

# EuroBioRef

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## SP5 – <Advanced Catalytic Conversion Processes to Chemicals and Integrated Separation Technologies> WP5.2 – <Acetals Production>

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#### Approval

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## Executive summary

### Description of the deliverable objective and content

The aim of this deliverable is to present the conclusion concerning the *Operando* studies which have been carry out for the acetals production catalysts during the 35 first months.

### Deviation from objectives and corrective actions

We are in line with the fixed objectives.

### Innovation brought and technological progress

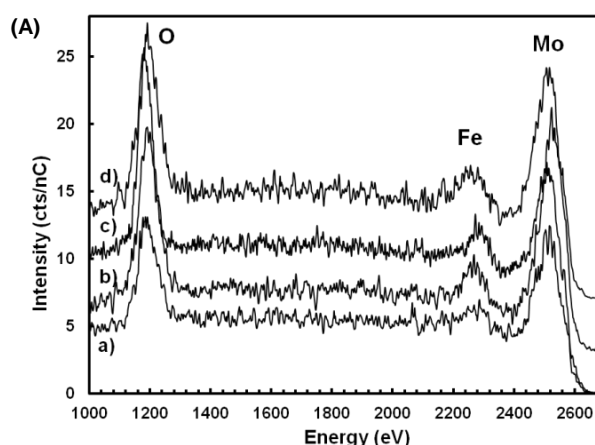
Intensive characterizations including X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS), *in-situ* electron paramagnetic resonance (EPR) and temperature-programmed desorption of ammonia (TPD-NH<sub>3</sub>) were carried out to determine the catalytic functions of FeMo formulations, which are concomitantly required to realize the reaction.

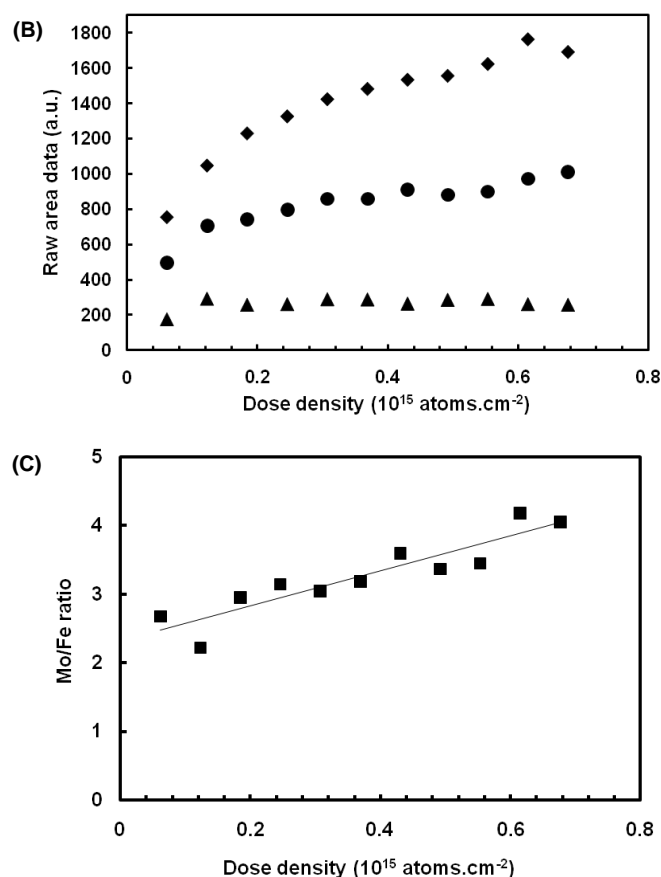
In order to adjust the composition of the catalysts we have synthesise a series of FeMo based catalysts. The textural and structural properties are reported in the table 1.

**Table 1** Physical properties of the calcined catalysts prepared with different Mo/Fe nominal atomic ratios.

Catalyst	$S_{BET}$ (m <sup>2</sup> .g <sup>-1</sup> )	Mo/Fe Ratio			$Fe/M_T^*$	Amount of crystalline phase (rel. %)	
		Theoretical	ICP-MS	LEIS		Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	MoO <sub>3</sub>
FM01	2	2.5	2.5	4.0	0.283	87	13
FM02	7	3	2.8	2.4	0.260	77	23
FM03	11	3.5	3.5	4.1	0.222	80	20
FM04	10	3.75	3.4	2.7	0.228	64	36

The outermost layer of FeMo catalysts possesses Mo and Fe species as observed through LEIS (see Figure 1 and Table 2).





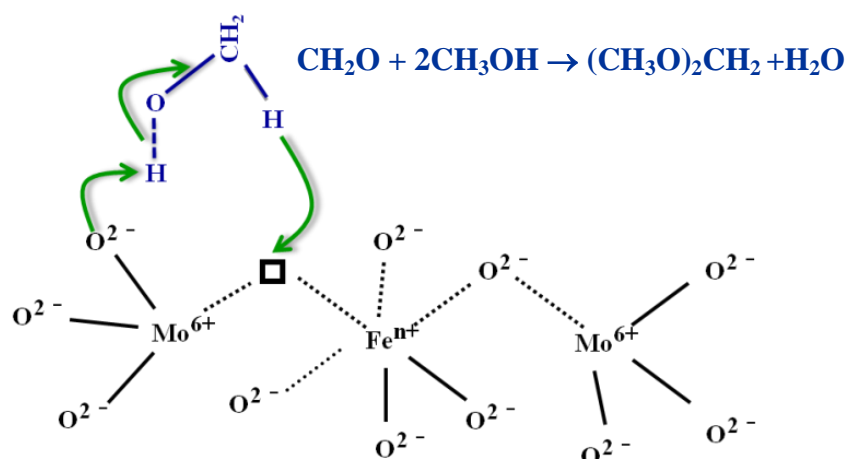
**Figure 1:** (A) 3 keV  $^4\text{He}^+$  LEIS spectra of iron molybdates: FM01 (a), FM02 (b), FM03 (c), and FM04 (d); (B) Evolution of relative intensities of Mo (◆), Fe (▲) and O (●) peaks with the  $\text{He}^+$  ion fluence from 3keV  $^4\text{He}^+$  LEIS spectra of FM04 catalyst during sputtering experiments; (C) Evolution of the Mo/Fe ratio from 3 keV  $^4\text{He}^+$  LEIS spectra of FM04 catalyst with the  $\text{He}^+$  ion fluence.

XPS analysis on the treated catalyst placing in a reductive environment (20 mol%  $\text{CH}_3\text{OH}$  in inert gas at  $255^\circ\text{C}$ ) shows no evidence of Mo reduced species, whereas partial reduction of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  occurs gradually (cf table 2). Nonetheless, XPS results imply the formation of methoxy groups due to dissociative adsorption of methanol on the sites connected with  $\text{Mo}^{\text{VI}}$ . Further XPS study on the same catalyst placing in the reactive mixture (20 mol%  $\text{CH}_3\text{OH}$  in air at  $255^\circ\text{C}$ ) revealed that  $\text{Fe}^{\text{II}}$  ions on the surface are partially re-oxidized to  $\text{Fe}^{\text{III}}$  and there is no change observed on Mo centers (table 1). These results are further confirmed by *in-situ* EPR measurement (figure not shown).

**Table 2:** XPS analysis results after one hour on stream with FM02 sample after different in situ treatments at 528 K in 20 mol. % of methanol in air.

Treatment condition	Binding Energy (eV)		Peak width (FWHM)		Relative atomic conc. of Fe $2p_{3/2}$ species (%)		Mo/Fe XPS atomic ratio
	Mo $3d_{5/2}$ ( $\text{Mo}^{\text{VI}}$ )	Fe $2p_{3/2}$ ( $\text{Fe}^{\text{III}}$ )	Mo $3d_{5/2}$ ( $\text{Mo}^{\text{VI}}$ )	Fe $2p_{3/2}$ ( $\text{Fe}^{\text{III}}$ )	$\text{Fe}^{\text{III}}$	$\text{Fe}^{\text{II}}$	
Fresh catalyst	232.3	711.2	1.9	4.3	100	-	3.0
Air ( $\text{O}_2/\text{He}$ )	232.0	712.2	1.6	4.8	100	-	5.1
$\text{CH}_3\text{OH}/\text{He}$	231.6	709.0	2.4	4.3	54	46	4.8
$\text{CH}_3\text{OH}/\text{O}_2/\text{He}$	232.6	712.2	1.6	3.9	71	29	3.4

Regarding the synergetic effect on the performances of FeMo catalysts (*cf.* task 5.2.1), the active sites involving both Mo and Fe species have been proposed. These sites are described as anionic vacancies produced by dehydroxylation. Formaldehyde is formed on such sites and is then reacted with two molecules of methanol to form DMM. The figure 2 provides a picture of this active site



**Figure 2:** Proposed active site for methanol transformation to DMM – ( $\text{Fe}^{n+}$ :  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ , and  $\square$ : anionic vacancy, number arbitrary).

The acidic function required for this consecutive acetalization is provided by the vacancies acting as Lewis acid sites. It was found from  $\text{NH}_3$ -TPD experiments that the catalyst reduction leads to an increase in the acidity. We incline to think that only the lattice oxygen is directly involved in the reaction. Gaseous oxygen present in the reactive medium is responsible for reoxidizing the catalyst surface with regeneration of the active sites.

#### Related IPR and publishable information

With these results, we have submitted a publication in Applied Catalysis B which is in review process. It has been accepted with minor revisions.

#### Conclusion

We report herein an efficient iron molybdate mixed oxides catalyst for the gas phase selective conversion of methanol to 1,1-dimethoxymethane (DMM) using a methanol-rich reactants mixture. Catalysts with different Mo and Fe contents were synthesized by the coprecipitation technique before being calcined at 723 K in air. The highest DMM yield with a selectivity of 85 % for 46 % conversion was obtained at 528 K over the catalyst with a bulk Mo/Fe ratio of 3.4 ( $\text{Fe}/M_T = 0.228$ ). This catalyst contained 64 % of crystalline  $\text{Fe}_2(\text{MoO}_4)_3$  and 36 % of crystalline  $\text{MoO}_3$ , with a relatively high surface area compared to the other catalysts of the studied series. The good performance in terms of DMM production can be ascribed to the concomitant redox and acid properties present in the Fe-Mo-O catalytic system, which are relevant to undergo consecutive partial oxidation and condensation reactions. Surface composition and reducibility were investigated by LEIS and XPS. With respects to the LEIS results, the outermost surface layer of the fresh catalyst presented both Mo and Fe species with a Mo/Fe ratio of 3. From the XPS analysis results, we deduced that the direct synthesis of DMM from methanol using the feed highly concentrated in methanol involves adsorption of methanol on the sites where Mo and Fe atoms are connected. This leads to the partial reduction of some Fe from  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  on the catalyst surface. The same phenomenon was also characterized by the EPR experiments. These catalytic active sites were proposed as anionic vacancies – which can be generated by surface dehydroxylation and are identified as Lewis acid sites surrounded by Mo and Fe atoms. Acidity of the catalyst was determined by  $\text{NH}_3$ -TPD. The number of acid sites and their strength were increased by pre-reducing the catalyst with  $\text{H}_2$ . As the catalyst is being continuously reduced under the reducing atmosphere applied during the reaction, due to the presence of methanol, a

significant increase in selectivity can be attributed to an increase in acidity, which is required in the acetalization reaction to form DMM, in addition to the redox properties. Owing to the reduction of the catalyst, the number of anionic vacancies became larger. This helped improving the catalytic conversion. Evidence was reported that gaseous oxygen is only responsible for reoxidizing the catalyst surface, especially Fe sites, suggesting that the studied reaction obeys the Mars-van Krevelen mechanism. At last, we observed a synergistic influence between Mo and Fe in the catalyst, particularly on methanol conversion. By advisedly optimizing the Fe-Mo-O catalyst formulation, an optimal DMM yield could be achieved, *i.e.*, the formulation with Mo/Fe ratio of 3.4 could reach the extrapolated yield value of 50 % yield.

Alternatively for methanol oxidation to formaldehyde, this study demonstrates also the importance of the methanol partial pressure but mostly the importance of the average oxidation state on the selectivity. For the formation of DMM, catalyst formulations should be tuned to keep the balancing of oxidation states – (*i.e.*, Fe<sup>III</sup> and Fe<sup>II</sup>) – present during the course of reaction.