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ARTICLE

# One-Pot *1,1*-Dimethoxymethane Synthesis from Methanol: A Promising Pathway over Bifunctional Catalysts

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## Abstract

Dimethoxymethane or DMM is a versatile chemical with applications in many industries such as paintings, perfume, pharmacy, and fuel additives. DMM can be produced through the reaction of methanol and formaldehyde in the presence of acid catalysts, or directly, through the selective oxidation of methanol over catalysts with redox and acid functionalities. In terms of sustainability, the so-called bio-methanol derived from syngas obtained via biomass gasification can be used in DMM synthesis. In this review article we have condensed and classified the research outputs published over the past decade aimed at producing DMM from methanol over different types of catalysts. The majority of studies described the reaction of methanol to DMM in a promising way using heterogeneous catalysts in gas phase for the ease of product and catalyst recovery as well as suitability for continuous processing. Likewise, the influence of parameters including catalyst component, feed composition, and temperature on the performance of catalysts utilised in DMM production is analysed and discussed. Further, some perspectives concerning the evolution of potential DMM market with respect to the characteristics of the best catalyst materials for high DMM productivity are expressed.

## 1 Introduction

The current fossil fuel exploitation to notably meet the world's energy needs has raised a global concern of the future risks linked to petroleum and natural gas reserves depletion. Finding alternative resources that are renewable and can be sustainably used in the future is really the challenge to be faced in the 21st century. Biomass is an important renewable feedstock for a large spectrum of products including fuels for transportation and high value-added chemicals.[1] If rationally handled, using biomass as a raw material provides a way of producing substances with less environmental impact, *e.g.*, through a reduction of greenhouse gas emissions, especially carbon dioxide. *1,1*-Dimethoxymethane, also known as methylal or DMM, is a versatile molecule that can be obtained from methanol produced from syngas generated from biomass conversion, the mainstream of methanol being currently obtained from natural gas-based and coal-based syngas. DMM has a wide range of market applications. High purity DMM is used in cosmetics and pharmaceuticals[2]. It is used in the synthesis of polyoxymethylene dimethylether (POMM), a more user-friendly embalming agent in substitution of the currently used formaldehyde, which is a well-known human carcinogen. DMM and POMM are considered as alternative fuels for low-temperature fuel cells, much safer than methanol, due to, *e.g.*, extremely low toxicity of DMM and POMM lower volatility[3,4,5,6]. DMM can also be used as a hydrogen storage material for compact hydrogen. More importantly, DMM finds also an

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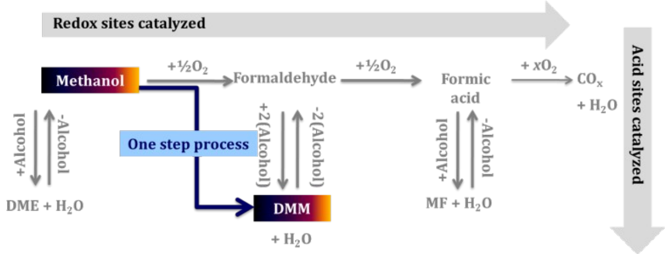
application as an oxygenated additive to diesel fuel, particularly helping in the reduction of particles emissions, of which the great harm to human health has been recently widely covered by the media[7,8]. DMM can also be used as an alternative source to concentrated formaldehyde at a higher concentration compared to the conventional way, *i.e.*, methanol to formaldehyde oxidation reaction[9].

## 2 Methanol oxidation reaction pathways to synthesize DMM

Methanol oxidation is a well-known probe reaction to characterize the surface acidity, basicity as well as the redox property of metal oxide catalysts[10,11], *e.g.*, molybdenum-based systems supported on silica and vanadia supported on titanium oxide. The possible pathways of methanol reaction over such catalysts are reported in Scheme 1. The redox-catalysed pathway leads to a sequence of oxidized species including formaldehyde, formic acid and carbon oxides (CO and $CO_2$), whereas the dehydration products including dimethyl ether (DME), DMM and methyl formate (MF) are formed *via* the acid-catalyzed pathway. The recent review of Wu et al described the various route to obtain the aforementioned products.[12] DMM and MF are obtained from the condensation of methanol with formaldehyde and formic acid, respectively. Formic acid is considered as an intermediate in the formation of MF or carbon oxides and it is rarely observed in the products mixture[13,14].



**Scheme 1 : Methanol oxidation pathways** adapted from [15].

### 2.1 Indirect oxidation of methanol to DMM

For the industrial scale production, DMM is conventionally produced *via* a two consecutive steps. Methanol is first oxidized in the gas phase to formaldehyde followed by a liquid phase acetalization of the so-obtained formaldehyde with methanol in a second reactor[16,17,18,19,20,21,22,23,24]. The oxidation reaction proceeds over metallic silver or an iron molybdate (FeMo) mixed oxides catalyst. The silver-catalysed process operates at atmospheric pressure using a feed rich in methanol (50 % v/v) at a temperature in the range between 560 and 600 °C[25]. The conversion of methanol per pass in the reactor is of 65-75 %. The unreacted methanol is separated from the reactive mixture and recycled back into the reactors to finally achieve 89 % yield in formaldehyde[26]. The iron molybdate mixed oxides is used in the oxidation process, where a much lower concentration of methanol, *i.e.*, 7 vol.% of methanol in air, is fed into the reactor under atmospheric pressure. An excess of air is used to ensure a maximum conversion of methanol and to avoid the explosive mixture compositions between 7 and 37 Vol. % of methanol in air[25]. The reaction temperature is kept below 400 °C to maintain the catalyst stability and limit side reactions, especially the dehydration of methanol to ether. The yield of formaldehyde obtained from iron molybdate mixed oxides is 95 % at 98-99 % methanol conversion. The average lifetime of the FeMo catalyst is about 6 to 12 months, which is longer than that of the silver catalyst that is typically of 2-4 months.[27] Moreover, the FeMo mixed oxides is less sensitive to contamination by impurities present in air such as $CO_2$, $CH_4$, and $N_2O$, as well as by impurities in methanol, *e.g.*, acetone, in comparison to the metallic silver.

The current production of DMM is carried out *via* the subsequent liquid phase condensation of formaldehyde and methanol in the presence of strong mineral acids (*e.g.*, $H_2SO_4$ or $H_3PO_4$)[28]. However, homogeneous catalysts are corrosive, difficult to separate from the products, and the removal of catalysts generates excessive amount of hazardous wastes. The research focused on the use of heterogeneous catalysts to manufacture DMM is therefore much preferable and this certain area of study has recently received much attention. Examples of solid acid catalysts that have been used in DMM synthesis include cation-exchange resins, sulfonated fluoroalkylene resin derivatives, and crystalline aluminosilicates[29]. Some applications are also patented. The Lambiotte & CIE process incorporates a catalytic distillation reactor using Amberlite® 15 wet resin to obtain almost quantitative yield of azeotropic methylal (93 % DMM and 7 % methanol). After neutralization with base, the azeotropic product is fed to an extractive distillation tower, where water is used as an extraction medium. After drying of the overhead product, very high purity of DMM, *i.e.*, 99 %, is obtained[30]. The BP Corporation also patented a two consecutive steps process for preparation of polyoxomethylene dimethyl ether (POMM) from methanol and/or dimethyl ether, with DMM as a main product[17,18,19,20,21,22,23,24,31].

### 2.2 Direct oxidation of methanol to DMM

The selective transformation of methanol to DMM is strongly sensitive to the nature of the active sites (*i.e.*, acid and oxidant nature) present on the catalyst surface and to their relative strength as shown in Figure 1[32]. These two sites should be spatially close. The formation of DMM requires a weak acidic center surrounded by low oxidizing power sites. When the site is more acidic, the residence time of formaldehyde species becomes long enough to form dioxymethylene as an intermediate,[33] which subsequently reacts with methanol to form DMM. However, the oxidizing power of the active center cannot be too high, else dioxymethylene species are oxidized before reacting with methanol. When the site is too acidic and has a strong oxidizing power site nearby, dioxymethylene intermediates are oxidized *(i)* to formate species, which then reacts with methanol to form methyl formate, or *(ii)* to carbon oxides on sites with a very strong oxidizing power. DME is a major product formed when strong acid centers with low oxidizing power are present.

Indeed, as claimed by Tatiboüet *et al* in [32], an appropriate system for the direct synthesis of DMM from methanol should be a catalyst with appropriate redox and acid functionalities in order to orientate the reaction through the desired pathways leading to DMM. Developing selective catalysts for a single-step conversion of methanol to DMM is challenging and this has become a strong research interest in the recent years. Thus, a variety of heterogeneous catalysts have been developed to selectively convert methanol to

DMM[34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54]. In the following paragraphs, we will focus on the direct synthesis of DMM by heterogeneous catalytic oxidation of methanol, which is a favourable option in terms of minimizing the energy consumption as well as reducing the environmental impact generated along the two-steps process. The production of DMM with a suitable bifunctional catalytic system also helps the industry lowering its Capital Expenditure (CAPEX) along with the production cost reduction.

### 2.2.1 Heteropolyacids (HPAs) and molybdenum-based catalysts

Heteropolyacids containing molybdenum, with P or Si central atoms, can catalyse the oxidation of methanol to formaldehyde with minor amounts of DMM[55]. Fournier *et al*. reported the use of bulk and supported *12*-molybdophosphoric acid catalysts providing up to 55 % of DMM selectivity at approximately 20 % conversion of methanol[34]. The authors suggested that the $\beta$-$MoO_3$ phase present in the catalyst is capable of reacting with water vapour produced by the reaction in the presence of phosphoric oxide to recreate the initial heteropolyacids. Liu and Iglesia investigated the performance of $H_{3+n}V_nMo_{12-n}PO_{40}$ polyoxometallate Keggin clusters supported on $SiO_2$ in the oxidation of dimethyl ether and methanol at low temperatures (180-240 °C). They reported a DMM selectivity of 58 % at a methanol conversion of 68 % over 9.2 wt.% $H_4PVMo_{11}O_{40}$ supported on $SiO_2$.[35] The accessibility of acid and redox sites increased when anchoring HPAs clusters on $SiO_2$ supports, improving both the DMM synthesis rate and the selectivity. After selectively 'poisoning' the protons on the surface with an organic base, they could inhibit the formation of DME and thereby increased the selectivity of DMM to 80 % at 180 °C. A high DMM selectivity of 76 % was also reported on 2 mol.% Mo supported on MCM-41, but it was achieved at a very low conversion of 0.7 % at 270 °C.[56] Nevertheless, this catalyst was rapidly deactivated owing to the significant leaching of Mo species from the channels of MCM-41.

### 2.2.2 Ruthenium-based catalysts

Liu and Iglesia examined the performances of $RuO_2$ clusters supported on $SnO_2$, $ZrO_2$, $TiO_2$, $Al_2O_3$ and $SiO_2$ in the selective oxidation of methanol to DMM at low temperatures between 27 and 127 °C,[36] at which the thermodynamics of the reaction is more favourable. A maximum DMM selectivity of 67 % was reported in this work over a 4.4 wt.% $Ru/Al_2O_3$ catalyst at 60 °C, using a high methanol pressure of 80 kPa, where the thermodynamic limitations are not essential. The oxidative dehydrogenation rate per exposed Ru atoms was the highest when $RuO_2$ was supported on $SnO_2$ due to the ease of $RuO_x$ clusters reduction. The performances in methanol oxidation on supported Ru oxide are presented in Table 1. Further, a recent paper deals with production of DMM from methanol in liquid phase using $MeCl_3$ catalysts where Me is Fe, Ni, Zr, Zn and Ru[57]. The reaction was carried out in a batch autoclave using molecular $O_2$ (3 MPa) as an oxidizing agent. The authors claimed that the Ru-based catalyst is the only system among the tested catalysts that is able to transform methanol into DMM with an interesting yield of 33.6 %.

### 2.2.3 Rhenium-based catalysts

Iwasawa and coworkers focused their studies on DMM formation over $ReO_x$ compounds and Re-based mixed oxides supported on $TiO_2$, $SiO_2$, $V_2O_5$, $ZrO_2$, $\alpha$-$Al_2O_3$, $\alpha$-$Fe_2O_3$, and $\gamma$-$Fe_2O_3$[37]. $SbRe_2O_6$ was highlighted for its good performances in the synthesis of DMM. The catalyst converted 6.5 % of methanol at 300 °C and provided a DMM selectivity as high as 92.5 %[38]. The conversion of methanol sharply increased with increasing temperature to 86.2 % while keeping a high selectivity of 85.4 % to DMM. The authors suggested that the performance of the crystalline $SbRe_2O_6$ catalyst are correlated to the rhenium oxide connecting with Sb-O chains. The stabilization of Re-oxide species by the specific connection with Sb oxide chains at the surface is a key issue relevant to the selective DMM formation. No structural change in the bulk and surface of the catalyst was observed during and after reaction at 300 °C, which was evidenced by XRD, Raman, XPS, and SEM results. Nevertheless, the low surface area of $SbRe_2O_6$ ($1\ m^2.g^{-1}$) and the loss of rhenium atoms by volatilization under $O_2$ are important hurdles for commercial applications[39]. A further study by Yuan and Iwasawa on supported Re oxide on different supports including $V_2O_5$, $ZrO_2$, $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$, $SiO_2$, $\alpha$-$Al_2O_3$, $Sb_2O_3$, $Bi_2O_3$, $MoO_3$ and $TiO_2$ in rutile and anatase forms evidenced that 10 wt.% Re/$\gamma$-$Fe_2O_3$ was the most efficient catalyst in DMM production with 91 % selectivity to DMM at 48 % conversion of methanol (Table 2). They suggested that the redox ability of Re oxides, *i.e.*, $Re^{VI-VII} \leftrightarrow Re^{IV}$, was responsible for the high catalytic activity, while an adequate Lewis acidity of the Re oxides was also necessary for the acetalization of formaldehyde with methanol to DMM. The oxide supports also prevented Re oxides from being sublimated and reduced to $ReO_2$ particles. Re/$\alpha$-$Fe_2O_3$, Re/$\gamma$-$Fe_2O_3$ and Re/$V_2O_5$ catalyst were very selective to DMM, *i.e.*, 91-95% DMM selectivities were obtained, in a wide range of conversions, *i.e.*, 16-48 %, at 240 °C. The selectivities of the Re-oxide catalysts were similar to that of $SbRe_2O_6$, but their catalytic activities are significantly higher. Following the studies by Iwasawa's group, Sécordel *et al.* concentrated their work on supported $TiO_2$ (anatase) and $SiO_2$ oxorhenate systems.[41] The catalysts were prepared by oxidative thermal spreading of metallic $Re^0$ on the support in the absence of water to prevent $HReO_4$ volatilization. The structures and the catalytic activity of the resulting materials were comparable to those of catalysts prepared using the incipient wetness technique. A maximum DMM selectivity of 77 % at 44 % methanol conversion was achieved over a Re/$TiO_2$ catalyst at 260 °C.

### 2.2.4 Supported vanadium-based catalysts

The oxidation of methanol over supported vanadium-based catalysts has been reported for the production of formaldehyde[58] and methyl formate.[59] In these reactions, DMM was usually observed as a by-product[48,78]. In general, the selectivity to DMM sharply decreases with the increase of conversion of methanol over the conventional $V_2O_5/TiO_2$ catalysts.[60] Fu and Shen demonstrated that the selectivity to DMM can be greatly improved by the addition of $Ti(SO_4)_2$ on traditional supported $V_2O_5/TiO_2$ catalysts even at high methanol conversions.[43] 89 % DMM selectivity was obtained at 60 % conversion with the modified 10%$V_2O_5/TiO_2$-$Ti(SO_4)_2$ catalyst, whereas only 11 % of selectivity were found at 41 % conversion for the $V_2O_5/TiO_2$ solid. This suggested that the surface acidity

**Table 1 : Catalytic performances in methanol oxidation on supported Ru oxides at 240 °C adapted from Ref. 36. a Based on the Ru content and the BET surface area; b With 96 kPa balance He; c Rate for primary methanol oxidative dehydrogenation to formaldehyde. Experimental conditions: $CH_3OH/O_2/He$ = 4.0/9.7/86.3 mol.%, GHSV = 40 $L.h^{-1}.g_{cat}^{-1}$, atmospheric pressure, fixed-bed reactor; $CO_x = CO+CO_2$**

| Catalyst (Ru wt. %) | Ru surface density ($Ru/nm^2$)[a] | Reactants ($CH_3OH/O_2/N_2$, kPa) | Temperature (°C) | ODH turnover rate ($mol/g_{atom\ Ru\text{-}surf}.h$)[c] | Selectivity (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | F | MF | DMM |
| $RuO_2/TiO_2$ (2.2 %) | 3.1 | 4/9/1[b] | 120 | 84.7 | 25.2 | 69.9 | 4.1 |
| $RuO_2/ZrO_2$ (4.1 %) | 2.1 | 4/9/1[b] | 120 | 88.9 | 6.6 | 70.7 | 5.6 |
| $RuO_2/SnO_2$ (4.1 %) | 2.5 | 4/9/1[b] | 120 | 142.3 | 20.0 | 60.7 | 15.5 |
| $RuO_2/SiO_2$ (4.3 %) | 1.1 | 4/9/1[b] | 120 | 41.5 | 12.4 | 31.0 | 56.1 |
| $RuO_2/Al_2O_3$ (4.4 %) | 1.3 | 4/9/1[b] | 120 | 71.0 | 11.6 | 30.1 | 57.4 |
| $RuO_2/SnO_2$ (4.1 %) | 2.5 | 80/18/2 | 60 | 19.9 | 1.6 | 57.3 | 40.8 |
| $RuO_2/Al_2O_3$ (4.4 %) | 1.3 | 80/18/2 | 60 | 9.5 | 9.4 | 23.4 | 66.8 |

of $V_2O_5/TiO_2$ was not strong enough to promote the condensation reaction. Accordingly, the production of a large amount of formaldehyde as well as of methyl formate was observed in agreement with the assumptions of Tatibouët *et al.*[10] With the acid modification, the condensation of formaldehyde with methanol was significantly promoted. A higher DMM selectivity of 92 % at 48 % conversion was reported, but, over the $V_2O_5/TiO_2$-$Ti(SO_4)_2$ catalyst containing less amount of $V_2O_5$ (5 wt.%). This performance was as good as that of 10 wt.% Re/$\gamma$-$Fe_2O_3$ obtained by Iwasawa and co-workers.[37,39] The $V_2O_5/TiO_2$-$Ti(SO_4)_2$ catalyst was more reactive than the supported Re/$\gamma$-$Fe_2O_3$, considering that the rate of methanol conversion over the former was approximately 50 % higher, while the reaction took place at a temperature 80 °C lower. Liu *et al*. revealed the high performance of $TiO_2$ nanotubes (TNT) impregnated with $V_2O_5$ and modified with $SO_4^{2-}$ ions for the selective production of DMM from methanol[44]. The conversion of methanol reached 64 % with 90 % selectivity to DMM at 130 °C over the catalyst formulation containing 20 wt.% of $V_2O_5$ impregnated in TNT with 6 wt.% $SO_4^{2-}$ ions addition. A high surface area ($S_{BET}$ = 305 $m^2.g^{-1}$) and open mesopores of TNT helped facilitating the transportation of methanol to the active sites during the reaction, leading to a higher conversion. The semiconducting property of TNT might favour the electronic interaction between the support and the active phases, leading to improved catalytic redox reactivity as well.[61] The addition of $V_2O_5$ increased the surface acidity of TNT, which was further enhanced by the addition of $Ti(SO_4)_2$. The authors also prepared mesoporous $VO_x$-$TiO_2$ mixed oxide with a high surface area using the evaporation-induced self-assembly (EISA) technique,[62] and post-treated the catalyst with ammonia solution to increase the thermal stability of mesoporous titania[63]. Incorporation of vanadia into the titania system significantly increased the conversion of methanol from 0.2 % to 8 % with a DMM selectivity as high as 93 %[45]. With increasing the reaction temperature, the conversion of methanol increased while the selectivity to DMM rapidly declined with increased selectivities to formaldehyde and methyl formate. Apparently, the surface acidity of the $VO_x$-$TiO_2$ catalysts was not strong enough for enabling the condensation reaction to form DMM at high temperatures. The addition of $SO_4^{2-}$ over the $VO_x$-$TiO_2$ surface resulted in a significant increase of both methanol conversion and DMM selectivity. The latter was attributed to the improvement in surface acidity pointed out by an increase in propylene and diisopropylether, the dehydration products from *iso*-propanol tests. This increase in the surface acidity upon addition of sulphate in vanadia-titania catalysts was also observed by Baraket *et al*. who prepared $VO_x$-$TiO_2$ catalysts *via* a sol-gel process. The catalyst having 30 wt.% of $V_2O_5$ on the $TiO_2$ support with modification of approximately 10 wt.% of $SO_4^{2-}$ gave 83 % selectivity to DMM at 150 °C with a 57 % methanol conversion.

Obviously, the DMM selectivity is strongly affected not only by the addition of sulphate, but also by the nature of the vanadia loading, and the sulphate-vanadia interaction. Following the work of Liu and coworkers[44], Cai *et al.* investigated the effect of acidic promoters including sulphuric, phosphoric, and phosphotungstic acids on $V_2O_5$-supported TNT.[64] They found that only the catalyst modified with sulphuric acid and treated by a calcination at 400 °C revealed significantly improved DMM selectivities with high methanol conversions. 92 % selectivity to DMM could be maintained at a high conversion of methanol of 58 % at 130 °C. The calcination created some sulphate groups strongly interacting with vanadium species, which enhanced the surface acidity strength without weakening the redox ability of the vanadium sites, unlike those catalysts modified with phosphoric and phosphotungstic acids that might cover some redox sites of vanadia species. Lu *et al*. prepared a series of supported $V_2O_5/TiO_2$ catalysts modified with $H_2SO_4$ for the selective oxidation of methanol.[49] The number of acid sites significantly increased with the amount of $SO_4^{2-}$ used in the acid modification. However, the acid strength was found to decrease simultaneously with the $V_2O_5$ loading. The content of $V_2O_5$ should not exceed 15 % in order that the catalytically active

**Table 2 : Catalytic performances in methanol oxidation on supported Re oxides at 240 °C adapted from Ref. 39**

| Catalyst | $S_{BET}$ (m$^2$.g$^{-1}$) | $CH_3OH$ conv. (mol.%) | Selectivity (mol.%) | | | | | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| | | | HCHO | $CH_2(OCH_3)_2$ | $(CH_3)_2O$ | $HCOOCH_3$ | $CO_x$ | DMM |
| Re/$TiO_2$ (rutile) | 5 | 53.7 | 1.9 | 83.1 | 0.7 | 9.1 | 5.2 | 45 |
| Re/$TiO_2$ (anatase) | 50 | 59.5 | 4.1 | 78.5 | 1.1 | 11.7 | 4.6 | 47 |
| Re/$V_2O_5$ | 6 | 21.5 | 0.0 | 93.7 | 4.3 | 0.0 | 2.0 | 20 |
| Re/$ZrO_2$ | 9 | 35.8 | 2.0 | 89.4 | trace | 7.6 | 1.0 | 32 |
| Re/ $\alpha$-$Fe_2O_3$ | 3 | 15.5 | 2.0 | 90.5 | 1.0 | 6.0 | 0.5 | 14 |
| Re/$\gamma$-$Fe_2O_3$ | 16 | 48.4 | 2.4 | 91.0 | 1.0 | 4.6 | 1.0 | 44 |
| Re/$SiO_2$ | 36 | 15.1 | 1.3 | 60.7 | trace | 11.9 | 26.1 | 9 |
| Re/$\alpha$-$Al_2O_3$ | 10 | 16.3 | 2.8 | 88.3 | trace | 5.9 | 2.9 | 14 |
| Re/$MoO_3$ | 5 | 9.1 | 0.0 | 80.0 | 19.0 | 0.0 | 1.0 | 7 |

vanadium species are highly dispersed on the $V_2O_5/TiO_2$ surface. The catalyst loaded with 15 wt.% $V_2O_5$ and 15 wt.% $SO_4^{2-}$ was declared as the best catalyst for DMM formation, with an adequate trade-off between the dispersion of vanadia species and the balance between redox and acid functions. 93 % selectivity to DMM at 49 % methanol conversion at 150 °C were obtained over this catalyst.

Acidic additives such as phosphorous-containing species have been applied to many oxidation reactions. These species can interact with surface vanadia species and have a significant influence on the surface acidity and catalytic properties.[65] Chen *et al*. studied the performances of $VO_x$ supported on TS-1 zeolite (25 wt.% Ti) doped with $SO_4^{2-}$ and $PO_4^{3-}$ ions.[50] The TS-1 zeolite was selected as a support due to its high specific surface area, excellent stability and high acidity. $VO_x$ deposited on the surface of TS-1 served as redox sites. Upon loading with $VO_x$, TS-1 exhibited a decrease in specific surface area, pore volume, and pore size, which suggested that $VO_x$ was deposited and highly dispersed in the TS-1 channels. While using a reactant feed within the flammable region*, i.e.*, methanol/$O_2$/$N_2$ = 1/2.5/7.5 (v/v), the authors reported a positive effect when adding $SO_4^{2-}$ into the $VO_x$/TS-1 catalyst, whereby the methanol conversion was significantly boosted (46 % compared to 24 % for the unmodified catalyst) with essentially the same selectivity (81 % *vs.* 83 %) at 150 °C. The higher DMM formation was attributed to a better reducibility coupled with a larger number of acidic sites. In the case of $PO_4^{3-}$-doped catalysts, the reduction occurred at significantly lower temperatures compared to those observed over $SO_4^{3-}$-doped catalyst. This phenomenon suggested that $PO_4^{3-}$ interacts with the surface vanadia species and enhances the reducibility of the catalyst. The addition of sulphate ions induced the formation of strong acidic sites, whereas the introduction of phosphate ions generated moderate acidic sites with enhanced amounts of acid sites in both cases. The addition of $PO_4^{3-}$ had an effect on the type of the surface acidity because only Lewis acidity was present on the $VO_x$/TS-1/$PO_4^{3-}$ catalyst. Zhao *et al*. investigated the influence of the calcination temperature on the activity of $VO_x/TiO_2/SO_4^{2-}$ catalysts[46]. The best catalytic performance was observed over the $VO_x/TiO_2/SO_4^{2-}$ sample calcined at 400 °C having a proper sulphur concentration of approximately 0.8 wt.%. The highest DMM yield (61.4 %) was obtained at 130 °C at 74 % methanol conversion and 83 % DMM selectivity. 400 °C is an optimal temperature for catalyst calcination in terms of maximizing the surface acidity. The catalyst contained polymeric $VO_x$ species with terminal V=O bonds, high Brønsted acidity, and enhanced reducibility after calcination at this temperature. The $VO_x$ species with terminal bonds was claimed to be the most active species for methanol adsorption and C-H bond breaking, particularly when compared to crystalline $V_2O_5$. Calcination at temperatures higher than 450 °C led to a higher formation of less active crystalline $V_2O_5$ species. Increasing the sulphur loading was found to have the effect of poisoning the catalytic sites. The samples with high contents of sulphur exhibited an appreciable amount of acid sites but the yield in DMM did not increase remarkably with increasing the acid sites concentration.

Kaichev *et al*. studied the reaction of methanol over vanadia supported on anatase $TiO_2$, and DMM was found dominant at temperatures below 120 °C with selectivities up to 95 % but at a relatively low conversion (less than 30%)[66]. At low temperatures, the formation of DMM competed with that of methyl formate, while the formation of formaldehyde was largely inhibited. The active sites were assigned to the highly dispersed $VO_x$ vanadia species on $TiO_2$. The freshly prepared catalyst was washed with nitric acid and this selectively dissolved the $V_2O_5$ crystallites resulting in the less active species for methanol oxidation, leaving only highly dispersed vanadia species over the surface of titania with approximately one monolayer, *i.e.*, 7.1 V atom/nm$^2$. The polymeric vanadium oxide was the dominant species in this monolayer coverage according to the Raman spectroscopy data.[67] These species consisted of a terminal V=O bond with at least one V-O-Ti linkage and one or two bridging V-O-V bonds.

The influence of the preparation method on the surface and the catalytic properties of $VO_x/TiO_2/SO_4^{2-}$ catalysts was further examined by Zhao *et al.*[68] by preparing samples with 25 wt.% of $V_2O_5$ and 0.2-6.5 wt.% of S *via* a co-precipitation technique with and without 1 % of polyethylene glycol, *via* a sol-gel method and *via* mechanical grinding before calcination at 450 °C in air. The catalyst prepared by the co-precipitation technique showed the highest conversion of methanol. An 86 % DMM selectivity was reported for a 61 % methanol conversion at 150 °C. The catalyst surface acidity was strong enough to catalyse the reaction of methanol to DMM, without producing a large amount of formaldehyde and methyl formate as oxidation products. The co-precipitation was also the best method in terms of maximizing the specific surface area. The sample prepared by mechanical grinding was found completely non-homogeneous. The same research group also prepared $VO_x/TiO_2/SO_4^{2-}$ catalysts with different loadings of vanadia, *i.e.*, 5, 15 and 25 wt.%, by successive incipient wetness impregnation.[69] The conversion of methanol increased with the vanadia content due to enhanced redox ability, in agreement with the results of TPR measurements, which showed an increase in $H_2$ consumption with vanadium loading. Meanwhile, the selectivity to DMM slightly increased upon the addition of $SO_4^{2-}$ ions due to enhanced surface acidity. The best catalytic behaviour was obtained over the catalyst doped with $SO_4^{2-}$ ions with 25 wt.% loading of $V_2O_5$. A 54 % DMM selectivity at a 58 % methanol conversion was reported at 150 °C.

Coprecipitation and incipient wetness impregnation are typical ways to prepare supported vanadium catalysts. In these techniques, additional heat treatment is required to obtain the desired phase composition and purity. This post treatment leads to a significant aggregation of the catalyst particles. This aggregation of particles may weaken the interaction between vanadia and the supports, leading to lower reducibility, which is thus unfavourable for methanol oxidation, the first step in DMM synthesis. This aggregation can also decrease the number of acidic sites, which does not help facilitating the second step where methanol is condensed with formaldehyde to form DMM. To overcome this problem, the preparation of catalysts at the nanoscale has been considered as an efficient pathway. Guo *et al*. synthesized sulphated $V_2O_5/TiO_2$ catalysts by a rapid combustion method.[70] A high DMM selectivity (92 %) at 44 % conversion of methanol was obtained at 120 °C at the optimum sulphate content of 4 mol.%, which was attributed to the largest number of acidic sites as well as the increased number of highly dispersed sulphate species. The coverage of aggregated sulphate when its content was beyond 4 mol.% on the surface of the catalyst decreased the reducibility of $VO_x$ also the population of the acidic sites, leading to a decrease in DMM selectivity.

### *2.2.5 Multicomponent metal oxide catalysts*

The development of multicomponents metal oxide catalysts has been of particular interest recently. Golinska-Mazwa *et al.* used binary oxides of Sb and V modified with ammonium niobate (V) and oxalate hydrate ($C_4H_4NNbO_9$) in the oxidation of methanol.[52] The authors suggested that a selective catalyst formulation for DMM production could be obtained with a proper synthesis procedure of $SbVO_x$ mixed oxide and further modification with Nb. The use of Pluronic P123 as a template in the synthesis of the catalysts helped increasing the specific surface area and pore volume of the final materials. The sample prepared in the presence of a template contained $\alpha$–$Sb_2O_4$ phase, a *p*-type semiconductor that allows the electron transfer from vanadium species in $SbVO_x$ to $Sb_2O_4$ at the interface of these two phases. This electron transfer induces the formation of oxygen vacancies and thus promotes the chemisorption of $O_2$. The $O^{2-}$ oxygen ion spills over the interface and partially reoxidizes the V species, increasing the catalytic activity. The conversion of methanol increased from 26 % on the Nb-free catalyst to 34 % on the Nb/$SbVO_x$ (P123-prepared) catalyst in the same time the selectivity to DMM increased drastically (39 % *vs.* 4 %). This behaviour is explained by the change in acidic strength resulting from the Nb-V interaction. The Nb-V interaction further induced a stronger formaldehyde chemisorption and helped retaining formaldehyde on the surface for further interaction with methanol molecules to form DMM.

The use of an amorphous mixed oxide catalyst of the general formula $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}O_x$, prepared by a simple straightforward coprecipitation procedure, for the selective oxidation of methanol in the gas phase was described by some of the present authors.[53] A DMM selectivity as high as 90 % could be obtained at a high methanol conversion of 68 % at 280 °C, after preactivation of the catalyst in pure oxygen at 340 °C for 1 h. This catalyst performed well in a wide range of methanol concentrations and reaction temperatures, *i.e.*, 220-280 °C, without a drastic loss in DMM selectivity, which is of interest for industrial applications.

Chen *et al*. prepared mesoporous Al-P-V-O catalysts by coprecipitation of $Al(NO_3)_3.9H_2O$, $(NH_3)_2HPO_4$ and $NH_4VO_3$ solutions[71] and tested the samples with different loadings of phosphorous and vanadium in the selective oxidation of methanol. The reducibility and surface acidity of the Al-P-V-O catalysts varied with the Al/V/P ratio. The highest yield in DMM (56 % conversion and 82 % selectivity at 110 °C) was obtained with the catalyst having 10 wt.% of P and 20 wt.% of V, with a proper balance of acid and redox characters, determined by respectively $NH_3$-TPD and $H_2$-TPR, suitable for DMM formation. Increasing the content of P helped enhancing the oxygen adsorption of the catalyst and increased the amount of lattice oxygen to provide more active oxygen sites for the catalytic reaction. As mentioned in their previous work, Chen *et al.* confirmed that a large number of weak acidic sites was required for DMM formation.[72] Indeed, the DMM selectivity over the Al-P-V-O catalysts was greatly altered by the presence of strong acid sites that favor the formation of DME and MF[73]. Thereby, the amounts of strong acid sites should be restrained to get a high DMM selectivity.

Meng *et al*. prepared a series of $V_2O_5$ catalysts supported on $\gamma$-$Al_2O_3$ with a fixed vanadia content of 14 wt.% but with various $MoO_3$ loadings.[74] The V-Mo/$Al_2O_3$ catalyst having 14 wt. % of $MoO_3$ selectively converted 54 % of methanol to DMM with a 92 % selectivity at 120 °C. This remarkable catalytic performance was attributed to the synergistic effect between the surface vanadium and molybdenum oxide species. The active redox sites were proposed to be the bridging V-O-Mo oxide, monovanadates and molybdyl species bonded to the support. The V-O-Mo oxide completed a redox cycle through an electron transfer between lattice oxygen and metal cations, improving the redox capability of the catalysts. The electron transfer between lattice oxygen and metal cations also played an essential role in regenerating the catalyst by restoring the active lattice oxygen, mostly enabled by V species. The V species exhibited superior performance in the adsorption of gaseous oxygen and a stronger re-oxidation ability compared with Mo species. The yield in DMM was improved when increasing the amount of weak acid sites and Brønsted acid sites upon $MoO_3$ addition.

The selective oxidation of methanol to DMM over a mixed oxide of $V_2O_5$ and $CeO_2$ was also of interest for Guo and co-workers[51]. The catalyst was prepared by a sol-gel method using $NH_4VO_3$, $Ce(NO_3)_3$, and citric acid as precursors. At 160 °C, 90 % of selectivity to DMM at 17 % conversion of methanol were reported over the catalyst with 15 wt.% of $V_2O_5$.

### *2.2.6 Iron molybdate catalysts*

A bulk iron molybdate mixed oxides (FeMo) catalyst[75] is being currently used in the industry for formaldehyde synthesis applying reactant feeds with low methanol concentrations (*i.e.*, of less than 7.5 mol.%)[76,48,77,78]. DMM is always detected as a by-product in the formaldehyde production, indicating the presence of an acid-catalyzed function that should be fine-tuned to focus the action of such a catalyst toward DMM selectivity. Nevertheless, the thermal stability of this catalyst has not to be demonstrated because the temperature range for industrial formaldehyde production seems to be coherent (*i.e.*, > 350°C) with that envisaged for DMM synthesis (*i.e.*, < 320°C). Naturally, the majority of literature dealing with FeMo-type catalysts focused on their use in the formaldehyde production. Industrial FeMo catalysts are composed of mixed oxides of $Fe_2(MoO_4)_3$ and $MoO_3$, with an excess of molybdenum in general to compensate the loss of volatile reduced Mo atoms during the oxidation reaction, with the aim of extending the lifetime of the catalyst. The ratio between Mo and Fe can exceed 5 in industrial catalysts. However, they usually present Mo/Fe ratios between 2.3 and 5[79].

Adkins and Peterson were the first authors to describe the use of FeMo mixed oxides as the active catalyst in formaldehyde production from methanol[80]. In their work, the FeMo mixed oxides were prepared by coprecipitation of ferrous iron malate, ammonium molybdate, and ammonium nitrate solutions. Porous steel was added to the mixing solution before evaporating water. Afterwards, the catalyst coated pellets were dried for several hours at 60 °C and calcined at 360-370 °C in a slow flow of dry air for 1 h. Later on, Kerr and coworkers prepared iron molybdates by coprecipitating sodium molybdate solution with ferric chloride solution[81]. The preparation method developed by Kerr *et al.*, as cited by Pernicone,[82] allows the user to vary the relative concentrations of Mo and Fe parent solutions to obtain catalysts with a reproducible Mo/Fe molar ratio.

At the laboratory scale, the researchers prefer to use ammonium molybdate and iron nitrate as Mo and Fe sources, respectively, to avoid the contamination of the catalyst by residual poisons such as sodium and chlorine.[83,84] According to Popov *et al*., the activity of iron molybdate catalysts drastically decreased by a factor of 10 to 12 when adding sodium salts during their preparation.[85] In this example, the presence of sodium decreased the surface acidity strength that helps preventing the competitive adsorption between methanol and water. Nonetheless, the industrial iron molybdate catalysts are still prepared from ammonium molybdate and ferric chloride solutions.

The coprecitation technique in aqueous solution is the most common way to prepare non-supported iron molybdate catalysts. A few parameters are known to influence the quality of the final catalysts including the concentration of the parent solutions, the temperature and the length of the precipitation step, the pH of the resulting solution after precipitation, as well as the temperature and time applied for the final calcination step.[84] Pernicone referred in his work that the catalyst activity especially strongly depends on the final pH of the precipitation solution,[82] in agreement with Wilson who also found that the specific surface area of catalysts mostly depend on the concentration of the ammonium molybdate solution.[86] Boreskov and coworkers believed that the Mo/Fe ratio was a critical factor for the activity and the selectivity of the FeMo mixed oxides system.[87] They observed an optimum activity for an atomic ratio of 1.7 in the reaction of selective methanol oxidation to formaldehyde, in agreement with Sun-Kuo *et al*.[88], while Acosta observed a ratio of 2.4[89]. Arruana and Wanke found an increase of 30 % in the activity of FeMo catalysts calcined at temperatures in the range of 257-547 °C under air flow during the first 18 h of thermal treatment, ascribing this increase to the progressive formation of Mo-rich surface layers[90]. The activity then declined when extending the prior thermal treatment to 572 h, possibly due to the sublimation of Mo. In a similar context, Trifirò *et al*. studied the structure-properties variations of $Fe_2O_3$-$MoO_3$ catalysts with the temperature of calcination and confirmed a decrease of specific surface area and a severe decrease in catalytic activity when the sample was calcined at 600 °C[91].

The coprecipitation technique is not the only way to prepare FeMo catalysts. Several alternatives have been reported in the literature. Soares *et al*. prepared FeMo mixed oxides *via* a sol-gel method in which the iron precursor (i.e. iron nitrate) solution was slowly added to the Mo precursor (*i.e.*, molybdenum hexacarbonyl) solution without precipitation.[92] They pointed out that the specific surface areas of the catalysts prepared by such a sol-gel technique were higher than those prepared by coprecipitation. Later on, they reported the preparation of Mo-rich iron molybdate by a sol-gel-like technique using iron nitrate and molybdenum hexacarbonyl solutions in a propionic acid medium[84]. In addition to the obtained higher specific surface area, the sol-gel-like catalyst was more tolerant to surface reduction and surface Mo loss by $MoO_3$ sublimation. Wach and Brands developed the *in situ* preparation of iron molybdates in a fixed bed reactor packed with particles of $MoO_3$ and $Fe_2O_3$ oxides in the absence of water. They claimed that the performances of the obtained catalysts were equivalent to those of an industrial catalyst tested in the same conditions.[93] Beale *et al*. successfully developed a one-step hydrothermal method to prepare crystalline $Mo_5O_{14}$ and amorphous $Fe_2(MoO_4)_3$ precursors, which then transformed to $Fe_2(MoO_4)_3/MoO_3$ mixed oxides with high specific surface areas at calcination temperatures above 300 °C[83]. In their work, appropriate amounts of iron nitrate nonahydrate and ammonium heptamolybdate were mixed and well-stirred to obtain a gel-like solution. The mixture was heated in a Teflon-lined autoclave at 150 °C for 24 h. The resulting precipitate was separated and dried at 60 °C overnight before calcination. The authors also claimed that this mixed phase sample showed a higher selectivity for formaldehyde production than a conventional sample prepared *via* coprecipitation. The preparation of iron molybdate thin films catalysts was suggested recently in the work of Ulrich and coworkers as a model catalyst for the selective methanol oxidation to formaldehyde reaction.[94] Well-ordered thin Fe-Mo oxide films were prepared by Mo deposition over a thin $Fe_3O_4$ (111) film grown on a Pt(111) single crystal and oxidized at elevated temperatures. Lately, Jin *et al*. synthesized iron molybdate catalysts comprising $Fe_2(MoO_4)_3$ nano-particles anchored on $MoO_3$ nano-rods applied for the same reaction[95]. $MoO_3$ nano-rods were impregnated with iron nitrate solution *via* the incipient wetness method. The nano-structured $Fe_2(MoO_4)_3/MoO_3$ was found to have comparable performances under the tested reaction conditions compared to the conventional coprecipitation catalyst.

Technically, the oxidation of methanol over FeMo catalysts is carried out in fixed-bed reactors, where it can be difficult to maintain a uniform temperature distribution. The use of fluidized bed reactors to minimize internal hot spots has then also been suggested. However, the mechanical resistance of non-supported FeMo catalysts is too weak, and they cannot be operated with this reactor type. As a solution to this issue, some authors have prepared FeMo mixed oxides deposited on supports, *e.g.*, $Al_2O_3$ and $SiO_2$, to provide the adequate resistance to the FeMo catalyst, either *via* incipient wetness or spraying the support material with a solution of Mo and Fe precursors in the presence of citric acid[96]. Studies on Mo-Fe-O supported over $Al_2O_3$ and $SiO_2$ revealed that supported catalysts were less active than non-supported ones[96,97,98,99]. The interaction between the support and the active Mo-Fe-O phase is a crucial factor, which can alter the nature of the catalyst, for instance, by modifying the electronic properties of the surface Fe species. Cairati *et al*. reported that the increase in the specific surface area of the supports had an adverse effect on the catalytic behavior and this effect is more significant for alumina than for silica[100]. However, what could be promising for a possible fluidized bed reactor operation is to use silica as the support and minimize its interaction with the mixed oxides, due to its high specific surface area, by using a high content of the active Mo-Fe-O phase. Such a concept was tested by Diaz *et al*[101]. The silica-supported Mo-Fe and Mo-Fe-P mixed oxides were prepared in the presence of citric acid as a chelating agent. The prepared catalysts presented good performances in fluidized bed reactors, with high activity and selectivity towards formaldehyde both at low and high methanol conversions.

Gornay *et al*. demonstrated the excellent performance of an industrial FeMo catalyst [$(MoO_3\text{-}Fe_2(MoO_4)_3$] in the single step DMM synthesis from methanol. In poor feed conditions (7.5 mol.% of methanol), the catalyst was selective to formaldehyde with a very low selectivity to DMM (3 %). When increasing the concentration of methanol to 40 mol.%, the FeMo catalyst became very selective to DMM (*ca.* 90 %) with almost unchanged conversion of methanol (60 % using rich feed vs. 56 % using poor feed, at 280 °C), giving a remarkable productivity of 4.6 $kg_{DMM}h^{-1}kg_{cat}^{-1}$, which is so far the highest value ever reported in the literature. The direct synthesis of DMM from methanol was also realized using two sequential microreactors at atmospheric pressure by He and Liu.[102] The coupling of the selective oxidation of methanol (3.5 kPa) in air to formaldehyde at 277 °C on an industrial iron molydate catalyst (Mo/Fe ratio of 3) with the subsequent acetalization of formaldehyde with methanol at 30 °C on H-ZSM-5 led to the continuous formation of DMM with a yield of 84 %.

## 3 Parameters influencing the catalytic performances in direct selective oxidation of methanol to DMM

In the previous sections, we have seen that the oxidation of methanol to DMM can be realized over a variety of catalysts with different performances among them and also when placed under different reaction conditions. In this section, we will discuss the parameters that have been identified as having an important impact on the catalytic performances, such as the catalyst composition, the reaction temperature and the reactant concentrations.

### *3.1 Effect of catalyst composition*

The composition of the catalytic material obviously plays an important role in the catalytic activity. However, it is not straightforward to extract the behavior of a catalyst as a function of its composition only, and it is quite risky to directly analyze the effect of the catalyst composition because different research groups have performed their experiments under different reaction conditions, over different metals supported on a variety of materials, for instance. In the literature, the majority of the tested catalysts is composed of metal oxides, *e.g.*, $MoO_3$, $V_2O_5$, etc., deposited on solid oxide supports, *e.g.*, $Al_2O_3$, $SiO_2$, $TiO_2$. In general, the active metals are chosen in the *d* block of the periodic table, and only a few noble metals were tested, if we except the case of Ru and Re.

There are several papers mentioning the influence of the supports on the activity of the deposited metal species[36,39].It is noteworthy that the support effect was discussed when using the catalysts at low methanol concentrations, *i.e.*, 3-4 % of methanol, in the reaction feed, which are probably not the best conditions to produce DMM for other catalytic systems. The performances of Ru supported on different materials have been analysed by Liu and Iglesia at the iso-conversion of methanol of around 20 %[33]. Except for the $TiO_2$ support, the Ru content was around 4.1 wt.%. The nature of the support influenced the products selectivities over the $RuO_x$-based catalysts. The formation of DMM was favoured over acidic surfaces ($Al_2O_3$ and $SiO_2$) whereas over $SnO_2$, $ZrO_2$, and $TiO_2$ supports, of which the amphoteric character is known, methyl formate was preferentially formed. In any case, the DMM selectivity never exceeded 60 %.

Yuan and Iwasawa compared the effect of supports on Re-based catalyst[39] at 240 °C, which means at various conversions. The content of Re deposited on each support was fixed at 10 wt.%. Irrespective of the support, the DMM selectivity was higher than 80 % (except for $SiO_2$; DMM selectivity = 60%). Since the conversion varied, we have calculated the DMM yield ((DMM selectivity*methanol conversion)/100) in order to somewhat be able to compare the catalyst performance in terms of both conversion and selectivity. The highest yields of 44-47 % are obtained when Re is deposited on the $TiO_2$ and the $\gamma\text{-}Fe_2O_3$ supports. The lowest DMM yields are obtained over supported $Re/SiO_2$, $Al_2O_3$ and $MoO_3$ catalysts. Considering these two studies, it is difficult to provide clear conclusions on how the support actually affect the reaction of methanol conversion to DMM, and it seems that the catalytic behavior relies on the active metals deposited on the supports and not only by the support itself.

We have prepared a series of FeMo catalysts with different Mo and Fe loadings and examined their respective activities. The performance indicators, *i.e.*, methanol conversion, DMM selectivity and DMM yield, were reported relative to the proportion of Fe in the samples (Figure 1). An optimal DMM yield of 50 % could be achieved over the catalyst with a Mo/Fe ratio of 3.2. However, under specific operating conditions for this type of catalyst, *i.e.*, at 255 °C at atmospheric pressure using a feed consisting of 40 mol.% of methanol in air, high DMM yields were obtained in a very narrow range of Fe contents. Indeed, 30 to 40 % yields in DMM were achieved with an $Fe/M_T$ ratio between 0.22 and 0.26 (with $M_T$ = Mo+Fe).

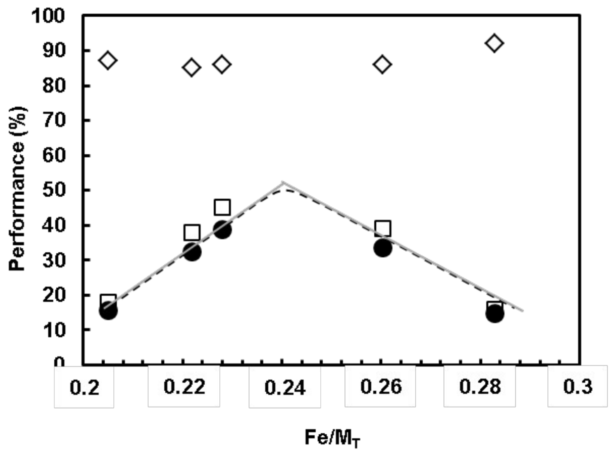


**Figure 1 : Performances at the steady state of FeMo catalysts as a function of the Fe/$M_T$ molar ratio (with $M_T$ = Fe + Mo); Methanol conversion (square), DMM selectivity (lozenge), and DMM yield (circle)[12].**

### *3.2 Effect of reaction temperature*

The oxidation of methanol to produce DMM is exothermic and the reaction is difficult to control due to possible temperature inhomogeneity within the reactor. The deeper oxidation of methanol to highly oxygenated products, *e.g.*, formic acid, methyl formate, or carbon oxides along with the fluctuations of reaction temperature would probably be a severe issue. For many oxidation reactions, and irrespective of the studied catalysts, increasing reaction temperature favoured the oxidation of methanol, promoting the reactivity of catalysts. In contrast, increasing the reaction temperature can cause a negative effect on the product selectivities. However, it is difficult to know if the selectivities are really affected directly by the increase in temperature or by the increase in methanol conversion induced by the high temperatures, unless full oxidation is not observed.

In general, DMM formation is favoured at low temperatures. High temperatures facilitate the formation of MF and DME. The majority of publications have mentioned a decrease in DMM selectivity at elevated temperatures, except over FeMo-based catalysts[75,77] and over the amorphous $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}O_x$ mixed oxide.[53] Interestingly, both aforementioned catalysts are two materials used in industrial plants initially for other applications, and have been synthesized in order to be stable for a long time (*i.e.*, a few years) within the studied temperature range. Over both catalytic formulations, a high DMM selectivity can be sustained while the temperature is increased unlike over the other types of catalysts, over which the DMM selectivity tends to drop at higher temperatures favouring the production of formaldehyde and methyl formate instead of DMM. This DMM selectivity stability is highly favourable in the industry in case of undesired temperatures fluctuations and enables increasing the reaction temperature to compensate from the unavoidable deactivation observed with the catalyst lifetime.

Kaichev *et al*. reported DMM as a major product in the selective oxidation of methanol at low temperatures between 100 and 120 °C using a highly dispersed monolayer supported vanadium catalyst[66]. The DMM selectivity constantly decreased at temperatures beyond 120 °C where methyl formate became the predominant product, especially at temperatures between 140 and 150 °C. Busca *et al*[60,76]. observed a decrease in methyl formate selectivity above 170 °C, and carbon oxides became the main product at 190-200 °C. Over a Re/$\alpha$-$Fe_2O_3$ catalyst, the selectivity to DMM increased to a maximum at 240 °C before decreasing at higher temperatures.

It is well admitted among researchers that this selectivity behaviour is due to a decrease in the surface acidity with temperature. Fu and Shen tried to alleviate this decrease in acidity by adding $Ti(SO_4)_2$ entities on the surface of their materials, which allows an attenuation of the phenomenon.[43] The decrease in surface acidity is associated with a decrease in methanol concentration over the catalyst surface induced by the increasing conversion. This increase in conversion, indeed, leads to a depletion of methanol in the reaction medium, which then suppresses/limits the DMM formation. This will also reduce the chance of formation of reactive intermediates, *i.e.*, methoxymethanol ($CH_3OCH_2OH$)[35,51] obtained by the reaction of adsorbed methoxy and methanol molecules at the surface of the catalyst, which is responsible for DMM formation. High temperatures also facilitate the desorption of methoxy groups adsorbed on the catalyst surface, reducing the amount of methoxy groups that further react with methanol molecules to form intermediate species. It is also true that the oxidation reaction of methanol becomes more thermodynamically favoured than the consecutive acetalization reaction leading to DMM when increasing temperature. The reverse phenomenon (*i.e.*, decrease in the surface acidity with the temperature increases) has been identified for the FeMo-based catalyst,[15] which can explain why this kind of material atypically keeps a very good DMM selectivity when increasing the temperature.

### *3.3 Effect of $O_2$ concentration in the reaction feed*

Regarding Scheme 1, the minimum methanol/$O_2$ ratio required to form DMM is 6. Only a few studies on the effect of the methanol/$O_2$ ratio are reported, probably due to the fact that the range of $O_2$ concentrations that can be probed while staying out the explosive region in the triangular flammability diagram is quite narrow[103]. Liu and Iglesia investigated the influence of the oxygen partial pressure over a $RuO_2/TiO_2$ catalyst.[36] The obtained results showed no evidence of a clear influence on both DMM selectivity and methanol conversion, while the authors scanned a wide range of $O_2$ pressures ($O_2$/methanol ratio from 1 to 9). The authors referred this behaviour to the well-known Mars–Van Krevelen mechanism, which involves lattice oxygen atoms on nearly stoichiometric surface[104]. Similar conclusions have been made over heteropolycations, *i.e.*, $H_5PV_2Mo_{10}O_{40}$, deposited on $SiO_2$[35]. This effect is also mentioned in the work of Yuan *et al*. who studied the effect of oxygen partial pressure on $SbReO_6$ activity at 300 °C[38]. In the range of the studied oxygen concentrations, they observed no significant change in both the methanol conversion and the DMM selectivity except at very high $O_2$ concentrations. The selectivity to DMM remained constant at 92-93 % at $O_2$ contents below 10 mol.% and slowly decreased to 84 % at a 42 mol.% $O_2$ content, which was accompanied by an increase in the formation of dimethyl ether.

### *3.4 Effect of $CH_3OH$ concentration in the reaction feed*

The majority of groups reporting the selective oxidation of methanol to DMM have focused their studies on poor-methanol conditions, *i.e.*, around 4-5 % of methanol in the feed, a typical reaction condition used in the industry to produce formaldehyde from methanol, which is additionally the first step to synthesize DMM from methanol (see Scheme 1). Several papers have verified the variation of methanol conversion and DMM selectivity with methanol concentrations in the feed. In a previous study, the present authors investigated the influence of the methanol partial pressure on the performances of Re/$TiO_2$, FeMo, and amorphous mixed oxide catalysts (Figure 2) in terms of DMM productivity, which reflects the ability of the catalyst to selectively convert methanol to DMM. In this way, one can consider the effect of methanol concentration to both performance indicators, *i.e.*, methanol conversion and DMM selectivity, at the same time.

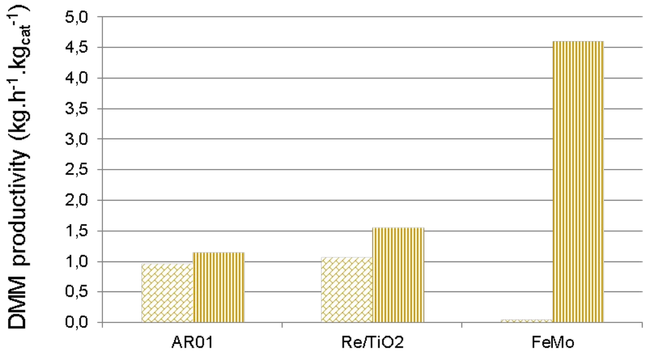


**Figure 2 Evolution of the DMM productivity** at 553K **for different types of catalysts: Re/$TiO_2$[105], FeMo[77] and mixed oxide amorphous material AR01[53] in rich and poor methanol concentration in the feed. Figure adapted from Ref [105].**

When considering the Re deposited on $TiO_2$[105] and the amorphous mixed oxides[53] catalysts tested in either poor- (4 %) or rich- (40 %) methanol condition, their productivity trends were similar, roughly in the same range, *i.e.*, between 0.5 and 1.5 $kg_{DMM}.h^{-1}.kg_{cat}^{-1}$. In the poor- methanol condition, for both catalysts, the DMM selectivity and methanol conversion were higher leading to the values plotted in the figure. However, when the catalysts were exposed to the rich-methanol condition, the DMM selectivity severely dropped and no drastic increase in DMM productivity was observed. The behavior of the FeMo catalyst was completely different[77]. The poor methanol conditions are the conditions used industrially to form formaldehyde from methanol over this kind of catalyst. When looking at Figure 2, it is not surprising to see almost no DMM productivity when a low methanol concentration is present in the feed over this catalyst. However, increasing the methanol concentration in the feed dramatically changed the selectivity towards DMM at almost the same methanol conversion, with no alteration in space velocity (GHSV) and reaction temperature (see table 3). This marked increase in selectivity caused the DMM productivity increasing up to 4.6 $kg_{DMM}.h^{-1}.kg_{cat}^{-1}$, which is so far, as aforementioned, the highest value ever reported. This behaviour is quite unique (*i.e.*, change of selectivity from formaldehyde to DMM by just changing the methanol concentration) for the FeMo catalyst. This fact has been assigned to the partial reduction of the iron atoms of the FeMo catalyst leading to an increase of its acidity which favoured the DMM production.

| | Methanol concentration (mol %) | Methanol conversion (%) | Formaldehyde selectivity (%) | DMM Selectivity (%) |
|---|---|---|---|---|
| Rich feed condition | 40 | 56 | 4 | 90 |
| Poor feed condition | 5 | 60 | 88 | 3 |

**Table 3 : Evolution of the DMM selectivity, formaldehyde selectivity and methanol conversion as a function of the methanol concentration in the feed over FeMo catalyst.**

## Conclusion and Outlook

Dimethoxymethane is distinguished by its versatility in many applications. This compound has a low boiling point, a low viscosity, and a good solubility in water as well as in some other solvents. Its low toxicity and its anti-carcinogenic nature are the desirable properties driving the use of DMM instead of organic solvents and in replacement of formaldehyde in embalming process. The use of DMM as a chemical intermediate for the manufacturing of polyacetal has been accounted for a substantial demand for this molecule. Further, DMM is extensively used in products such as medicines, paints, and cosmetics. The potential of DMM as an excellent diesel modification additive has been considered as well.

In this paper, we have reported numerous efforts made for over a decade to selectively convert methanol to DMM. Most of the studies considered this reaction in the gas phase, as this seems more practical compared to a liquid phase operation when considering the industrial point of view in terms of plant installation, catalysts, and products recovery.

Many catalytic systems are reported in the literature, *e.g.*, oxides, supported metals, etc., and the most active ones are Mo based amorphous materials, supported Re and Ru and FeMo-based catalysts. The latter benefits from being very robust, already produced at the industrial scale, and quite cheap compared to the three other ones. The FeMo catalyst also maintains its considerably high methanol conversion in rich-methanol condition, *i.e.*, approximately 40 % of methanol concentration in the feed, and offers a significantly high DMM selectivity, which results in a remarkable productivity as high as 4.6 $kg_{DMM}.h^{-1}.kg_{cat}^{-1}$. These advantages along with the fact that the FeMo catalyst is currently used in formaldehyde production plants enables envisioning a revamping of existing formaldehyde units practically working with this catalyst, switching them to DMM production units. This could be rather easily executed by changing the reactant feed composition, *i.e.*, shifting from low concentration of methanol (4-5 mol.%) to high concentration (40 mol.%), and lowering down the process temperature to be approximately 280-300 °C as illustrated in Figure . A very important point, concerning the Operational Expenditure (OPEX) of such kind of plants is the use of air as oxidant instead of pure oxygen which can decrease drastically the operating cost.

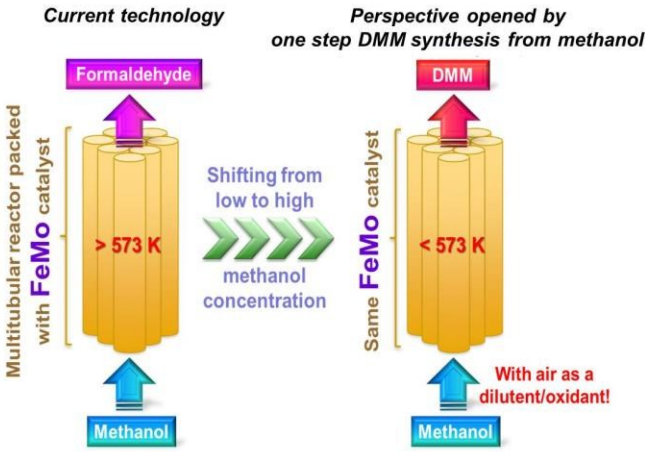


**Figure 3 : Concept of transformation of a formaldehyde production plant into a DMM production plant with a FeMo mixed oxides as a versatile catalyst.**

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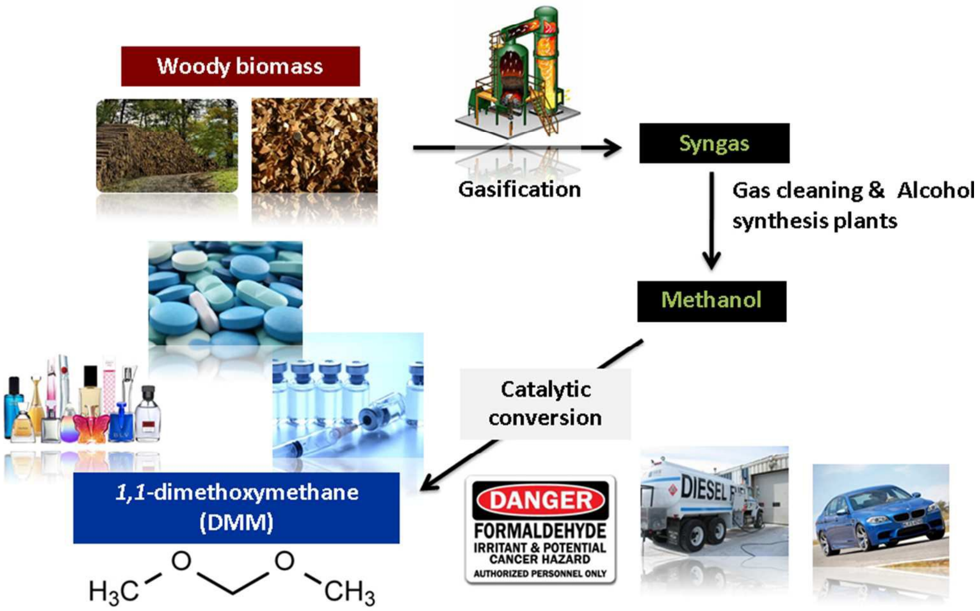

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