



Highly productive iron molybdate mixed oxides and their relevant catalytic properties for direct synthesis of 1,1-dimethoxymethane from methanol

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ABSTRACT

The one-step gas phase conversion of methanol to 1,1-dimethoxymethane (DMM) was studied over highly productive iron molybdate mixed oxides in a fixed-bed reactor working at atmospheric pressure. When placing the Fe–Mo–O catalyst under a reaction mixture highly concentrated in methanol, the DMM selectivity was drastically boosted. This specific and unique feature encouraged us to extensively characterize this family of particular catalysts. LEIS analysis revealed the presence of both Mo and Fe species on the outermost atomic layer of the catalysts. X-ray photoelectron spectroscopy (XPS) and *in situ* EPR measurements showed that the Fe centres are responsible for the redox properties. The acidic properties of the FeMo mixed oxides were then attributed to anionic vacancies acting as Lewis acid sites produced by dehydroxylation of the catalyst surface. XPS analysis also showed that oxygen from the gas phase was responsible for reoxidation of the catalyst surface with regeneration of the active sites, which suggests a Mars–van Krevelen mechanism. The good catalytic performances were then attributed to a synergistic effect between Mo and Fe species. A Mo/Fe molar ratio of 3.2 for an optimal remarkable yield in DMM of 50% was found.

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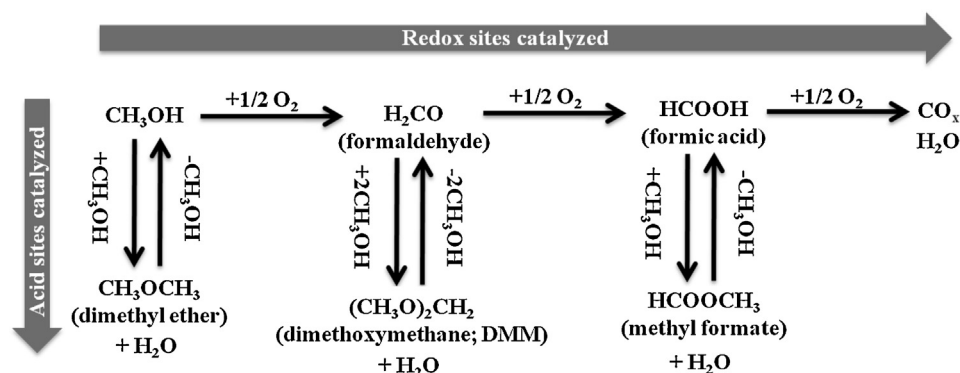
1. Introduction

The disastrous environmental issues caused by the extensive consumption of fossil-based sources, especially for energetic needs, has driven numerous studies to find alternative sustainable resources. In this context, it is now well understood that biomass, which is an abundant and renewable feedstock, has a great potential for being used as a raw material for a large spectrum of high value-added chemicals, including fuel applications. Among the various envisioned target molecules, 1,1-dimethoxymethane is of topical interest. It can be synthesized from the so-called

'bio-methanol' obtained *via* biomass-derived syngas conversion, which is an elegant way of cascade upgrading, and does not rely only on bio-based sourcing. DMM is distinguished by its versatility for various applications. It is widely used as a solvent and a starting material in the fragrance and pharmaceutical industries [1]. It is applied as a starting monomer in the synthesis of polyoxymethylene dimethylether (POMM), which could be used as a safe embalming agent in substitution of the currently used formaldehyde [2], a well-known human carcinogen. It finds also an 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 [3,4]. At last, DMM and POMM are also considered as alternative safer fuels for low-temperature fuel cells, much safer than methanol, due to, e.g., for POMMs lower volatility [5–8]. It appears then that DMM has a lot of advantages from the environmental point of view, which explains the recently renewed interest concerning this molecule.

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Scheme 1. Methanol oxidation pathways [29].

Production of DMM at the industrial scale is being currently carried out in a sequential way *via* two consecutive steps: gas phase methanol partial oxidation to formaldehyde, which is followed, in a second dedicated reactor, by liquid phase acetalization of the so-obtained formaldehyde with methanol molecules, including using reactive distillation process [9,10]. Synthesizing DMM *via* a single step direct route starting from methanol would obviously be preferred, thus minimizing the Capital Expenditure (CAPEX) and the production cost but also energy consumption besides reducing the environmental impact generated along the two-steps process. In this respect, developing selective catalysts for the one step partial oxidation of methanol to DMM is challenging, and has become a relatively widespread research subject in the recent years [11–28]. It has been reported that the direct reaction is strongly sensitive to the nature of the catalytic active sites [29]. Indeed, as shown in Scheme 1, the redox-catalyzed pathway leads to a sequence of oxidized species, namely formaldehyde, formic acid and carbon oxides, whereas the acid-catalyzed pathway yields dehydration products, *i.e.*, dimethyl ether, DMM and methylformate, respectively obtained from condensation of methanol with its aforementioned oxidation products. An appropriate system for the direct synthesis of DMM must thus be a bifunctional catalyst with adequate balance between redox and acid sites of the proper respective strength, in order to guide the reaction through the desired pathway among the possible ones in Scheme 1.

Various studies aiming at realizing the one-step methanol oxidation to DMM over a variety of catalytic systems, *i.e.*, molybdenum-based catalysts [11], heteropolyacids (HPAs) [12], oxides of ruthenium [13] and of rhenium [15–18], as well as vanadium-based catalysts [19–27] can be found in the literature. In the studies reporting the use of bulk and supported 12-molybdophosphoric acid catalysts, up to 55% of DMM selectivity was obtained at low methanol conversion of less than 20% [11]. Liu et al. investigated the performances of supported $\text{H}_{3+n}\text{V}_n\text{Mo}_{12-n}\text{PO}_{40}$ polyoxometallate Keggin clusters. They reported a selectivity to DMM of 58% at a methanol conversion of 68% over 9.2 wt.% supported $\text{H}_4\text{PVMo}_{11}\text{O}_{40}/\text{SiO}_2$ [12]. These authors further examined the performances of a completely different system, namely RuO_2 supported on TiO_2 , Al_2O_3 and $\text{TiO}_2\text{-Al}_2\text{O}_3$. They reported a maximum DMM selectivity of 67% at a lower conversion of 20% over a 4.4 wt.% $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst [13]. Iwasawa and co-workers focused their investigations on ReO_x and Re-based mixed oxides supported on various solids, *i.e.*, TiO_2 , SiO_2 , V_2O_5 , ZrO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, and $\gamma\text{-Fe}_2\text{O}_3$. Among the tested catalysts, $\text{Re}/\gamma\text{-Fe}_2\text{O}_3$ was the most efficient one with 91% selectivity to DMM at 48% conversion of methanol [15]. Following the results of Iwasawa's group, Sécordel et al. concentrated their study on supported TiO_2 -anatase and SiO_2 oxorhenate catalysts prepared by thermal spreading of metal Re^0 . A maximum DMM selectivity of 77% at

44% methanol conversion was claimed over a Re/TiO_2 catalyst [17]. Additionally, an attempt to use vanadium-containing catalysts has been described by several groups. Fu et al. reported a maximum DMM selectivity of 92% at 48% methanol conversion over the acid-modified $\text{V}_2\text{O}_5/\text{TiO}_2\text{-Ti}(\text{SO}_4)_2$ catalyst [19]. Later on, Lu et al. studied the $\text{V}_2\text{O}_5/\text{TiO}_2$ system [21–23] and further improved its catalytic reactivity by addition of SO_4^{2-} . 93% selectivity to DMM at 49% methanol conversion was reported over the catalyst loaded with 15 wt.% V_2O_5 and 15 wt.% SO_4^{2-} [24]. The performances of supported $\text{VO}_x/\text{TS-1}$ zeolite doping with SO_4^{2-} and PO_4^{3-} ions were then determined by Chen et al. Despite the fact of using a reactant feed within the flammable region – *i.e.*, $\text{methanol}/\text{O}_2/\text{N}_2 = 1/2.5/7.5$ (v/v), the authors reported a positive effect when adding SO_4^{2-} into $\text{VO}_x/\text{TS-1}$ catalyst that the so-obtained methanol conversion was significantly higher (46% compared with 24% for the unmodified catalyst) with essentially the same selectivity (81% vs. 83%) [25]. Guo et al. reported 90% of selectivity to DMM at 17% conversion of methanol over the $\text{V}_2\text{O}_5/\text{CeO}_2$ catalyst loaded with 15 wt.% V_2O_5 [26]. Developments of Sb-, V-, and Nb-containing catalysts for the oxidation of methanol were also discussed by Golinska-Mazwa et al. It was found that, by using a proper synthesis procedure for SbVO_x mixed oxides further modified with Nb species, it was possible to obtain selective catalysts for DMM production [27]. A maximum yield in DMM was stated at 39% conversion of methanol with 36% DMM selectivity.

In this study, we used an iron molybdate mixed oxides catalyst $[\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3]$ [30], which is being currently used in the industry for formaldehyde production using reactant feeds with low methanol concentrations of less than 7.5 mol.% [22,23,31,32]. We optimized this catalytic system for DMM production, based on the hint that in our experiments DMM was always detected as a by-product, indicating the presence of an acid function that should be tuned to focus the selectivity. Then, in a previous study, we evaluated the performance of iron molybdate catalyst towards DMM formation in comparison with those of two very efficient catalysts used as benchmarks, namely Re/TiO_2 and an amorphous mixed oxide of Mo, V, W, Cu, and Sb [28,33]. It was demonstrated that the selectivity to DMM could be drastically increased by simply placing the iron molybdate catalyst under a reaction feed highly concentrated in methanol (40 mol.% of CH_3OH in air) while keeping the same methanol conversion as that observed in a methanol-poor feed (7.5 mol.% of CH_3OH in air). A remarkably high productivity of $4.6 \text{ kg}_{\text{DMM}} \text{ h}^{-1} \text{ kg}_{\text{cat}}^{-1}$, the highest value ever reported in the literature, was achieved with 56% of methanol conversion and 96% of DMM selectivity at 553 K. This performance boost observed upon shifting from methanol-poor to methanol-rich feed was not observed over the supported Re and the amorphous mixed oxide catalysts. Thus, the present work aims at investigating the redox and acid properties of the iron molybdate catalytic system to

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