperature of $823-923$ K and pressure of $21-81$ kPa. The CH_4 conversions increased with reaction temperature and partial pressures, but the catalyst was subjected to an early deactivation due to the formation of CNF resulted in high reaction rates at higher temperatures as shown in Fig 8.
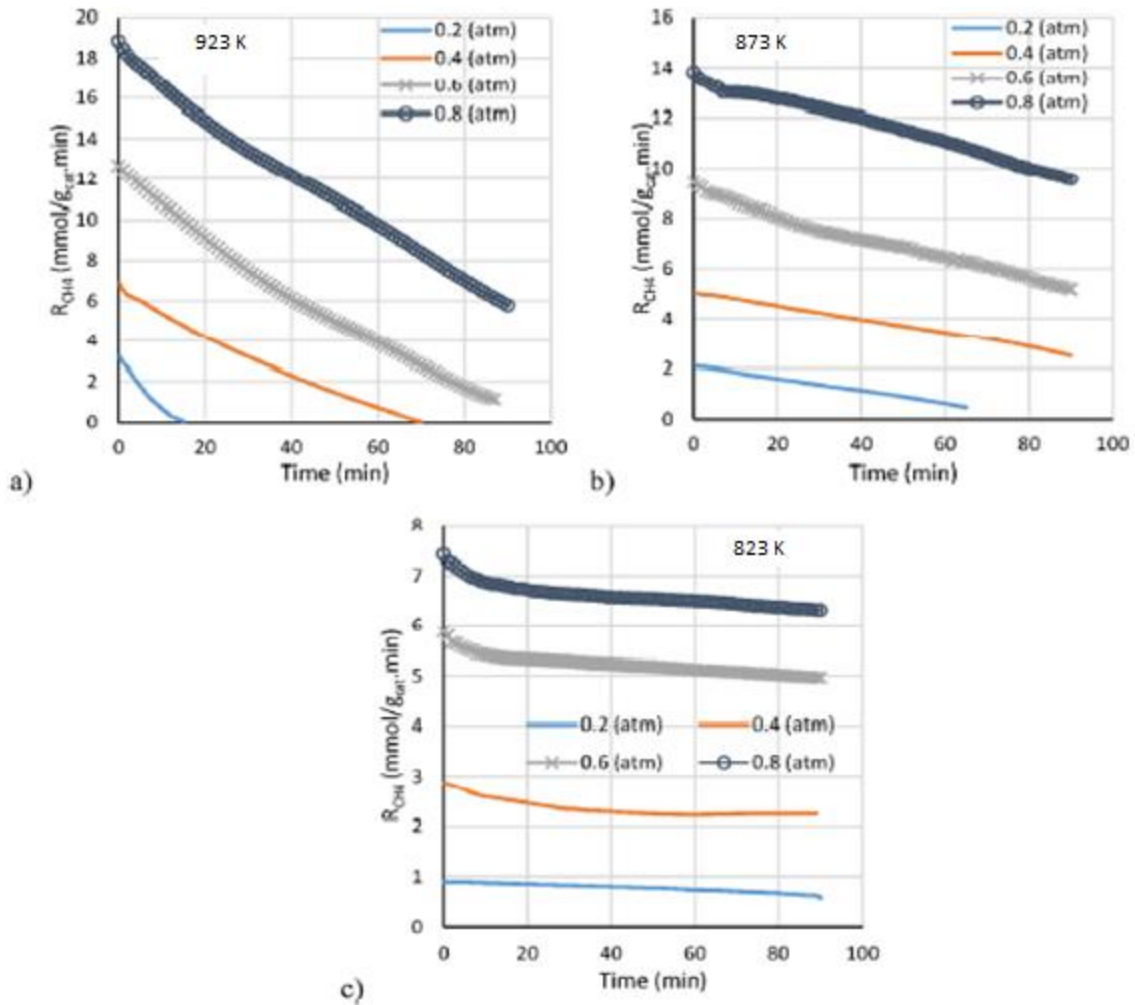
Fig 8: Reaction time vs CH₄ decomposition; Reproduced with permission from U. Ashik,

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The authors reported that as the TCD of CH_4 occurs in various steps and the reaction kinetics of each step is still under study, this makes the overall mechanism of TCD extremely complicated. Empirical model law based on power law was used in this study for computing the reaction order and activation energy. In another study, the reaction kinetics over Ni−Cu−Co was studied, and the activation energy was calculated by Arrhenius plot shown in Fig 9 [117].

Recent studied made by [118] reported that the initial step of CH_4, i.e. breakage of bonds in TCD over the metallic catalyst is the rate determining step since the activation energy decreased from

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440 kJ mol^{-1} to 65 kJ mol^{-1} over Ni (100) catalyst at high temperatures. Similarly, Maryam et al.

[119] carried kinetic modelling of CH$_4$ decomposition at a temperature range of 823−923 K over

Ni−Cu/MgO and estimated around 50.4 kJ mol^{-1} of activation energy. The results also revealed

that the catalyst deactivation was dependent on TOS, reaction temperature, and partial pressures.

Nasir et al. [96] stated that a reaction order and activation energy of 2.65 and 61.77 kJ mol^{-1}

respectively was obtained by carrying out TCD over Ni/Zeolite catalyst. The kinetic data indicated

that the optimum reaction temperature and partial CH$_4$ pressures must be maintained to get the

highest performance from the catalyst in terms of catalyst activity and stability.
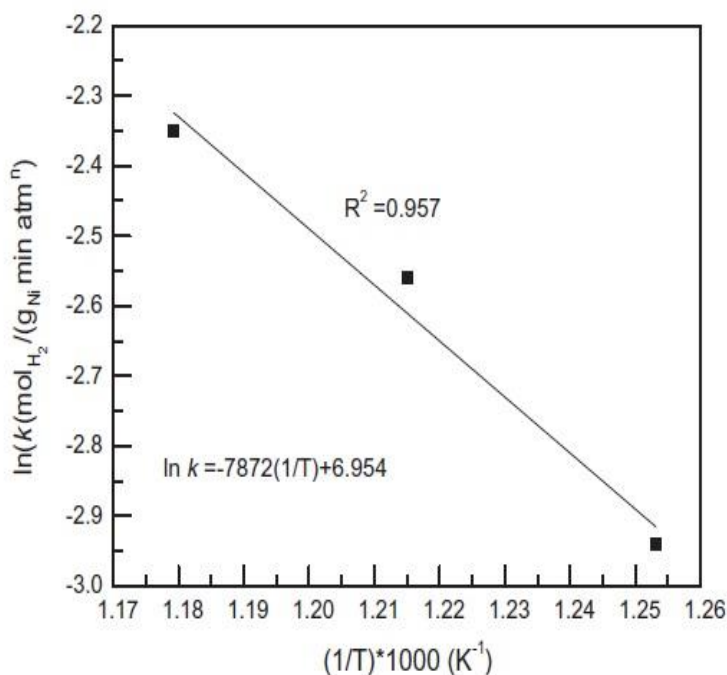
Fig 9: Activation Plot of Ni−Cu−Co; Reproduced with permission from H. Y. Wang, Copyright 2014

Elsevier [117]

The activation energy and order of reaction of some of the highly active catalyst in TCD of CH_4 has been shown in Table 5.

Table 5: Activation Energy of First-order TCD over Metal Based Catalyst by Empirical Model

Catalyst	Activation Energy E_a (kJ mole^{-1}) [a]	Ref
Ni	65.4	[117]
Ni	64.6	[120]
Ni/Zeolite	61.77	[96]
Ni/TiO$_2$	60	[121]
Ni/SiO$_2$	29.5	[122]
Ni−Cu/Al$_2$O$_3$	46	[123]
Ni−Cu/MgO	50.4	[119]
Ni−Cu−Co	67.5	[117]

[a]Dependent Upon Reaction Parameters

The comparison of different hydrogen production techniques has been furnished in Table 6. The liberation of ample amount of greenhouse gases marks SRM, DRM and POM unfavorable techniques for H_2 production. Moreover, the separation of H_2 from synthesis gas requires heavy equipment that increases the overall cost of the process. TCD is a nonoxidative technique in which CH_4 is decomposed into H_2 and elemental carbon as a by-product. Furthermore, among all suggested processes TCD occurs at the lowest reaction temperature because metallic catalysts are used.

Table 6: Comparison in between H_2 Production Techniques

	SRM	DRM	POM	TCD
Reaction	$CH_4 + H_2O \rightarrow CO + 3H_2$	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$CH_4 + 0.5\ O_2 \rightarrow CO + 2H_2$	$CH_4 \rightarrow C + 2H_2$
Advantages	1.75-85% Efficiency 2.Ancient Technique	1. Two green House gases are consumed, i.e. CH_4 and CO_2 2. Clean fuel is a product	1.60-75% Efficiency 2. Low Residence Time 3.High Reaction Yield	1. Green and Nonoxidative Technique. 2.Highly ordered carbon produced as a by-product.
Disadvantages	1.Costly process. 2.High reaction temperature and pressure required 3. H_2 must be removed from synthesis gas	1. Carbon formation and sintering. 2. H_2 must be removed from synthesis gas.	1. Costly technique as it requires the cryogenic unit to sperate O_2 from Air 2. H_2 must be removed from synthesis gas	1. Deactivation of the catalyst due to encapsulation of low active carbon.
H_2/CO Ratio Operating Temperature	H_2/CO Ratio: 3:1 973-1273 K	H_2/CO Ratio: 1:1 1223-1373 K	H_2/CO Ratio: 2:1 923-1023 K	H_2/CO Ratio: - 823-1023 K
Operating Pressure	3-25 bar	1 bar	100 bar	1 bar

6. Outlook

TCD has been termed as one of the effective technique to produce CO_X free H_2 that can replace all existing fuels due to clean and abundant energy. The hydrogen produced by this process can be directly employed as feedstock in fuel cells while carbon obtained as by-product can be used as advanced materials and catalysts. The main problems encountered in this process as stated in literature surveys are high reaction temperature, and rapid catalyst deactivation as the formation of carbon destabilizes the adsorption capacity of clean material thus lowering its catalytic activity and stability. In recent years, cumulative efforts have been devoted for the commercialization of TCD, and reaction kinetics, catalyst developments and process parameters have been investigated broadly. However, this process needs further directions. The current article enlightens that TCD can be developed by further theoretical and experimental investigations. It is considered that the future perspective of TCD research is to concentrate on the synthesis of trimetallic catalysts having suitable metals comprising of appropriate compositions. The impregnation of Mo, Co, Fe, Cu, Pd, Cr and Pt on the Ni-based catalyst can serve the purpose of industrializing TCD. Furthermore, the mixtures of CH_4 with other hydrocarbons like C_6H_6, H_2S, CO_2, alkanes, and alkanols can be utilized as efficient feedstocks for TCD as it gives better hydrogen yields and improve carbon types towards MWCNTs. The synthesis methods, calcination temperatures, and activation temperatures are also essential to enhance the performance of the catalysts. The suitable synthesis techniques and activation conditions can give a high dispersion of metal on support, robust metal support activation and high resistance to coke. Additionally, the reactor designs must be explored deeply to optimize this process. It is believed that a practical research done on these parameters can give better results in the respective fields. This will help to get ample energy by the combustion

of H_2 by industrializing TCD of CH_4. It is also worth mentioning that, industrialization of TCD will assist to tackle the issue of clean energy crisis and GHG emissions which is the root cause of global warming. Moreover, the carbon produced as a by-product will serve as a value-added product as catalyst and power generation.

7. Conclusion

TCD has been considered as green and economical method to produce pure H_2 and elemental carbon as a by-product without the need of a costly separation method as compared to other techniques, i.e. DRM, SRM and POM. However, a high reaction temperature of TCD and fast deactivation of the catalyst has restricted this process for commercial applications. For this purpose, the metal-based catalysts, i.e. noble and transition metals have been extensively researched to lower the reaction temperature and improve the catalyst stability. Ni, Cu, Co, Fe, and Pd are the most studied transition metals impregnated on Al_2O_3, FeO, MgO, CeO_2, and La_2O_3. Of all metallic catalysts, Ni-based materials proved to be better due to its low cost, easy availability and excellent catalytic efficiency as compared to other metals. While parameters such as reaction temperature, GHSV, and metal loading also affect the process yields. The co-feeding of CH_4 with other feedstock C_2H_4, C_3H_6, C_2H_5OH and CH_3OH producing more active carbon as a by-product is proposed to be effective solution to overcome the rapid catalyst deactivation. Lastly, the kinetic study is presented in which the research done by some notable's groups were mentioned based on activation energies. An empirical model based on the power law is considered as the most appropriate model that fits in TCD, and hence the order of reaction and activation energy is calculated.

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