EuroBioRef

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WP5.2 – <Acetals Production>

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Dissemination level

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Executive summary

Description of the deliverable objective and content

Deviation from objectives and corrective actions

Innovation brought and technological progress

Related IPR and publishable information

Conclusion
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 acetics 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-NH₃) 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 synthesize 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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{BET}$ (m².g⁻¹)</th>
<th>Mo/Fe Ratio</th>
<th>Fe/M₇⁺</th>
<th>Amount of crystalline phase (rel. %)</th>
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<td></td>
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<td>Theoretical</td>
<td>ICP-MS</td>
<td>LEIS</td>
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<tr>
<td>FM01</td>
<td>2</td>
<td>2.5</td>
<td>2.5</td>
<td>4.0</td>
</tr>
<tr>
<td>FM02</td>
<td>7</td>
<td>3</td>
<td>3.5</td>
<td>2.4</td>
</tr>
<tr>
<td>FM03</td>
<td>11</td>
<td>3.5</td>
<td>3.5</td>
<td>4.1</td>
</tr>
<tr>
<td>FM04</td>
<td>10</td>
<td>3.75</td>
<td>3.4</td>
<td>2.7</td>
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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 $^4$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 He$^+$ ion fluence from 3keV $^4$He$^+$ LEIS spectra of FM04 catalyst during sputtering experiments; (C) Evolution of the Mo/Fe ratio from 3 keV $^4$He$^+$ LEIS spectra of FM04 catalyst with the He$^+$ ion fluence.

XPS analysis on the treated catalyst placing in a reductive environment (20 mol% CH$_3$OH in inert gas at 255 °C) shows no evidence of Mo reduced species, whereas partial reduction of Fe$^{III}$ to Fe$^{II}$ 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 Mo$^{VI}$. Further XPS study on the same catalyst placing in the reactive mixture (20 mol% CH$_3$OH in air at 255 °C) revealed that Fe$^{II}$ ions on the surface are partially re-oxidized to Fe$^{III}$ 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.

<table>
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<th>Treatment condition</th>
<th>Binding Energy (eV)</th>
<th>Peak width (FWHM)</th>
<th>Relative atomic conc. of Fe 2p$_{3/2}$ species (%)</th>
<th>Mo/Fe XPS atomic ratio</th>
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<tr>
<td></td>
<td>Mo 3d$_{5/2}$</td>
<td>Fe 2p$_{3/2}$</td>
<td>Mo 3d$_{5/2}$</td>
<td>Fe 2p$_{3/2}$</td>
</tr>
<tr>
<td>Fresh catalyst</td>
<td>232.3</td>
<td>711.2</td>
<td>1.9</td>
<td>4.3</td>
</tr>
<tr>
<td>Air (O$_2$/He)</td>
<td>232.0</td>
<td>712.2</td>
<td>1.6</td>
<td>4.8</td>
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<tr>
<td>CH$_3$OH/He</td>
<td>231.6</td>
<td>709.0</td>
<td>2.4</td>
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<td>232.6</td>
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<td>1.6</td>
<td>3.9</td>
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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.

\[
\text{CH}_2\text{O} + 2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{O})_2\text{CH}_2 + \text{H}_2\text{O}
\]

**Figure 2:** Proposed active site for methanol transformation to DMM − (Fe\(^{n+}\): Fe\(^{3+}\) or Fe\(^{2+}\), and □: 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 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 (Fe/M\(_T\) = 0.228). This catalyst contained 64 % of crystalline Fe\(_2\)(MoO\(_4\))\(_3\) and 36 % of crystalline 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 Fe\(^{III}\) to Fe\(^{II}\) 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. Acidicity of the catalyst was determined by NH\(_3\)-TPD. The number of acid sites and their strength were increased by pre-reducing the catalyst with 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$^{III}$ and Fe$^{II}$) – present during the course of reaction.