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Novel La$_3$Fe(MoO$_4$)$_6$ phase: magnetic properties and ethanol reactivity

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Single crystals of the new oxide La$_3$Fe(MoO$_4$)$_6$ were grown from fluxes of oxide precursors, and a polycrystalline sample was also prepared by a solid state reaction. La$_3$Fe(MoO$_4$)$_6$ crystallizes in the orthorhombic space group Pbc$a$ with unit cell parameters $a = 19.3164(11)$, $b = 10.4143(5)$ and $c = 22.0594(12)$ Å. This crystal structure exhibits a singular architectural type built on infinite chains of Fe(MoO$_4$)$_6$, each of them being surrounded by two isolated MoO$_6$ tetrahedra and three isolated La$^{3+}$ cations. Fe$^{3+}$ ions in La$_3$Fe(MoO$_4$)$_6$ are antiferromagnetically ordered below $T_N = 6.6$ K in chains and between chains, as refined from neutron diffraction data. Further the redox stability of this compound - pure powder – was checked using temperature-programmed X-ray diffraction under controlled atmosphere: under air, we observed a reversible phase transition above 523K. The same phenomenon was observed under reductive atmosphere, followed by a destruction of the as-formed phase above 923K owing to iron III to II reduction. Reactivity of ethanol was then evaluated to get insights on the redox properties of the material under working conditions. After 4 hours of reaction at 648K, the ethanol conversion was 97 % with a selectivity to acetaldehyde of ~ 60 %, the other products being formaldehyde (~ 10 %) and CO$_2$ (~ 30 %), underlining a better acetaldehyde selectivity than that of the La-free conventional Fe$_2$(MoO$_4$)$_3$ catalytic formulation.

Introduction

The prospection for new inorganic materials is usually driven by the ulterior motive of increasing performances of particular applications. The scientists dream about the possibility to design new materials with targeted properties. Nevertheless, if developing a predictive strategy route is a smart approach, it is pretty often unsuccessful due to technical difficulties for synthesis and because the properties are often not as promising as though t. In this context, the nature of the atoms inherent to the material itself was tuned and their association in the structure studied enabling properties modification. For example, piezo-electricity, pyroelectricity, and ferroelectricity [1],[2] properties are strongly related to the achievement of noncentrosymmetric (NCS) [3] compounds favored by introduction of lone-pair (LP) cations or polyanions inducing an external s2 electron favorably arranged in NCS crystal structures [4],[5]. Rational substitution of a cation by another one less charged that will thus induce vacancies in the structure is the classical technique used to increase ionic conductivity in materials [6]. This modification can further potentially lead to changes in the catalytic reactivity of the as-formed compounds.

Catalytic conversion of alcohols is nowadays of topical interest, as some of them are readily obtained from bio resources. Among them, ethanol is now massively produced for biofuels needs, but it is also being more and more considered as a platform molecule from which families of chemicals can be derived. [7] For instance, ethanol can be used as a starting material in the synthesis of different byproducts such as aldehydes [8],[9], acetals [10],[11], ethers, esters or alcohols with longer carbonated chains through the Guerbet chemistry [12],[13]. Such products are then of high importance in the context of the biorefineries development, as intermediate reactants in the downstream production of alternative fuel or chemicals. [14] Within this frame, FeMo-based mixed oxides (namely Fe$_2$(MoO$_4$)$_3$) are known for their specific redox behavior making them good catalysts for alcohols oxidation [15],[16].

In the present paper, we synthesized and characterized the structure of a new lanthanum molybdenum iron oxide La$_3$Fe(MoO$_4$)$_6$. As preliminary study, AFM coupling at very low temperature were evidenced. Further, we examined the catalytic properties of this new material including La in a FeMo oxide-based host structure. On a mechanically milled compound, a conversion of 97 % was observed at 650K with a selectivity to acetaldehyde of 62 %.This clearly outperforms a conventional FeMo catalyst, which exhibits a much lower selectivity to acetaldehyde due to uncontrolled ethanol reaction from ca. 575K.

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Experimental section

Synthesis of La₆Fe(MoO₃)₆: Single crystals: The flux growth technique was used to obtain single crystals. Indeed, this method has been shown to be particularly well suited in the exploratory crystal growth and discovery of novel complex oxides [17]. The temperature of synthesis is imposed by the nature of the inorganic chemical used as the solvent for crystallization, here MoO₃.

The crystals were found in the polycrystalline residue from the melt of 34 wt% of the (80% La(OH)₃ + 10% Cr₂O₃ + 10% Fe₂O₃) mixture in 66 (wt%) of MoO₃ which was taken as a flux. The protocol of heat treatment was deduced from the careful examination of ref. [17]. The starting mixture was loaded into a gold tube, sealed and then heated at 1175K during 96 hours and finally slowly cooled (40ºC/h) during 20h. The furnace was then switched off and crystals were handily selected under a 60x Nikon binocular.

Powder sample: The corresponding powder was obtained as a pure polycrystalline phase from the stoichiometric mixture of La(OH)₃ (preferred to La₂O₃ which is highly hygroscopic) and Fe₂O₃ and MoO₃ heated at 1175K in an alumina crucible, after several intermediate grindings. The sample was promptly removed from the furnace at elevated temperature to avoid any residual presence of Fe₂O₃, La₆Fe(MoO₃)₆ was obtained as a single phase, as proved by the good pattern matching shown in Figure 1. The lattice parameters refined from this powder diffraction pattern (using JANA 2006 software [18]) led to a=19.3212(3) Å b=10.4381(2) Å and c=22.1252(3) Å in good agreement with the lattice parameters refined from the single crystal data (see below).

Structural crystal characterization:

Single crystal XRD study: Single crystals of this new phase have been collected using a Bruker Apex Duo diffractometer with a MoKα microfocus tube (λ=0.71073 Å). The intensity data have been extracted from the collected frames using the program SAINT-Plus 8.27b. The lattice parameters have been refined from the complete data set. Absorption corrections have been performed using multiscan methods using SADABS [20]. The crystal structure was solved by charge flipping method using SUPERFLIP [21] and the data was refined with the JANA2006 [18] crystallographic suite. After absorption correction, the 10170 reflections (I>3σ(I)) were merged in the Laue group mm2 leading to merging factor Rint=3.2% for 8270 reflections with I>3σ(I). The refined orthorhombic lattice parameters of the titled compound are: a=19.3164(11) Å, b=10.4143(5) Å, c=22.0594(12) Å. Analysis of the data set revealed that the systematic absences were consistent with the orthorhombic space group Pbca. All relevant details of data collection and pertinent data of the refinements are gathered in Table S1.

X-ray powder diffraction analysis of the powder sample has been performed at room temperature in the angular range of 2θ 1-80° with the scan step width of 0.02° using a D8 Advance Bruker AXS diffractometer in Bragg Brentano geometry equipped with a 1D LynxEye detector. Full pattern matching was performed on JANA 2006 [18].

High-temperature X-ray diffraction (HTXRD): The temperature stability of the title compound was checked using HTXRD techniques on a Bruker D8 Advance diffractometer equipped with a high-temperature Anton Paar XRK900 chamber and a one dimensional X-ray detector (LynxEye) using Cu Kα radiation under two different atmospheres, namely air and diluted H₂/N₂ (3%) to simulate an oxidative and a reductive media, respectively. Data were collected over the range 10-70° in 2θ, with a 0.021° step and a time of 59min per diagram from room temperature to 1075K. Diffractograms were obtained every 50K on heating and cooling.

Textural characterization: The specific surface areas (SSAs) of the calcined catalysts were determined using the single-point BET (Brunauer, Emmett, Teller) method, with N₂ adsorption at liquid N₂ temperature and subsequent desorption at room temperature on a Micromeritics ASAP 2010 apparatus. The samples were outgassed at 473 K for 30 minutes prior to analysis.

Magnetic characterization: Magnetic susceptibility was measured using a MPMS SQUID-VSM (Quantum Design) magnetometer. The temperature dependence variation of the magnetization was carried out under a magnetic field of 0.1 T after cooling the sample in a field of 0.1 T (FC, field cooling) or in zero field (ZFC, zero field cooling). Magnetization versus H was measured between +3 and -3 T at 2 K.

Magnetic structure: Neutron diffraction experiments (ND) were carried out from room temperature to low temperature (1.5K) on the G4.1 beam line of LLB (Saclay, France) with a wavelength λ=2.43 Å. The ND patterns were recorded in the angular range 2θ=9°-80° with a 0.05° step, using approximately 8 g of powder introduced in a vanadium tubular sample holder.

Catalytic test: Materials and apparatus: Reaction of ethanol oxidation was performed using a fixed bed reactor. Before the experiment, 200 mg of sample was mixed with 200 mg of SiC in order to homogenize the temperature inside the catalytic bed. The catalytic tests were carried out in a glass reactor consisting of a 10 mm diameter tube connected online with a GC-MS apparatus, which enabled analysis runs every 3 min. The reactor was placed in
an oven of which the temperature was finely controlled using two
thermocouples. The reaction was performed in a range of
temperatures between 600 and 675°C under atmospheric pressure.
The total gas flow rate was maintained with a GHSV of 2256 h⁻¹

Figure 2: a) Projection of the structure of La₃Fe(MoO₄)₆ along the b axis. It
is built on isolated MoO₄ tetrahedra (dark green), isolated La³⁺ cations and
Fe(MoO₄)₆ infinite chains built through the connection of FeO₆ octahedra (dFe-O from
1.9124(20) to 2.0132(18) Å) sharing corners with four MoO₄ (dMo-O from
1.719 (2) to 1.8032(19)Å) tetrahedra. These chains are surrounded by cationic tunnels hosting La³⁺ (2 independent
crystallographic sites so 16 cations per unit cell along b-axis) and
isolated MoO₄ tetrahedra. The resulting electroneutral formula is
La₃Fe(MoO₄)₆. In this (La Fe Mo O) quaternary system, this compound is, beside La(Fe₀.667Mo₀.333)O₃[22], the second one
referenced in the ICSD database.

The refined obtained crystal structure is shown on figure 2. It can be
described as an association of one dimensional (1D) chains of
[Fe(MoO₄)₆] running along the a-axis, the chains being themselves
built through the connection of FeO₆ octahedra (dFe-O from
1.9124(20) to 2.0132(18) Å) sharing corners with four MoO₄ (dMo-O from
1.719 (2) to 1.8032(19)Å) tetrahedra. These chains are surrounded by cationic tunnels hosting La³⁺ (2 independent
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referenced in the ICSD database.

The 1D [Fe(MoO₄)₆] units encountered in the title compound can be
compared to other iron molybdenum oxides reported in literature.
Rb₃FeMoO₁₅ [23] exhibit 1D Fe[MoO₁₅] chains more or less
identical but with one oxygen atom in common with two MoO₄
tetrahedra (figure 3a)). FeO₆ octahedra and MoO₄ tetrahedra are
also involved in 2D layers in KFe(MoO₄)₂ [24] by sharing corners
(figure 3b)). In the other three examples: Fe₃(MoO₄)₉ [25], Cs₂Fe₃(MoO₄)₆ (figure 3c)) [26] and Cs₃FeMoO₁₅ (figure 3e))
[23], the connectivity between iron octahedra and molybdenum
tenrahedra is realized by assembling oxygen corners together,
building a final 3D framework, more or less distorted by co-addition
of counter cations.

Crystal structure of La₃Fe(MoO₄)₆

A colourless needle like single crystal was isolated from the
inhomogeneous melt and mounted on a glass fibre. As
aforementioned, the observed extinction conditions undoubtedly
suggest the Pbca space group. The heavy atoms (3 La, 6 Mo and 1
Fe atoms) were easily localized using the Superflip21 method,
whereas the remaining atoms (24 O) were deduced from the
inspection of successive difference Fourier maps. The structure
refinement rapidly converged to the conventional reliability factor
R₁= 0.0218.

during the reaction, and the gas composition was kept as 13.2 Vol.%
of ethanol, 6 Vol.% of oxygen and 40.8 Vol.% of helium taken as a
carrier gas. The catalytic performances were evaluated by
calculating the following parameters:

\[
\text{Ethanol conversion (\%): } \chi = \frac{(n^i - n)}{n^i} \times 100
\]

where nᵢ is the initial number of moles of ethanol and n is the
number of moles of unconverted ethanol.

\[
\text{Selectivity to products (\%): } S = \frac{n_{x} \times 100}{n_{CEth} \times n_{x} \times n_{CEth}}
\]

where nₓ is the number of carbons in the x product, nx the number
of moles of the formed x product, and n_CEth the number of carbon
atoms in one ethanol molecule (i.e., 2).
Figure 3: Several connections between FeO$_6$ octahedra and MoO$_4$ tetrahedra observed in the literature and compared to La$_3$Fe(MoO$_4$)$_6$. a) Rb$_3$FeMoO$_4$ building 1D units (corner sharing between FeO$_6$ and MoO$_4$ tetrahedra are highlighted in yellow), b) FeK(MoO$_4$)$_2$ with 2D Fe(MoO$_4$)$_2$ cationic layers and finally c) Cs$_2$Fe$_2$(MoO$_4$)$_3$. d) Fe$_2$(MoO$_4$)$_3$ and e) Cs$_3$Fe(MoO$_4$)$_3$ building a 3D network.

The atomic positions, anisotropic displacement parameters and the principal distances are given in Supplementary Information S2 and S3. The crystal-structure data for La$_3$Fe(MoO$_4$)$_6$ phase were deposited with the depository number CSD-429247.

Structural complexity of La$_3$Fe(MoO$_4$)$_6$ structure has been quantified using Shannon information theory [27]. Theoretically, structural complexity is strongly related to the atomic arrangement of the unit cell and using Shannon's law, $I_{total}$, which classifies it as a very complex structure. It is noteworthy that, only 0.02% of inorganic structures are identified as very complex as detailed in [27].

High temperature X-ray study and stability

To simulate the different cycles and to check the stability of the solid prior to catalytic experiment, an in situ X-Ray diffraction study versus temperature was performed under air and also under reductive atmosphere. Accordingly, the sample was heated from room temperature to 1073K and then cooled to room temperature under two different atmospheres.

Under Air: Figure 4a) shows diffractograms measured on the polycrystalline sample of La$_3$Fe(MoO$_4$)$_6$. All detected X-Ray lines are consistent with the orthorhombic unit cell of the studied phase. With increasing temperature one can notice: 1- a displacement of peaks positions related to a modification of the b-axis parameter occurring suddenly around 523K (figure 4c)) whereas no significant modification of a and c parameters are observed apart from ad

Figure 4: a) High-temperature X-ray diffraction data for La$_3$Fe(MoO$_4$)$_6$. A reversible transition is observed at 523K during the heating and cooling process as shown on inserts, blue diagrams correspond to the initial phase and red ones to the HT phase, b) cell volume and c) b-axis parameter evolution versus temperature for La$_3$Fe(MoO$_4$)$_6$ giving the thermal expansion coefficient.
classical dilatation phenomenon and 2- above 523K some extra peaks appear (for instance at 23.36, 23.89 and 29.66°). This phenomenon is reversible on cooling and may be due to a partial decomposition of the tittie phase leading to a modification of b- parameter and with appearance of a new phase. A more detailed study is out of the scope of this preliminary study. After this accident, the refinement of unit cell parameters indicates a classical dilatation phenomenon and 2- above 523K so some extra peaks appear (for instance at 23.36, 23.89 and 29.66°). This temperature evolution of both the cell volume and of the different lattice constants, allowed the determination of the volume and of the linear thermal expansion coefficients \( \alpha: \alpha_a=28.6 \times 10^{-6}, \alpha_b=11 \times 10^{-6}, \alpha_c=16.1 \times 10^{-6}, \alpha_d=14.5 \times 10^{-6} (K^{-1}) \). The thermal expansion of the material appears isotropic in all directions.

Magnetic properties

It is well known that iron molybdates may exhibit interesting magnetic properties depending on the connectivity and dimensionality between FeO\(_6\) and MoO\(_6\) subunits. For instance, (Cs,Rb)Fe(FeO\(_6\))\(_2\) is an example of triangular antiferromagnet with onset of 120° long range magnetic order below 4.5K. It was announced as a possible multiferroic type II material with spontaneous polarization induced by the antisymmetric magnetic exchanges \([28][29]\). In La\(_3\)Fe(FeO\(_6\))\(_6\), the Fe connectivity is rather low and may suggest paramagnetism only. However, the present study shows a rather different signature, as detailed below.

The temperature dependence of the magnetic susceptibility of polycrystalline La\(_3\)Fe(FeO\(_6\))\(_6\) is shown on figure 6. It evidenced a paramagnetic behaviour until a Neel like anomaly at \( T_N = 6.6 \) K. Below this anomaly, AFM ordering occurs despite the poor connectivity of the Fe sub lattice (Fe-Fe = 9.65Å along a, 5.25Å along b, 11.03Å along c). The curie-Weiss law was refined between 300K and 25 K law giving \( \mu_{\text{eff}}=6.2\mu_B/\text{Fe}^{3+} \) and \( \theta_{\text{CW}}=-13.8 \) K. The \( \mu_{\text{eff}} \) value is slightly higher than the theoretical value \( (\mu_{\text{eff}}=5.92\mu_B/\text{Fe}^{3+}) \), probably related with the presence of small impurities (the Morin transition of hematite is detected on \( \chi''(T) \) at 260K). The low negative value of \( \theta_{\text{CW}} \) is in good agreement with expected AFM ordering below TN. The magnetization at 2 K shown on insert of figure 6 is coherent with an AFM behaviour but shows an anomaly occurring at \( H \sim 2 \) Tesla, which could be due to minor FeO\(_6\) impurity. In this dilute Fe\(^{3+}\) system, the magnetic structure of La\(_3\)Fe(FeO\(_6\))\(_6\) is particularly interesting and especially the orientation and values of local moments of Fe\(^{3+}\) ions, in order to...
conclude on the effects induced by very indirect exchanges Fe-(O)₅-Fe.

A neutron diffraction study was performed at low temperature (from RT to 1.5K) on the G41 diffractometer, LLB laboratory, Orsay, France. The onset of the magnetic ordering was confirmed through the appearance of magnetic satellites between 4K and 1.5K on the neutron diffractograms. The three main magnetic peaks appear at 14.86° (011), 16.44° (111) and 20.78° (211) and can be indexed in the crystal unit cell (propagation vector: k = (0,0,0)).

Figure 6: ZFC/FC plots of M/H versus temperature at 103 Gauss. It shows a paramagnetic behavior down to the Neel temperature: T_N = 6.6 K. Inset: magnetization M(H) at T=2 K in μB/f.u.(G).

There is one single magnetic ion (Fe³⁺) in the Pbca unit cell, on Wyckoff site 8c (x, y, z). A symmetry analysis performed using the propagation vector k = 000, on the Pbca space group at site 8c shows that the magnetic components of all 8 sites are related by symmetry:

the magnetic representation Γ can be decomposed into 8 irreducible representations of dimension 1, contained 3 times each in Γ: Γ = 3 Γ₁ + 3 Γ₂ + 3 Γ₃ + 3 Γ₄ + 3 Γ₅ + 3 Γ₆ + 3 Γ₇ + 3 Γ₈.

To solve the magnetic structure, only the MₓMᵧ and Mₚ component of a single site, and the appropriate representation are therefore needed. Only two representations lead to calculated magnetic intensities in relation with the experimental patterns Γ₃ and Γ₇.

where Sᵢd is the component along the d-axis of atom Feᵢ. These two representations differ by spin reversal of half of the Fe ions, i.e. S₁, S₄, S₅ and S₇. Taking into account the very weak magnetic satellites, the agreement factors are overestimated and should be carefully considered. However the best refinement was obtained with the representation Γ₇ (R_magn =24.9%) compared to Γ₃ (R_magn = 38.5%). In addition due to its very low value the Sᵧ component was considered in a second stage, and its refinement in the Γ₃ model is unstable and does not converge. It follows that Γ₇ appears most plausible leading

Figure 7: a) NPD study at 4K and 1.5K. Main magnetic Bragg reflections are
labelled, b) refinement of the neutron diffraction pattern at 1.5K using the obtained magnetic structure (k=0,0,0), orientation of magnetic moments in c) (a,b) and d) (a,c) planes. Local 3-fold geometry of magnetic moment in polyhedral is also enhanced.

Fig. 8 represents the evolution of the ethanol conversion versus the temperature for both samples (i.e., native and after 4 hours of attrition). As expected, the ethanol conversion increased with temperature. However, while, e.g., at 650K over the attrited La$_2$Fe(MoO$_4$)$_6$ powder a 97% ethanol conversion was observed, the native non-premilled La$_2$Fe(MoO$_4$)$_6$ sample was less active with a conversion of only 34% in the same conditions due to a lower SSA (0.4 m$^2$/g vs. 5.6 m$^2$/g for the former - Table S4). Ethanol oxidation on non-attrited La$_2$Fe(MoO$_4$)$_6$ exclusively leads to the production of a chemical product obtained after partial oxidation, namely acetaldehyde. Over the ball-milled sample other products were observed (Fig.8). The main product was still acetaldehyde, but CO$_2$ and formaldehyde were also formed. To explain the apparition of formaldehyde, we propose the following interpretation: the CH$_3$CHOH(CHOH)$_2$COH aldol can be formed from ethanol and then retroaloldised to formaldehyde and acetone, as already reported [33].

Catalytic properties

Two samples of La$_3$Fe(MoO$_4$)$_6$ - described hereafter - were tested for the ethanol oxidation reaction at 600, 625 and 650K. For all the experiments, the carbon balance was always in the range of 100+/-3%. The first one was a La$_3$Fe(MoO$_4$)$_6$ sample used as-prepared (at high temperature and hence with big crystal sizes, figure 8a)), while the second one resulted from mechanically ball milling of the same solid prior to the catalytic test (in order to decrease the crystal size and hence to increase the specific area and thus reactivity, figure 8b)). After synthesis, the material was attrited 4 hours (Netzch PE 075, 1000 rpm) in ethanol using zirconia balls (2 mm diameter). This treatment leads to an increase in the SSA, of which the evolution over time is given in Table S4. Note that an efficient attrition procedure needs at least 20 g of powder.

Figure 8: SEM micrographs of a La$_2$Fe(MoO$_4$)$_6$ sample prepared by solid state reaction a) before and b) after 4 hours attrition with precision of specific surface area (SSA), c) comparison of ethanol conversion for La$_2$Fe(MoO$_4$)$_6$ prepared with and without attrition and d) selectivity to different products for La$_2$Fe(MoO$_4$)$_6$ prepared with attrition.

For comparison, we also measured under the same conditions the performances of an industrial FeMo catalyst (with a comparable SSA of 6 m$^2$/g) conventionally used for formaldehyde production from methanol [34]-[37]. Fig. 9 gives the products selectivity as a function of the reaction temperature for this sample. Full conversion (100%) of ethanol was observed for the whole range of temperatures. At 600K, the main product was acetaldehyde (i.e., selectivity of 55%). An increase in temperature led to the formation of other products such as carbon dioxide, formaldehyde, diethyl ether, furan, etc., which was detrimental for acetaldehyde selectivity. This was not observed on the La$_2$Fe(MoO$_4$)$_6$ which keeps a good selectivity to acetaldehyde when increasing temperature.
Conclusions

The second lanthanum iron molybdenum oxide referenced to date has been synthesized as a single crystal and pure powder. Its composition (Fe+Mo for redox and La for basicity) and its stability in temperature under several atmospheres are in favour of potential catalytic applications. Preliminary results of ethanol reactivity conversion are very promising because the title compound exhibits, after only a simple mechanical attrition milling, a conversion rate of almost 100% with a good selectivity to acetaldehyde (and rather low amount of CO₂). In comparison with a conventional FeMo catalyst, the new La₃Fe₂/₃Mo₁/₃O₇ is more selective for acetaldehyde production, even at high temperatures. Beside these catalytic properties, some antiferromagnetic properties have also been highlighted. We believe that the approach given in this manuscript is a good example of exploratory research enabling the prospection of new compounds with targeted properties, in different fields of applications.

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Notes and references


Figure 9: Comparison of selectivity to different products for FeMo catalyst in different temperatures


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This paper reports the synthesis, crystal structure and properties of the new La₃Fe(MoO₄)₆ phase. A neutron study enabled refinement of the magnetic structure evidencing AFM coupling at 1.5K. It also exhibited a promising ethanol conversion with a better selectivity to acetaldehyde than a conventional FeMo.