

## Effective FeMo catalyst for the direct synthesis of dimethyl- and diethyl acetals

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### Introduction

Dimethyl- and diethyl acetals are high value added chemicals which can be produced from biomass-derived alcohols. 1,1-dimethoxymethane (DMM) is a chemically stable compound with various applications, *e.g.*, a solvent, a fuel additive, or a safe embalming agent in substitution of the currently used formaldehyde [1]. 1,1-diethoxyethane (DEE) has been widely used as a solvent, as a starting chemical for fragrance and pharmaceuticals [2] as well as a good diesel fuel additive, with the advantage of keeping or even increasing the cetane number [3], while being of help in the efficient combustion of the resulting blend [4]. The production of DMM and DEE at the industrial scale is carried out in a sequential manner *via* two consecutive steps: alcohols partial oxidation to the corresponding aldehyde followed by acetalization of the alcohol with the previously obtained aldehyde [5]. From an economic point of view, producing the acetals in a one step process would be much more preferable. Developing selective catalysts for the one step partial oxidation of methanol to DMM, as well as for the partial oxidation of ethanol to DEE, has become a topical research subject in the recent years. In this study, we evaluated the catalytic performance of an industrial FeMo catalyst [MoO<sub>3</sub>-Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>] [6], which is (i) a bifunctional catalyst containing both redox and acid properties and (ii) effectively used in the production of formaldehyde using reactant feeds with low methanol concentrations of less than 7.5 %. The performance of FeMo catalyst was compared with that of Re-based as well as amorphous Mo-based catalysts, which both previously exhibited interesting performances [7]. Under a high methanol feed composition (40 mol %), the FeMo catalyst reveals a remarkably high DMM productivity [10]. Regarding its promising activities towards DMM production, the FeMo catalyst was also applied in the direct conversion of ethanol to DEE due to the similarities between methanol/ethanol partial oxidation reaction pathways.

### Experimental

Preparation of the MoO<sub>3</sub>-Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> catalyst followed a procedure described in the 70's by Pernicone [8,9] based on coprecipitation method between molybdenum and iron precursors. By systematically tuning different synthesis parameters (Mo/Fe ratio, calcination temperature, concentration of the precursors' solution, etc...), the FeMo catalyst formulation for the direct synthesis of DMM from methanol was specifically optimized. Differential Scanning Calorimetry analysis (DSC 131 Setaram) was carried out using a heating rate of 5 K.min<sup>-1</sup> under air atmosphere on the FeMo catalyst freshly prepared and dried. X-Ray diffractogram of the calcined sample was recorded from 2θ = 10° to 2θ = 70° (step: 0.02°; integration time: 1.5 s) on a D8 Advance apparatus (Bruker AXS). The catalyst was also placed in a high temperature chamber to record XRD diffractograms as a function of increasing temperature under air every 100 K up to 573 K and then every 25 K up to 773 K, applying a heating rate of 5 K.min<sup>-1</sup>. The performance of the Re/TiO<sub>2</sub> and of the Mo<sub>12</sub>V<sub>3</sub>W<sub>1.2</sub>Cu<sub>1.2</sub>Sb<sub>0.5</sub>O<sub>x</sub> catalyst formulations, of which their preparation method and the main characteristics are described elsewhere [7, 10], towards DMM production were evaluated at atmospheric pressure in a fixed-bed reactor and compared to that of FeMo. Two different feed compositions were selected outside the flammability zone: the 'poor' feed composition with CH<sub>3</sub>OH/O<sub>2</sub>/He = 7.5/8.5/84 and the 'rich' feed composition with CH<sub>3</sub>OH/O<sub>2</sub>/He = 40/13/47 (mol %). The gas hour space velocity (GHSV) was adjusted to 22 NL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Reactants and products were analyzed using an online gas microchromatograph (SRA3000) equipped with two columns (plot U and molecular sieves) and two TCDs. The carbon balance was higher than 95 %, which was satisfactory. Note that the Re/TiO<sub>2</sub> and Mo<sub>12</sub>V<sub>3</sub>W<sub>1.2</sub>Cu<sub>1.2</sub>Sb<sub>0.5</sub>O<sub>x</sub> catalysts were activated at 623 K for 1 h in an oxygen flow prior to use in the catalytic tests while the FeMo catalyst was used without any pretreatment, as in its conventional use for formaldehyde production.

### Results and Discussion

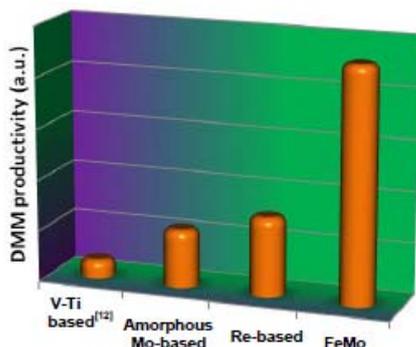
DSC analysis on the prepared FeMo catalyst sample evidences a small exothermal peak close to 615 K and two more intense peaks close to 661 and 675 K, respectively, corresponding to the presence of three crystalline phases confirmed by XRD analysis, namely Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (JCPDS # 15-0371), MoO<sub>3</sub> (JCPDS # 05-0507), and β-Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (JCPDS # 85-2207). The crystallization phenomena seem to take place at roughly the same temperature as can be deduced from the DSC analysis and are then confirmed by the diffractograms recorded in temperature [10,11]. The presence of Mo excess in the catalyst compared to the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> stoichiometry is found to be relevant to the formation of DMM. The catalytic performance at 553 K of FeMo compared with the Re-based and amorphous Mo-based catalysts are presented in Table 1. A selectivity into DMM is strongly sensitive to the composition of the feed in particular for the FeMo catalyst of which the selectivity changes drastically with the increasing quantity of methanol. Among the catalysts we have tested, a remarkably high DMM productivity of 4.6 kg<sub>DMM</sub>.h<sup>-1</sup>.kg<sub>cat</sub><sup>-1</sup> was obtained over the FeMo

catalyst at 553 K at a methanol conversion of 56 % with the selectivity of DMM reaching 90 %. This is thus, by far, the highest productivity ever reported in the literature.

**Table 1:** Catalytic performance obtained at 553 K with different concentrations of methanol in the feed

Methanol (mol %)	Catalyst	Conversion (%)	Selectivity (%)				
			DMM	F	DME	MF	CO <sub>x</sub>
7.5	Re/TiO <sub>2</sub>	65	74	1	12	7	6
	Mo <sub>12</sub> V <sub>3</sub> W <sub>1.2</sub> Cu <sub>1.2</sub> Sb <sub>0.5</sub> O <sub>x</sub>	57	89	3	5	1	1
	MoO <sub>3</sub> -Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	60	3	88	7	2	1
40	Re/TiO <sub>2</sub>	20	80	0	10	10	1
	Mo <sub>12</sub> V <sub>3</sub> W <sub>1.2</sub> Cu <sub>1.2</sub> Sb <sub>0.5</sub> O <sub>x</sub>	18	68	13	15	31	1
	MoO <sub>3</sub> -Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	56	90	4	5	1	0

DMM: dimethoxymethane, F: formaldehyde, DME: dimethylether, MF: methyl formate, CO<sub>x</sub>: CO+CO<sub>2</sub>



**Figure 1:** Comparison of catalytic activities in terms of DMM productivity.

Extrapolating from the fact that FeMo catalyst exhibits the best performance for DMM production, we expected also its interesting performance in the production of DEE according to the reaction pathways which are identical between methanol and ethanol. Regarding the preliminary test carried out at atmospheric pressure in a fixed-bed reactor using a gas feed composition comprising 30.8 Vol.% of ethanol and 7 Vol.% of O<sub>2</sub> in helium, we obtain a high selectivity towards DEE of 47% at 31% ethanol conversion at 526 K over the FeMo catalyst, resulting in a remarkable DEE productivity of 1.04 kg<sub>DEE</sub>·h<sup>-1</sup>·kg<sub>cat</sub><sup>-1</sup>. Our exploratory study of the FeMo catalytic performance in the direct conversion of ethanol into DEE and of the influence of various reaction parameters, *i.e.*, GHSV and partial pressure of reactants is currently under progress.

## Conclusions

With an industrial MoO<sub>3</sub>-Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> catalyst used for formaldehyde production, we observe a remarkably high productivity of DMM using a high concentration of methanol in the feed with air as a diluent/oxidant. With the same catalyst formulation applying to the direct synthesis of DEE from ethanol, we observe also an excellent catalytic performance ever reported.

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