Review

Methanol to Formaldehyde: An Overview of Surface Studies and Performance of an Iron Molybdate Catalyst

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Abstract: Formaldehyde is a primary chemical in the manufacturing of various consumer products. It is synthesized via partial oxidation of methanol using a mixed oxide iron molybdate catalyst ($Fe_2(MoO_4)_3$–MoO_3). This is one of the standard energy-efficient processes. The mixed oxide iron molybdate catalyst is an attractive commercial catalyst for converting methanol to formaldehyde. However, a detailed phase analysis of each oxide phase and a complete understanding of the catalyst formulation and deactivation studies is required. It is crucial to correctly formulate each oxide phase and influence the synthesis methods precisely. A better tradeoff between support and catalyst and oxygen revival on the catalyst surface is vital to enhance the catalyst's selectivity, stability, and lifetime. This review presents recent advances on iron molybdate's catalytic behaviour for formaldehyde production—a deep recognition of the catalyst and its critical role in the processes are highlighted. Finally, the conclusion and prospects are presented at the end.

Keywords: iron molybdate; molybdenum oxide; methanol conversion; formaldehyde production; mixed oxides

1. Introduction

Methanol is one of the most critical chemical intermediates used in the petrochemical sector. It is a raw material for synthesizing several hydrocarbons and numerous oxidation products [1–4] There is continuous discussion about methanol's successful utilization in methanol's partial oxidation to formaldehyde [5,6]. More than 30% of methanol is used in formaldehyde production every year [7,8].

Formaldehyde is an essential raw material and is widely used in many industrial chemical products such as resins, 1,4-butylene glycol (BDO), poly formaldehyde and pesticides [9,10]. In recent years, the annual demand for formaldehyde has exceeded 30 megatons, and formaldehyde production has been remarkably stable [8,11,12]. In 2017, around 52 million formalin tons (37% by weight aqueous solution of CH_2O) were produced, and the annual global consumption of formaldehyde is expected to increase by nearly 5% over the next few years [13–15]. This increase in the demand for formaldehyde will continue to grow with the manufacturing industry's development, increased demand for disinfectants, cosmetics and pharmaceuticals [16–18].

The commercial generation of formaldehyde first began in 1910 under the silver-catalyzed process and continued for nearly 40 years. In this process, the methanol and air mixture was subjected to 600 °C under the silver catalyst [14,19–21] and proceeded according to Equation (1).

$$CH_3OH \rightarrow CH_2O + H_2 \ \Delta H = 84 \ kJ/mol \tag{1}$$
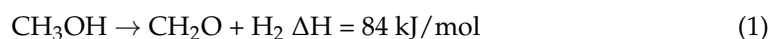
Silver catalysts have been used in the form of molten metals or dispersed on supports. However, the high temperatures required for the desired selectivity cause the particles to be aggregated and sintered, thus negatively affecting the formaldehyde yield [6,14,22].

Furthermore, the silver process strictly depends on the reaction conditions, methanol to oxidant ratio, the temperature and the feed's water presence. Therefore, different alternative preparation methods were investigated to increase the selectivity and stability at lower temperature conditions [14,19,22–25].

In 1931, Adkin et al. proposed a new iron-based catalyst (FeMo) to directly oxidize methanol into formaldehyde with an impressive catalytic performance [26,27]. The FeMo-based approach for the production of formaldehyde proceeds according to Equation (2) [28].

$$CH_3OH + \frac{1}{2} O_2 \rightarrow CH_2O + H_2O \ \Delta H = -159 \ kJ/mol \tag{2}$$
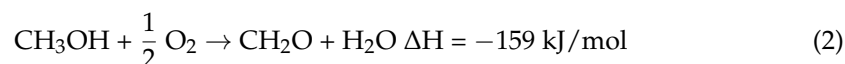
Compared to the silver process, the iron-based catalyst needs a low methanol: air mixture at a lower temperature, and it also limits further oxidation [6,22,29–31]. Oxygen-saturated methanol vapors were injected into a packed bed reactor, and nearly 90% yield was obtained, compared to 86% in the silver-based process [14,32]. The FeMo was found to be more resistant to poisoning; this resulted in an extension of the catalyst's lifespan of 6–12 months [33,34]. Iron molybdate processes have been recorded to operate at a low concentration of methanol, which ultimately makes the process safer and reduces the risk of explosion by fire [35]. The iron molybdate (oxide-based technology) provides a consistent product throughout the catalyst's lifetime and lowers the operating cost [6]. Consequently, in the 1950s, iron molybdate catalysts were used as industrial catalysts to oxidize methanol to formaldehyde [26,34,36–39].

Commercially available iron molybdate catalysts always contain $Fe_2(MoO_4)_3$ and MoO_3 [35,40–43]. The catalytic behaviour of the iron molybdate strongly depends on the Mo/Fe ratio [40,44–46]. The activity and selectivity of methanol to formaldehyde has been carried out with the different stoichiometric ratios from 0.02 to 4. However, a stoichiometric ratio higher than 1.5 has been found the most active and selective composition [44].

Mo segregates from catalytic material at the reactor inlet and the hotspots [47,48]. The volatilized Mo leaves behind an unselective Fe rich species [49,50] and condenses back as a separate layer; this proceeds to form undesired phases and, thus, deactivate the catalyst and reduce the surface area and selectivity [33,37,39,51,52]. It encourages the reactor's shutdown, and, consequently, can cause catalyst replacement. The early shutdown of the reactor is due to an increased pressure drop affected by molybdenum oxide precipitation from the gas phase to downstream of the reactor [37,41].

Therefore, considering the economic benefits and a broader positive impact on society, the development of an efficient catalytic system is required to overcome these limitations. Understanding the active sites within the catalytic materials is essential to implement the improvements. After a series of efforts, it was confirmed that the excess molybdenum is needed to compensate the sublimation of MoO_3. This provides stable, active and selective catalytic performance [29,33,53–56]. Due to the higher density of catalytically active $Fe_2(MoO_4)_3$ as compared to the anisotropic MoO_3, many scientists attribute the activity to isotropic $Fe_2(MoO_4)_3$ Still, there is a counter-argument that the MoO_3 that is present in the catalytic samples will not only regenerate lost molybdenum and prevent catalytic deactivation due to sublimation of MoO_3 [34,41,57,58], but also has a role in keeping a good selectivity for formaldehyde [55,59]. Therefore, it is essential to address the role of each oxide phase; for example, whether $Fe_2(MoO_4)_3$ acts as the only support for MoO_3, or whether it has intrinsic activity in the process [47,48,60].

Given the excellent performance of ferric molybdate catalysts, it is not easy to find a more selective composition [35,48]. This fact shows that the catalyst's chemical composition is the same as that first reported in 1931. The current study describes previous studies that identified catalytic activity and selectivity for the iron molybdate catalyzed process. In addition, the literature discusses the typical iron molybdate synthesis, its deactivation and whether $Fe_2(MoO_4)_3$ or MoO_3 plays a predominantly active role or if there is a common active centre between them.

Iron Molybdate an Active Catalyst for Methanol to Formaldehyde Production

Iron molybdate $Fe_2(MoO_4)_3$ has been widely used for various applications such as methanol/propylene oxidation, gaseous methane to liquid fuels such as methanol, and gas sensors and magnetic devices [32,47,50,61–64]. It is a well-established catalyst and is used in the partial oxidation of methanol to formaldehyde. Due to its high selectivity and activity, it can also be used as a catalyst with different supports and formulations for the treatment of alcohols and hydrocarbons and the storage of hydrocarbons and supercapacitors [63,65,66]. Iron molybdates are found in nature as ferrous molybdate ($FeMoO_4$) and ferric molybdate ($Fe_2(MoO_4)_3$). However, only ferric molybdate is active and plays a critical role in methanol's selective oxidation [34]. A Mo/Fe (2–3) stoichiometric ratio is required to achieve industrial molybdate synthesis, which primarily consists of $Fe_2(MoO_4)_3$ and MoO_3. To synthesize the ferric molybdate phase, the Mo/Fe ratio must be equal to or greater than 1.5. However, increasing the Mo/Fe ratio from 1.5 will cause it to start forming the most desired mixed oxides—$Fe_2(MoO_4)_3$/MoO_3 crystals [67]. Some physical properties of pure and mixed oxides iron molybdate catalyst are reported in the Table 1.

Table 1. Represents the physical property and selectivity of each oxide in iron molybdate catalyst.

Physical Properties [25,28,34,68,69] and Selectivity of Pure Oxide Phases			
Phases	**Mol. Weight [g/mol]**	**Color**	**Selectivity Towards**
Fe_2O_3	159.69	Red-brown	CO_2 [32,70,71]
MoO_2	127.94	Dark blue-violet	Primarily CO and small amounts of CO_2 [32,72]
$FeMoO_4$	215.78	Light green	CO [32,37]
MoO_3	143.94	White-yellow	Formaldehyde [32,47,73]
$Fe_2(MoO_4)_3$	591.56	Brown-yellow-green	Primarily formaldehyde [32,47,74]

The production of formaldehyde from methanol is not only limited to the iron molybdenum catalysts. As mentioned earlier, silver and many alternative catalysts have also been used as industrial catalysts in formaldehyde production [22,35,42,75–82].

Currently, worldwide formaldehyde production is divided almost equally between the silver catalyzed process and the use of oxide-based catalysts [12,14,22]. The silver-based process uses methanol-rich feed, whereas the oxide-based process (Formox process) has less methanol-rich contents. The oxide-based catalyst has achieved 93% selectivity compared to the <90% of silver-based catalyst. However, the silver process has a somewhat lower investment cost than the oxide-based process, but the selectivity is an essential parameter because the cost of methanol covers 94% of production cost compared to power and catalyst cost, which are 4% and 2%, respectively [22,36,83].

Typical performance data of oxidative dehydrogenations, ammoxidation, and selective hydrocarbon oxidations are presented in Table 2. The data shows that MoO_3/$Fe_2(MoO_4)_3$ has shown remarkable performance with 92–95% selectivity covering a 99% conversion rate at lower temperatures than the various other catalysts.

The data shows that the other catalyst has lesser selectivity and conversation and requires a high temperature.

Table 2. Comparison of different oxide catalysts for selective hydrocarbon oxidation and oxidative dehydrogenation.

Process	Catalyst	Selectivity (%)	Conversion (%)	Temperature (°C)
Methanol to formaldehyde [84]	Fe-Mo-O	92–95	>99	250–380
Propene to acrylonitrile [85]	Bi-Mo-O	80–83	98	420–450
Propane to acrylonitrile [86]	VSbWOx/SiO$_2$-Al$_2$O$_3$	67	60	500
Propane to acrylic acid [87]	Mo-V-Nb-Te-O	50–60	80	350–400
Propane to propene [88]	V-O/MCF	68	41	550
Xylene to phthalic anhydride [89]	V-O/TiO$_2$	80–82	99.9	350–450
Ethene to ethylene oxide [90]	Ag/Al$_2$O$_3$	80–90	7–15	200–300
Propane to propylene [86]	V-silicalite	30	70	550
Propane to acrylonitrile [91]	Mo-V-Nb-Te-O	72	76	420
Ethylene/Acetic acid to Vinyl acetate [92]	Pd-Cu-K on Al$_2$O$_3$	92	8–12	-
Ethanol to butanol [93]	20% Ni/Al$_2$O$_3$	25	80	250
Propane to propylene [86]	V-MgO	38	62	540
Ethane to ethylene [94]	Ni-NbO	51	90	400
Ethane to ethylene [86]	MoVTeNbO	85	88	400
Propene to acrolein [95]	Bi-Mo-O	83–90	<98	300–400
Butane to maleic anhydride [96]	V-P-O	65–73	75–85	350–420

Substantial research has been performed on the catalyst to find alternative compositions [84,97,98]. As a result, molybdates and vanadates gained much of the focus as these materials were found most efficient and selective for partial oxidation of methanol. Figures 1 and 2 show the performance of various molybdates and vanadates, and it is concluded that commercial iron molybdates have the most productive performance compared to other materials.

The primary chemical composition of the iron molybdate catalyst has not changed over the years. Despite this fact, fourfold productivity has been achieved due to some process improvements since the early 1960s, as shown in Table 3 [99,100].
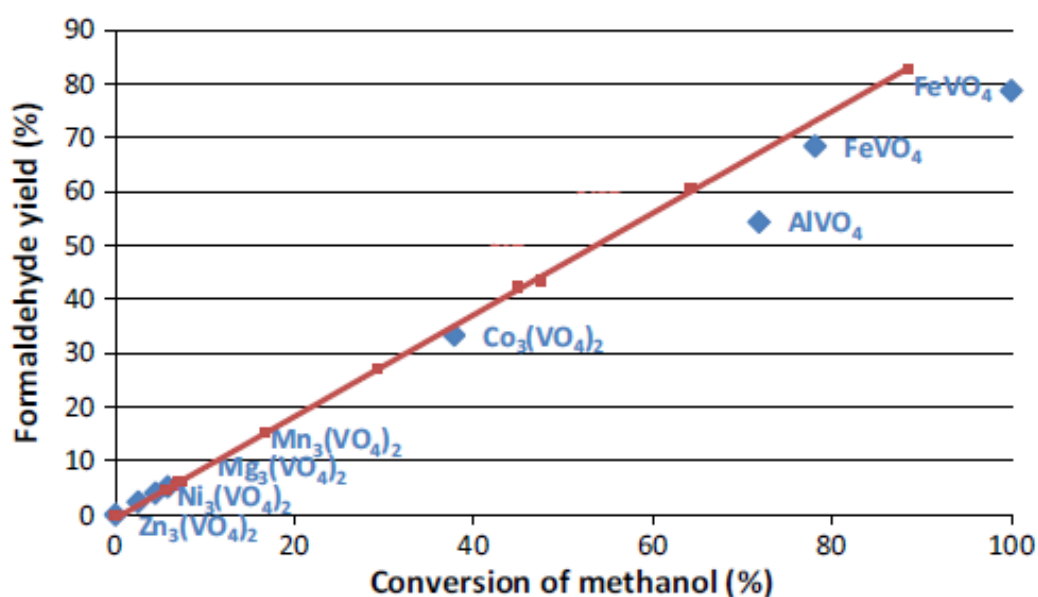

Figure 1. Comparisons of the yield and conversion of formaldehyde over the various vanadates in the Formox (oxide-based catalyst) process. Reprint from [99]. Copyright (2021) from Springer Nature.
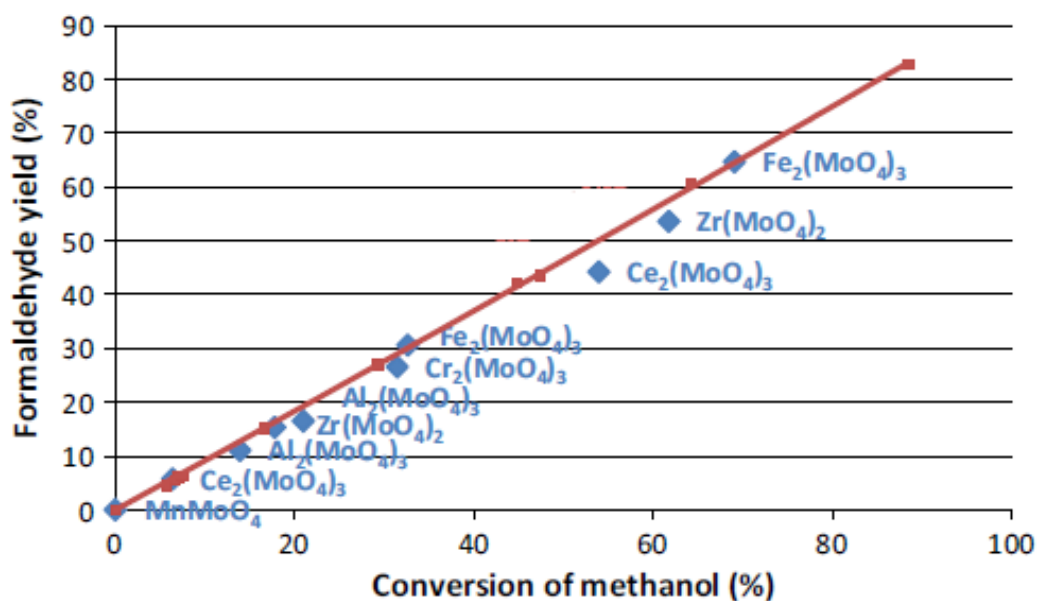
Figure 2. Comparisons of the yield and conversion of formaldehyde over the various molybdates in the Formox process. Reprints from [99]. Copyright (2021), with permission from Springer Nature.

Table 3. Represents the development of the Formox process over the iron molybdate catalyst from the year 1959 [99,100].

Years	Process Development	Results
1959	Dried granules of catalyst were used, and the feed consisted of 6.5 vol% methanol in the air.	First Production Scale
1972	Gas recirculation, 7.5 vol% methanol, and 10–11 vol% O_2 pre-calcined granules.	The gas recirculation and lower oxygen concentration increased productivity and reduced emissions.
1984	Introduced the ring-shaped catalyst.	Improved gas velocity, lowered the pressure drop and eventually expanded the productivity.
1984	Introduced the emission control system.	Better environmental impact and steam generation system.
1997	New loading system for faster and consistent loading with increased pressurization (0.3 bar).	Enhancement in productivity.
2003	New design standards and introduction of catalyst activity profile (CAP) with higher methanol inlet.	Productivity improvements.
2005	Pressurization to 0.5 bar g.	Productivity improvements.
2009	Launched CAP 2.0.	Higher yield, lower pressure drop, less aging.
2011	CAP 2.0, introduction of turbo charger.	Reduced power consumption, reduced operational cost.
2012	Launched CAP 3.0.	Yield and lifetime improvement and enabled the operation at even higher methanol inlet (up to 11 vol%).
2016	Complete loading/reloading service concept.	Reduced the downtime, lowered the risk issues related to unclean tubes.
2018	Addition of new high pressure plant design features 2.0 bar with a newly developed catalyst system.	Better performance, flexibility and rise in productivity.

Due to the various advantages discussed already, $Fe_2(MoO_4)_3$ has established itself as a leading commercial catalyst for formaldehyde production [26]. This is due to its nature to oxidize methanol at fairly low-temperature conditions and retain catalytic activity for repeated use. However, it is essential to identify whether $Fe_2(MoO_4)_3$ supports MoO_3 or whether it has an intrinsic activity. It has been believed that $Fe_2(MoO_4)_3$ has outstanding properties, such as the oxygen mobility of the mass lattice. This permits the catalyst to guarantee oxygen revival at the surface at any time throughout the reaction and maintains the catalyst selectivity [47].

2. Synthesis of Iron Molybdate

The synthesis process of iron molybdate significantly affects the choice of the reactor (fixed or fluidized bed) used in the partial oxidation of methanol. The bulk usage of catalysts and the impact of mechanical abrasion influence the reactors. Therefore, many efforts have been counted to use various synthesis procedures to control and modify the catalyst surface to withstand the mechanical abrasion [34,101,102].

$Fe_2(MoO_4)_3$ is most commonly synthesized by the coprecipitation method in the industry using $FeCl_3$ and ammonium heptamolybdate aqueous solutions [34,103,104]. Later, the precipitate is washed, filtered and calcined at 400–500 °C to obtain the $Fe_2(MoO_4)_3$ and MoO_3 crystals with a surface area of 5–8 m^2/g [104,105]. Many studies focused on iron molybdate catalyst prepared by coprecipitation methods to influence the catalyst's selectivity and activity. The catalyst prepared by coprecipitation was found to be very selective [26,28,55,69,106–110] and successfully produced formaldehyde from methanol with high yield [14]. However, the high cost of the expensive reagents used in coprecipitation synthesis, the large amount of water required in commercial manufacturing, the evolution of gases as impurities during calcination and the small surface area that hinders the reoxidation rate of the spent catalyst are significant problems associated with coprecipitation synthesis [107,111,112]. In addition, slight changes in the synthesis process significantly alter the catalyst properties and adversely affect the surface properties. Therefore, it is essential to find alternative synthesis methods that involve low-cost reagents, reduced water consumption, and a more homogenous consistency with less impact on environmental pollution [24].

Soares et al. [106,113] proposed the sol–gel method as it is considered one of the most suitable low-temperature methods that prepares the iron molybdate without coprecipitation. It was observed that the catalyst prepared with the sol–gel method had a better distribution/dispersion of excess MoO_3 over $Fe_2(MoO_4)_3$ as it prevents the Mo volatilization and increases the selectivity of formaldehyde. However, the sol–gel method's catalyst was less active than the coprecipitation method because of the early irreversible surface reduction during the calcination process. It is essential to conduct the calcination below 400 °C in the sol–gel technique to avoid agglomeration, loss of mechanical strength and surface reduction [34,106,113].

Beale et al. [111] used a single-step hydrothermal approach to prepare the iron molybdate catalysts with a different atomic ratio at reasonably low temperatures compared to other methods. The catalysts produced via hydrothermal processes had mixed Mo_5O_{14} and FeMo crystalline structures and were unstable at a temperature above 300 °C. The catalyst surface can easily be modified, and its potential synthesis at low temperatures could prepare the material with varying catalytic performance. In the hydrothermal process, the iron and molybdate solution was thermally treated at 150 °C in an autoclave reactor. Later the crystals were washed, filtered and dried to obtain the iron molybdate with excess molybdenum crystals without calcination.

Recently, Kong et al. [16] prepared the iron molybdate by the mechanochemistry approach using the grinding mill from 30–120 min. It was solvent-free and simplified compared to the traditional coprecipitation method, thus can easily be implemented in industrial-scale applications. The small ball size material and longer grinding time, for example, 120 min, had better crystallinity and selectivity of formaldehyde (97.56%) in comparison with larger particles and materials prepared with less milling time. The leading production of formaldehyde was attributed to $Fe_2(MoO_4)_3$ uniformity and to the grinding time.

Nikolenko et al. [50] prepared an iron molybdate catalyst with an ammonium molybdoferrate (II) precursor instead of the conventional Fe(III) precursor used for commercial iron molybdate catalysts. The Fe (II) synthesized iron molybdate has reduced the detrimental impurities (Fe(III) oxide) and protected the catalyst surface; it also reduced the acidity of the prepared solution. The catalyst prepared with Fe (II) showed similar activity to a commercial catalyst in the partial oxidation of methanol to formaldehyde.

Iron molybdate catalysts can be prepared with the kneading and evaporation method [104]. In this process, ammonium molybdate is dissolved in water, followed by the dropwise addition of iron nitrate powder. Following that, the mixture was subjected to evaporation, and the final product was dried and calcined. Li et al. [114] have examined wet and dry methods to prepare the iron molybdate crystals and observed the $Fe_2(MoO_4)_3$ and MoO_3 crystals after the calcination. The wet method recorded the higher performance and had a better and uniform encapsulation of Mo species. However, the bridging of Mo with Fe through oxygen could not be verified in this work.

Popov et al. [115] used molybdic acid and Fe oxalate to prepare the iron molybdate catalyst using centrifugal milling. The milling process reduced the synthesis temperature. However, the article lacks the necessary details to highlight additional advantages.

Hasan et al. prepared the catalyst (iron molybdate) with the mechanical mixing of MoO_3 and Fe_2O_3; the materials were mixed, ground and then calcined at 600–700 °C for 10–70 h; however, they had less surface area and were eventually found to be inactive and not selective [104,116].

Iron molybdate also has been prepared using amorphous reagents without coprecipitation. Ferric nitrate, excess citric acid, and ammonium heptamolybdate were used as regents, followed by the calcination at 400 °C over 6 h. However, no such comparison of this method with conventional coprecipitation has been reported in the literature [117].

Role of pH

It is recognized that physical and chemical interaction strongly influence the catalytic behaviour and Mo/Fe stoichiometric ratio [33,48–51,118]. For example, the preparation methods, the precursor's initial concentration, and the pH during precipitation are significant factors [34]. In a typical laboratory coprecipitation method, the precipitation of $Fe_2(MoO_4)_3$ with a Mo/Fe atomic ratio greater than 1.5 is usually carried out between pH 1.5 and 2.0. The pH of the solution is maintained primarily using HNO_3, while the preparation temperature can fluctuate from room temperature to the boiling temperature of the mother solution. Several authors obtained a different Mo/Fe atomic ratio by changing the same ratio in the parent solution [34,119,120].

However, Alessandrini et al. [119] reported that the variations in the Mo/Fe atomic ratio of the catalyst follow the same degree of variation of the parent solution only when the pH of the precipitate remains constant. If the Mo/Fe contents in the catalyst are less than the Mo/Fe contents in the parent solution, this increases the final pH of precipitates. Similar unfollowing was also noticed when HCl was used to maintain the pH instead of HNO_3.

On the contrary, Kolovertnov et al. [120] prepared the iron molybdate catalyst with the coprecipitation method at constant pH = 2; the obtained catalyst had a different Mo/Fe atomic constitution compared to the parent solution.

Wilson et al. [121] synthesized the iron molybdate catalyst and noticed that the Mo/Fe ratio of the catalyst does not depend upon the temperature of precipitation and the addition of order in the mother solution. Moreover, the precipitation steps do not affect the composition. Instead, the washing of precipitates before the drying significantly increased the catalyst's Mo/Fe atomic ratio because Fe has more solubility than molybdenum. However, the article fails to mention that the reported rise in Mo/Fe contents due to washing is limited to the bulk or surface of the catalyst.

Energy-intensive annealing and maintaining a pH of less or equal to 2 are the significant disadvantages reported in the literature. In addition, it was noted that increasing the pH from 2 caused a significant loss of Mo contents in the mother solution.

Therefore, Nikolenko et al. [50] prepared an iron molybdate catalyst with an ammonium molybdoferrate (II) precursor instead of the conventional Fe(III) precursor used for commercial iron molybdate catalysts. The Fe (II) synthesized iron molybdate was successfully prepared between pH 5 and 6, thus reducing the prepared solution's acidity. In

addition, the catalyst prepared with Fe (II) showed similar activity to a commercial catalyst in partial oxidation of methanol to formaldehyde.

Although the iron molybdate catalyst has been synthesized for many years, there is still scope to expand and improve the catalytic system and develop an understanding of the synthesis process [48,66,118].

3. Role of $Fe_2(MoO_4)_3$ as an Active Phase in Partial Oxidation of Methanol

Classifying the active phase is slightly more complicated as $Fe_2(MoO_4)_3$–MoO_3 compounds containing mixed oxides show excellent formaldehyde selectivity with different activity levels [34]. It has been observed that improved catalytic activity of the iron molybdate catalyst is mainly due to the increase in the number of catalytically active sites of $Fe_2(MoO_4)_3$ [122]. In contrast, the reduced activity of MoO_3 is due to the minimal surface of MoO_3. Therefore, $Fe_2(MoO_4)_3$ has been identified as the active ingredient, and excess molybdenum is considered a bystander phase [29,110,119].

In 1965 Kolovertnov et al. started studying Mo-Fe-O catalysts with various Mo/Fe atomic compositions in methanol's partial oxidation to formaldehyde [96]. The authors noticed that the Mo/Fe atomic ratio of 1.7 is the optimum combination to convert methanol to formaldehyde [123]. After that, Boreskov et al. validated the findings of Kolovertnov and derived the maximum activity at Mo/Fe = 1.7, as well as nominating $Fe_2(MoO_4)_3$ as an active phase and observing that Mo excess is mandatory to regenerate the active sites [123]. Soares et al. [113] carried out partial methanol oxidation under the two different atomic compositions (Mo:Fe 1.5:1) and (Mo:Fe 3:1). The temperature programmed desorption (TPD) confirmed that the $Fe_2(MoO_4)_3$ is 2–4 times more active than bulk MoO_3 at the stoichiometric stage. Their studies confirmed that $Fe_2(MoO_4)_3$ is the active phase because increasing Mo's amount can increase selectivity, but the fundamental activity per unit surface is unchanged [124].

Okamoto et al. [57] dispersed Mo over the $Fe_2(MoO_4)_3$ and confirmed that $Fe_2(MoO_4)_3$ was an active phase with a Mo/Fe ratio of 1.7. However, Sun-Kou et al. [58] hold $Fe_2(MoO_4)_3$ as an active phase under the Mo/Fe (>1.7) and concluded the $Fe_2(MoO_4)_3$ is responsible for an increase in the electronic properties of the catalytic surface. Table 4 represents the consequence of the Mo/Fe ratio on the conversion and selectivity of formaldehyde.

Table 4. Activity, selectivity, and specific surface area of the iron molybdate catalyst under various Mo/Fe ratios [69].

Mo/Fe Ratio in the Catalyst	Conversion at 180 °C	Selectivity	Surface Area (m²/g)
0 (Fe_2O_3)	2	0 (322 °C)	2.1
0.2	55	18 (204 °C)	55.4
0.5	50	27 (210 °C)	38.7
1	38	47 (244 °C)	16.3
1.5	35	73 (249 °C)	7.8
2.2	29	90 (256 °C)	6.7

Alessandrini et al. [119] introduced Mo (VI) to the crystal network of iron molybdate (mixed oxides) and recognized MoO_3 as an essential factor in improving catalyst homogeneity and texture. The stoichiometric phase (Fe) is the active phase, indicating that an excess of Mo does not affect Mo-Fe-O's specific activity. However, excess Mo was needed to obtain a catalyst with a large surface area and prevent iron-rich phases during the reaction [34].

Weckhuysen and Wachs state that MO bonds are so stable under reaction conditions that they cannot directly be involved in the selective oxidation reaction [125]. Van Truong et al. [126] found an increase in the catalyst's surface area and mechanical strength while introducing excess Mo in the crystal structure. Söderhjelm et al. [69] reported a mixture of crystal phase MoO_3 and $Fe_2(MoO_4)_3$, a top-performing catalyst, and confirmed

that MoO_3 is more selective than pure $Fe_2(MoO_4)_3$ but less active than $Fe_2(MoO_4)_3$. Wachs and Routray [127] and Routray et al. [29]. experienced similar activity for both $Fe_2(MoO_4)_3$ and MoO_3 using the methanol-TPSR (temperature-programmed surface reaction).

Recently, Gaur et al. [41] studied the structural changes in iron molybdate (Mo/Fe = 2.0) during the partial oxidation of methanol to formaldehyde. It was observed that exposing the catalyst to the feed during the initial time on stream, the α-MoO_3 volatilized while $Fe_2(MoO_4)_3$ remained stable. It was further seen that α-MoO_3 volatilization was enhanced with the rise in methanol formation, and it increased the temperature and reduced the oxygen contents. The extensive characterization in the studies confirmed the vital role of catalyst selectivity and stability.

It is concluded from the literature discussed that $Fe_2(MoO_4)_3$ is an active phase. However, the correct formulation of Mo/Fe is vital to balance the presence of Mo and Fe. The presence of Mo is essential to prevent the formation of undesired products and increase selectivity.

4. Role of Excess MoO_3 in Iron Molybdate Catalyst

From 1980, the industrial application of MoO_3 encouraged significant research on hydrodesulfurization, hydrocracking and the selective oxidation of alcohols [104,128,129]. Specifically, MoO_3 served as an ideal addition for the partial oxidation of methanol to formaldehyde.

MoO_3 is a highly valued material due to its capacity to improve formaldehyde selectivity when used with an iron molybdate catalyst [59].The typical structural unit cell of MoO_3 is represented in Figure 3 [130].
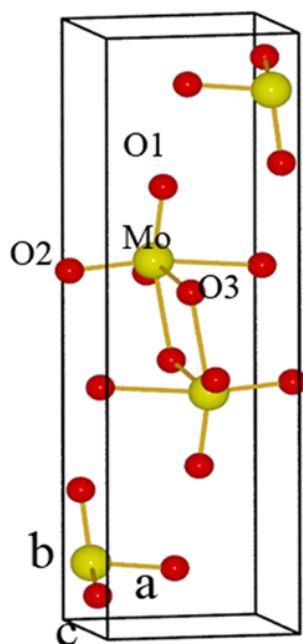

Figure 3. The crystal structure of MoO_3 unit cell. Reprint from [130]. Copyright (2021), with permission from Springer Nature.

Söderhjelm et al. proposed that each mixed oxide has a unique role in the partial oxidation of methanol [69]. For example, MoO_3 divides the molecule O_2 into atomic oxygen, while $Fe_2(MoO_4)_3$ uses this dissociative oxygen to oxidize methanol to formaldehyde. MoO_3 is an active phase and restored lost Mo in the partial oxidation of methanol [69].

Bowker et al. [131] examined the interaction of methanol with novel synthesized Fe_2O_3 and Fe_2O_3/Mo catalysts. Initially, the hematite converted the methanol to adsorbed methoxy and later oxidized it to the formate. However, the Mo in Fe_2O_3 made the material highly selective for formaldehyde production and blocked the formate pathway. Further-

more, Bowker's group [44,55,70,132] concluded that the Mo impregnation (2.2 Mo/Fe ratio) increased formaldehyde selectivity > 90% with 90% methanol conversion. After the segregation of the Mo contents, the authors noticed the sudden decline in formaldehyde selectivity, and, eventually, CO was found to be a significant product. In another study, Bowker et al. [107] used a computational approach in the continuity of his work to study iron-oxide-supported mono-, bi-, and multilayered Mo-rich surfaces in the methanol reaction. Covering a wide Mo load range, one Mo coating produced CO as the main product; bicharged Mo layers produced formaldehyde efficiently; furthermore, an increase in Mo content lead to the formation of formats.

Yeo et al. [32] synthesized an iron molybdenum catalyst by a physical grinding method and have found that iron molybdenum catalysts are highly selective for the oxidation of methanol to formaldehyde. Detailed surface studies have revealed that molybdenum-rich surfaces are crucial to ensure high selectivity and a large surface area.

Dias et al. [133] impregnated monolayers of MoO_3 over the $Fe_2(MoO_4)_3$ and recorded that incorporating MoO_3 does not affect methanol conversion and thus is not very active, but MoO_3 layers with the optimal Mo content increased the yield of formaldehyde. Similarly, Pham et al. synthesized α and β-MoO_3 and compared their performance. The studies confirmed that β-MoO_3 had higher catalytic activity and selectivity for formaldehyde as compared to α-MoO_3. Moreover, the prepared β-MoO_3 was active up to 320 °C for more than 15 h [134].

Raun et al. [33] prepared iron molybdate loaded with the different phases (h-MoO_3 & α-MoO_3). The structure, morphology, and crystal size of the MoO_3 crystal significantly affect the catalyst's durability. It is also believed that the H-MoO_3 immediately rearranged its phase to the α-MoO_3 phase and its increased stability is due to the presence of comparatively large h-MoO_3 crystals (2–10 μm) rather than α-MoO_3 (1–2 μm) as given in Figure 4. While Bowker et al. highlighted the role of Mo contents on the product fraction as represented in Figure 5.
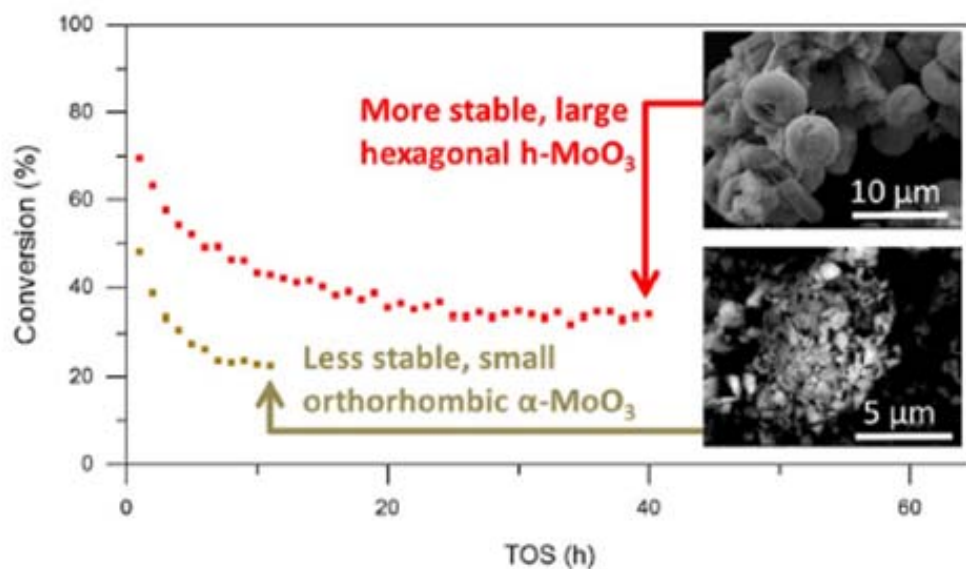

Figure 4. The detailed examination of the iron molybdate surface produced with a new physical milling method confirmed that the presence of molybdenum content affects both the structure and the catalysts' performance. Reprints from [51]. Copyright (2021), with permission from Springer Nature.
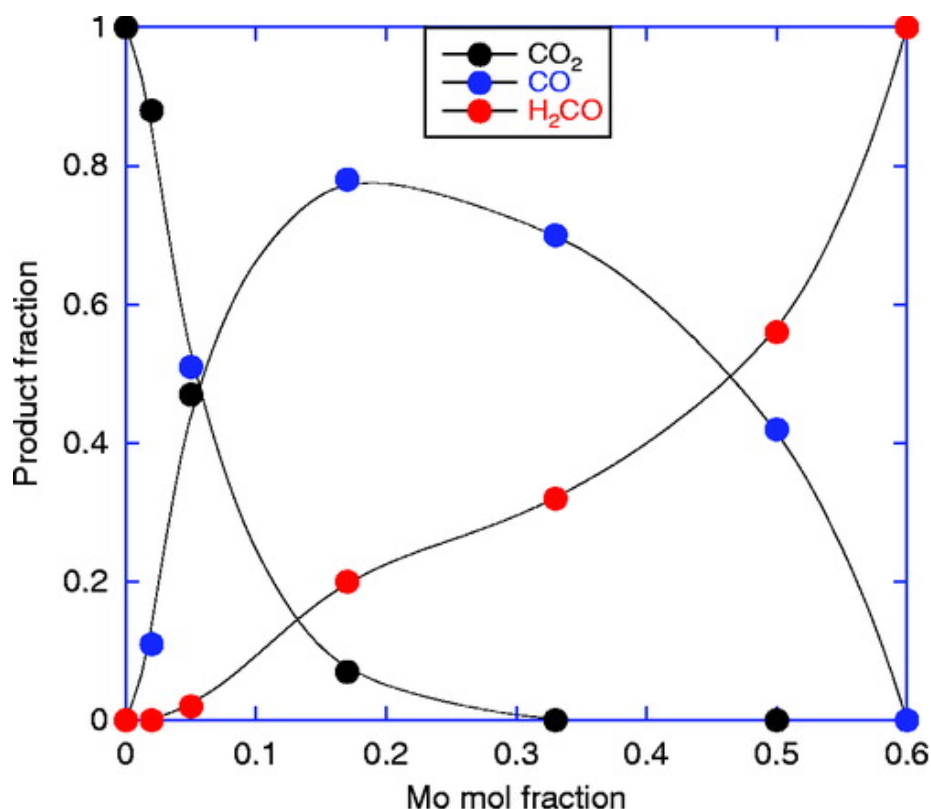
Figure 5. The product's dependence yields on Mo's mass loading. Reprint from [107]. Copyright (2021), with permission from Taylor & Francis Online.

House et al. [44] studied the activity and selectivity of $Fe_2(MoO_4)_3$ catalysts at a Mo:Fe ratio of 0.02 to 4 in the partial oxidation of methanol. To obtain high catalytic activity and selectivity for formaldehyde, the Mo: Fe ratio should be more than 1.5. The Mo contents are believed to increase oxygen availability on the catalyst's surface and change the catalyst's acidity. As oxygen availability increases, the Mo-rich catalysts improve the surface reoxidation. Therefore, it is confirmed that excess molybdate is significant for the regeneration reaction [55,132]. The $Fe_2(MoO_4)_3$ acts as the acceptor. Simultaneously, the MoO_3 serves as the donor phase; thus, it changes the active phase's electron density [61].

Andersson et al. prepared a novel structure (spinel-type) iron molybdate catalyst and compared its performance with traditional iron molybdate used in the partial oxidation of methanol. The spinal type had a lower Mo/Fe ratio because it could accommodate the reduced molybdenum and eventually increase the surface's reoxidized sites. The conventional type catalyst had lesser stability than spinel type and had a higher Mo/Fe ratio [99]. The $Fe_2(MoO_4)_3$ is the active phase, and MoO_3 is necessary to limit the generation of iron-rich phases and is needed to compensate for Mo's loss during the process [34,57,59,106,110,120]. The $Fe_2(MoO_4)_3$ acts independently with limited activity, and MoO_3, a donor stage, ensures rapid oxygen availability and accelerates the entire catalytic selectivity [127].

Raun et al. [33] synthesized an iron molybdate catalyst by a hydrothermal process with an atomic ratio of Mo/Fe = 2 and measured the catalyst's performance up to 600 h, as showed in Figure 6. During the first 10 h, the catalyst activity decreased by 50% due to the evaporation of α-MoO_3. The onset of declined activity is due to decreased MoOx contents on the catalyst surface, as reported by Dias et al. [133].
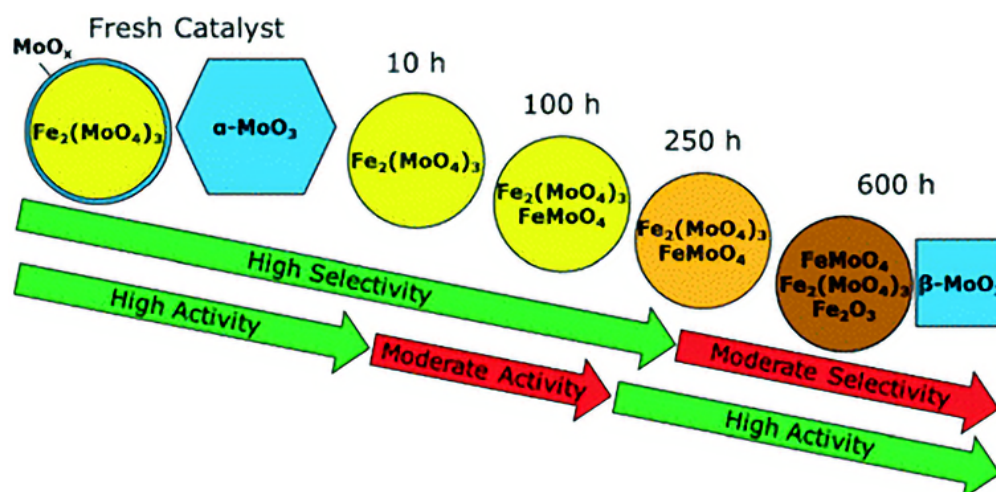
Figure 6. Deactivation behaviour of an iron molybdate catalyst during selective oxidation of methanol. Reprint from [33]. Copyright (2021), with permission from Royal Society of Chemistry.

Recently, Thrane et al. [42] confirmed the volatilization and sintering of excess molybdates at a higher temperature. The molybdates were prepared with alkali earth metals (Ba, Ca, Sr and Mg) and tested in the partial oxidation of methanol to formaldehyde. The study found the same pattern of volatilization in the prepared materials as conventional iron molybdate. The surface areas of stoichiometric molybdate were found to be higher compared with excess molybdates samples. It was confirmed that excess molybdenum was sintered and volatilized during the reaction, thus ultimately reducing the catalyst's area. The $MgMoO_4$ was found to be active but less stable among all the tested catalysts with 75% conversion and 97% corrected selectivity at 400 °C.

The Mo segregation in the iron molybdate catalyst substantially reduces the product selectivity in the partial oxidation of methanol. Therefore, it is exciting to load the Mo surface on the iron molybdate with varying combinations to study the details of catalytic activity and deactivation studies of iron molybdate catalyst. The layers of MoO_3 in the $Fe_2(MoO_4)_3$ act as an active phase. Simultaneously, the crystalline excess of MoO_3 is needed to compensate for the Mo volatilization in the reaction and maintain the methanol's selectivity.

5. Role of Catalyst Support

The selective oxidation of methanol to formaldehyde has been broadly affected by the catalytic performance and the active phase area. Machiels et al. [135] and Tatibouet et al. [1,136] synthesized MoO_3 over the graphite and presented the relationships between the surface acidity and the redox sites, and obtained formaldehyde and dimethyl ether, respectively.

Castillo et al. [137] achieved 99.5% formaldehyde selectivity at 94% conversion over mechanically synthesized MoO_3 and α-Sb_2O_4 phases. The Sb_2O_4 was responsible for achieving high selectivity because Sb_2O_4 facilitated the reoxidation and maintained the oxygen deficiency over the catalyst surface.

Briand et al. [138] reported a relationship between activity and electronegativity of the cation on the support. The authors proposed that cation's electronegativity significantly affects electron density and the adsorption–desorption of reactants and products. It was suggested that the cation's electronegativity increases in the following order: ZrO_2 > MnO > TiO_2 > Nb_2O_5 > Cr_2O_3 > Al_2O_3 ~ NiO > SiO_2, and SiO_2 supported MoO_3 enhanced the activity at higher Mo coverage (high Mo density) than the lower Mo contents. The better tradeoff between the Mo contents and the electronegativity of the cation support is significant to achieve better performance (activity).

Chen and Wachs [139] synthesized the MoO_3/Ta_2O_5 (tantalum pentoxide) catalyst and stated that the redox and acidic sites were responsible for forming formaldehyde and

dimethyl ether, respectively. The authors noticed the distortion of the Mo species over a 1% MoO_3–Ta_2O_5 catalyst.

Mo-Fe-O mixed oxides were also supported with different supports (SiO_2 or Al_2O_3) to provide adequate strength. However, the addition of supports declined the catalytic activity related to the unsupported catalyst; the drop in activity was attributed to the interaction between the support and active sites that changed the catalyst's electronic properties [101,121,140,141]. Moreover, the catalyst activity over the alumina supports remained constant despite the temperature rise. The silica-supported iron molybdate catalyst's selectivity decreased with increased temperature [140,142]. It is concluded that supported iron molybdate is less active than the unsupported catalyst. These results authenticated that an increase in the surface has a negative impact on iron molybdate, and these effects are more pronounced on alumina than silica. These results were also approved by Hill and Wilson [143]; when iron molybdate catalysts were synthesized on SiO_2, SiC and TiO_2 supports, it was concluded that Mo-Fe active sites reacted with support, and that was more evident in higher surface area materials.

Recently, Ortiz et al. [81] synthesized the iron molybdate and iron metal over the silica support and performed the partial oxidation of methane/methanol to formaldehyde. It was observed that the pH during synthesis significantly influenced the metal dispersion over the SiO_2; this better dispersion increased the formaldehyde formation in the partial oxidation of the methane. However, the metal distribution over the silica was found not to be that active for partial oxidation of methanol. Instead, bimetallic $FeMoO_x/SiO_x$) prepared by the conventional sol–gel and acid-treated (FeO_x/SiO_2) methods were found to be active in the partial oxidation of methanol to formaldehyde.

The aforementioned literature supports the idea that iron molybdate supported on the smaller surface gives better performance and activity. However, when using a low surface area material, the more the excess presence of MoO_3 results in rapid volatilization [37].

Rozanov et al. [34,144] concluded that the higher surface area support could enhance the catalytic activity and realized that sulphate, pyrophosphate, phosphate and chloride could have significant impacts while preparing iron molybdate over the silica. These materials may remain during the synthesis process after the calcination and increase the catalytic activity.

Similarly, in another study, Peyrovi et al. [145] synthesized the Fe-Mo catalyst over the γ-Al_2O_3 support prepared by impregnation and coprecipitated methods. The coprecipitated catalyst had a large particle size (29 nm) compared with the impregnated catalyst (16 nm). As a result, the coprecipitated catalyst had better performance, with 97% of methanol conversion and 96% selectivity at 350 °C, with an optimum Mo/Fe ratio of 1.7. This increased performance was attributed to the large particle size and effective contribution of the support.

Therefore, a better tradeoff between surface area, essential Mo/Fe stoichiometric ratio and the confinement effects of the support over MoO_3 are vital to consider while synthesizing the iron molybdate catalyst over the different supports.

6. Promoters

The industrial iron molybdate catalyst's stability, mixed oxides' volatilizations, production cost, deactivation of the catalyst, mechanical abrasion of the catalyst in the reactor during repeated use, particle sintering at higher temperatures and short life (1–2 years) are significant concerns.

The promoters' addition to the iron molybdate catalyst could significantly enhance the catalyst's activity and selectivity to balance the operating cost. Not many studies have been reported on promoters in the literature. However, the addition of small amounts of chromium, aluminium, cobalt, nickel and tellurium influences the catalyst's activity and selectivity [25,146].

Klissurski et al. [147] prepared the chromium doped iron molybdate Mo/(Fe + Cr) with the coprecipitation method. Chromium has increased stability and selectivity compared

to the conventional catalyst when tested at 400–420 °C for 100 h. The chromium-doped catalyst had constant stability over the course of 100 h while the traditional iron's molybdate had a 20% reduction in stability.

Sanchez et al. [148] prepared the chromium-impregnated iron molybdate catalyst by the coprecipitation method and compared its performance with industrial iron molybdate catalyst. It was observed that the addition of chromium declined the Mo/Fe atomic ratio and increased the surface area and yield compared to non-doped chromium molybdate under the same conditions.

Estevez et al. [149] recorded the chromium-based iron molybdate catalyst under various Mo/Fe atomic ratios. The Cr and different Mo/Fe atomic ratios significantly influenced and showed a higher conversion but low selectivity at the low-temperature condition. The authors argued that the rise in conversion could be due to chromium or the Mo/Fe atomic ratios.

Pesheva et al. [150] used chromium and aluminium as promoters in the iron molybdate catalysts and recorded an improvement in the catalyst's stability. It was concluded that the promotor's reducibility is vital in the catalysts' stability and proposed the following sequence in increasing order of stability: MoFeO < MoFeCrO < MoFeCrAlO

From the literature, it has been observed that the addition of Cr has increased the catalyst's stability and lifetime, both of which are beneficial for industrial iron molybdate catalysts.

Ivanov et al. [151] prepared the tungsten (0–15.9 wt.%) doped iron molybdate catalyst by coprecipitation method. The prepared catalyst was subjected to reaction at 350 °C to record the formaldehyde yield. The 4.9 wt.% tungsten-based catalysts recorded 93.4% formaldehyde yield compared to 90.2% yield under the conventional iron molybdate catalyst. However, the deactivation mechanism was not covered in this study. The literature [34,152] underlines the additional research on the Sn, P, Mn and Sb to investigate the regenerative, active, selective and stable promoters. The introduction of promoters during the synthesis process requires an excellent knowledge of the surface chemistry of the catalyst.

Role of Fe

Fe facilitates the transfer of H_2O and O_2 between the gas and the catalyst and also reoxidized reduced Mo [60]. It is believed that the iron's presence in sublayers and surface layers of iron molybdate catalyst affects both the activity and selectivity of formaldehyde. It has been concluded that iron occupancy in the sublayers of the catalyst increases the activity [25]. These results were also confirmed by Rellán-Piñeiro and López [60] using the DFT calculation and guaranteed that iron presence affects both the electronic structure and oxygen contents, thus creating the vacancies to raise the yield and selectivity of methanol. The progress in selectivity is due to the lower adsorption energy of formaldehyde than methanol. However, the iron present in the surface layers lowers the selectivity, leading to the further oxidation of the formaldehyde.

7. Role of Oxygen

The reaction of methanol to formaldehyde over the iron molybdate is optimally carried out from 800 to 900 K. The oxygen availability is of utmost importance and it should be sufficiently present in the gas phase. Limited oxygen presence caused the removal of oxygen from the catalyst surface at a high temperature and left the oxidized surface to prevent methanol reduction [153].

Choksi et al. investigated lattice oxygen's interdependence on methanol oxidation and redox processes and examined methanol oxidation kinetics over oxygen at several partial pressures. The oxygen's partial pressure determines the surface's conditions; it also dramatically affects the reaction rate and changes the rate-determining step [154]. Raun et al. investigated the effects of temperature and water concentration on molybdenum loss in iron-molybdenum pellets with a molar ratio (Mo/Fe = 2.4). The optimum presence of water steam prevents Mo's evaporation and its consumption rate [52].

Zarei et al. [76] analyzed the functional properties, hydrodynamic effects and geometric properties of the catalyst under methanol to formaldehyde conversion. It was observed that changes in the water to methanol proportion affect and increase the conversion factor from 50.21 to 82. Moreover, the appropriate presence of oxygen in the water selectively converts methanol to formaldehyde.

House et al. [55] highlighted the effect of oxygen on the selectivity and conversion of methanol. The oxygen content should be kept relatively high in the catalyst's bed edge to reduce the methanol and increase the selectivity to formaldehyde. The catalyst's conversion could be reduced to zero due to the loss of a significant amount of oxygen in the catalyst bed. Andersson et al. [99] highlighted the role of oxygen contents in the feed on the reaction pathway in Table 5 and proposed the highest, lowest and optimum oxygen contents required in the methanol reaction (Figure 7). If the oxygen contents are low, this will deteriorate the catalyst's surface.

Table 5. Oxygen usage per converted methanol in a MoO_3 / $Fe_2(MoO_4)_3$ system. Reprint from [99]. Copyright (2021), with permission from Springer Nature.

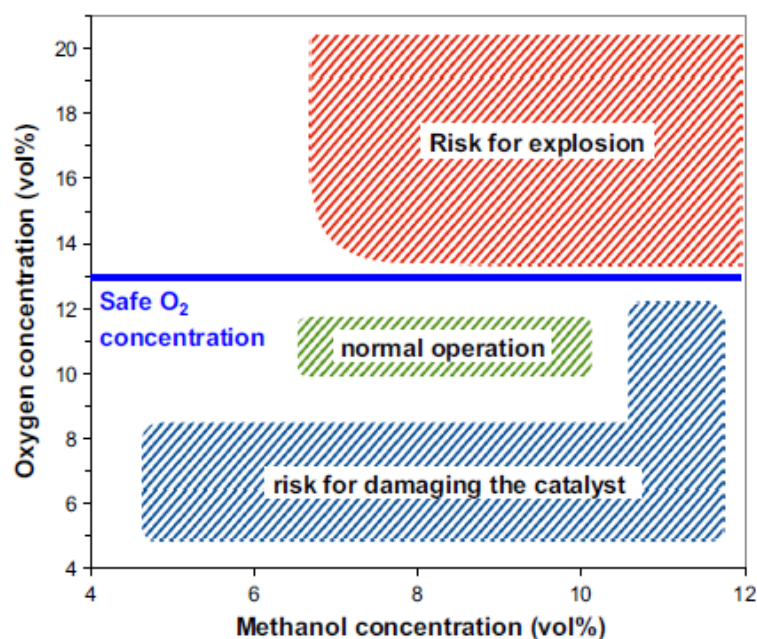| Reaction	Oxygen to Methanol Molar Ratio
$CH_3OH + \frac{1}{2} O_2 \rightarrow CO_2 + 2H_2O$	1.5
$CH_3OH + 1 O_2 \rightarrow CO + 2H_2O$	1
$CH_3OH + \frac{1}{2} O_2 \rightarrow CH_2O + H_2O$	0.5
$2 CH_3OH \rightarrow CH_3O CH_3 + H_2O$	0
$CH_2O + 2 CH_3OH \rightarrow (CH_3O)_2 CH_2 + H_2O$	0

Figure 7. Feed concentration (methanol and oxygen) are presented in a small window. Reprint from [99]. Copyright (2021), with permission from Springer Nature.

While high oxygen contents could cause exposition. Therefore, an optimum presence of oxygen is required for the conversion of methanol to formaldehyde.

As from Figure 7, the reduction of the oxygen is the best way to give a larger margin to avoid the risk of explosion and damaging the catalyst. However, too low an oxygen concentration will also negatively impact the catalyst lifetime.

8. Deactivation Studies

When designing and developing the industrial processes, it is necessary to understand the reaction and deactivation process of the catalytic system. The iron molybdate catalyst

has a typical operation span from 6–12 months. Thus, it is an exciting topic for researchers to study.

Ivanov et al. [155] used a pseudoisothermal reactor and investigated the iron molybdate catalyst's deactivation under 300 °C. The composition of the iron molybdate surface significantly changed after the sublimation of Mo.

Andersson et al. [99] represented the loss of Mo and V under the different molybdates and vanadates in the partial oxidation reaction (Table 6). The volatilization was analyzed after the catalyst was used for 96 h. The reaction temperature was 300 °C.

Table 6. Volatilization of vanadium and molybdenum from a selection of vanadates and molybdates, respectively. Reprint from [99]. Copyright (2021), with permission from Springer Nature.

Catalyst	Mo and V Loss (% per m^2)
$Fe_2(MoO_4)_3$ -MoO_3	9.3
$Fe_2(MoO_4)_3$	2.3
$Cr_2(MoO_4)_3$	6.2
$Zr(MoO_4)_3$	9.7
$FeVO_4$	1.9
$AlVO_4$	4.8
$Mn_3(VO_4)_2$	2.9

It has also been noticed that Mo condensed back as a separate layer on the catalyst surface and formed a Fe rich ($FeMoO_4$) catalyst, which further reoxidized to the Fe_2O_3, and ultimately decreased the surface area and selectivity toward formaldehyde [106].

$$3FeMoO_4 + \frac{3}{4} O_2 \rightarrow Fe_2(MoO_4)_3 + \frac{1}{2} Fe_2O_3 \tag{3}$$
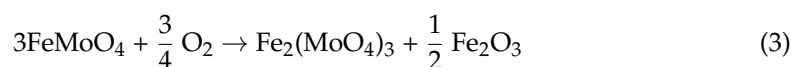
The formation of rust (iron oxide) may stick to the reactor's metal surfaces and damage the material's durability. In addition to that, the Fe_2O_3 becomes part of the methanol feed and is oxidized with the methanol to generate heat. The excess heat resulting from Fe_2O_3 oxidization causes the deflagration of catalysts in industry [156].
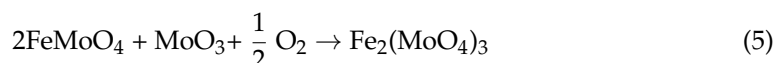
Soares et al. [106] prepared the $Fe_2(MoO_4)_3$ using the coprecipitation and sol–gel method and held water responsible for deactivating the catalyst surface. The authors confirmed that the volatile $MoO_2(OH)_2$ species formed during the reaction, which prevents reoxidation. The authors proposed that Mo volatilization is a significant cause of the deactivation of catalyst prepared by the coprecipitation method. In contrast, the sol–gel prepared catalyst deactivates primarily due to the loss of surface oxygen during the calcination. A better distribution achieved by sol–gel methods prevented the Mo volatilization and validated the presence of surface reduction in the absence of excess MoO_3.

Andersson et al. [37] reported the aging and deactivation of an iron molybdate catalyst and also proposed the deactivation mechanism presented under the Equations (3)–(5) when partial oxidation of methanol is carried out under the iron molybdate catalyst.

The catalyst was entirely characterized after the complete reaction in their studies, and a significant drop in activity was recorded. The MoO_3 was found to be precipitated in the same way as a needle like structure. Mo loss in the iron molybdate catalyst reduces its activity. Therefore, an excess of Mo is always needed to compensate for this loss to increase the catalyst life.

$$CH_3OH + Fe_2(MoO_4)_3 \rightarrow CH_2O + H_2O + 2FeMoO_4 + MoO_3 \tag{4}$$
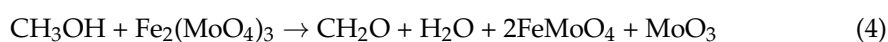
The excess MoO_3 proceeds the reoxidation reaction as follows:

$$2FeMoO_4 + MoO_3 + \frac{1}{2} O_2 \rightarrow Fe_2(MoO_4)_3 \tag{5}$$

However, in a MoO_3 deficient environment, Fe_2O_3 assists the CO_2 production. As explained earlier in reaction (3)

$$3FeMoO_4 + \frac{3}{4} O_2 \rightarrow Fe_2(MoO_4)_3 + \frac{1}{2} Fe_2O_3 \qquad (6)$$
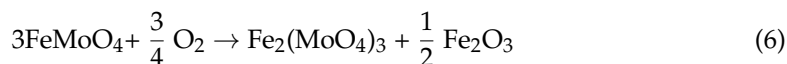
Sun-Kou et al. [58] reported that the correct Mo: Fe ratio (1.7:1) is essential to achieve both active and stable catalysts, and excess Mo above the optimum level might not participate in the process because of the high loss rate.

Mitov et al. [157] proposed that the deactivation of the iron molybdate proceeds via anion mobility, which led to the disruption of the catalytic surface at 300 °C and disruption increase at higher temperatures. However, Jacques et al. [158] concluded that water formation during the reaction blocks the active sites and causes H obstruction on the surface. Jacques et al. [159] also observed the reduction in stability and performance at 350 °C when MoO_3 volatilized and led to the formation of the MoO_2 phase. The excess MoO_3 is essential to reduce methanol and oxidized the O_2 at a high rate.

The iron molybdate catalyst life also depends on temperature, pellet size, methanol to oxygen ratio and working conditions [69,160]. The volatile species formed in partial oxidation of methanol lead to Mo's volatilization, thus deactivating the catalyst surface [37,106,110,160,161]. It leads to particle sintering in high-temperature zones, increases the pressure drop and decreases catalytic activity [161–163]. The deactivation changes the iron molybdate $Fe_2(MoO_4)_3$ into the Fe_2O_3 and $FeMoO_4$-phase [37,106,161]. Braz et al. also agreed that high-temperature zones in the reactor facilitate the volatilization in the partial oxidation of methanol, resulting in the loss of Mo [39].

9. Conclusions

Based on a review of the literature, the role of MoO_3 and $Fe_2(MoO_4)_3$ has been discussed. It is concluded that the correct Mo/Fe ratio is mandatory to achieve the selective formation of formaldehyde. $Fe_2(MoO_4)_3$ has been identified as the active ingredient, and excess molybdenum is considered a bystander phase. The optimum stoichiometric ratio (Mo/Fe) maintains oxygen availability on the catalyst's surface and affects the catalytic acidity required for the selective conversion of methanol to formaldehyde. $Fe_2(MoO_4)_3$ acts as an active phase with optimum Mo needed to compensate for the loss of molybdenum during the reaction. The presence of Mo contents maintains the electron density and serves as the donor phase. It provides the needed oxygen to support the activity and limits the generation of iron-rich phases. However, excess Mo above the optimum level might not participate in the reaction because of the high degradation rate. Similarly, different phases of MoO_3, active support to maintain the electronic properties and confinement of metals, the addition of effective promoter and its reproducibility, optimum methanol to oxygen contents, synthesis methods and newly shaped catalyst particles (spinal type) compared to conventional catalysts essentially affect the conversation and selectivity in the partial oxidation of methanol. The limited supply of Mo, insufficient oxygen contents, the presence of water, high-temperature zones and methanol itself act as reducing agents and remove oxygen from the surface, leading to several deficient Mo-based iron molybdate catalysts, which are neither selective nor active towards formaldehyde.

It is crucial to consider the reaction conditions, preparation methods to influence the catalyst particle's shape ($Fe_2(MoO_4)_3$–MoO_3) and maintain the active MoO_3 bystander for an extended period. Incorporating a computer-based simulation to accurately analyze the bonding energy between the catalyst surface and oxygen for quick reduction and fast reoxidation is essential to extend the catalyst's life and selectivity towards formaldehyde. New materials should give a better yield, be less volatile, and give consistent selectivity for repeated use.

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