Direct conversion of methanol into 1,1-dimethoxymethane: remarkably high productivity over an FeMo catalyst placed under unusual conditions

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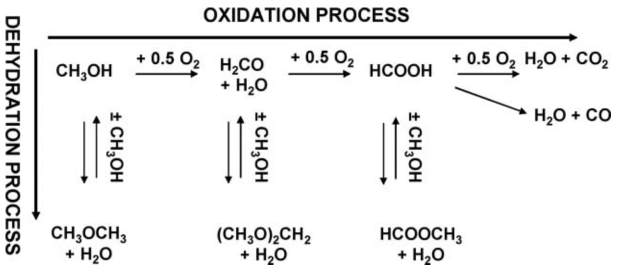
Received 8th June 2010, Accepted 27th August 2010
DOI: 10.1039/c0gc00194e

We report here the highest productivity ever observed in the direct conversion of methanol into 1,1-dimethoxymethane (*ca.* 4.6 kg_{DMM} h^{-1} kg_{cat}^{-1} at 553 K), this result being obtained over an FeMo catalyst. This catalyst is industrially used to selectively convert methanol into formaldehyde but has never before been applied to the present reaction. Placing this FeMo catalyst under unusual reaction conditions, *i.e.*, using a feed rich in methanol, completely changed its behaviour in terms of selectivity: the massive production of 1,1-dimethoxymethane, instead of formaldehyde, was observed.

Methanol is mainly produced by the conversion of syngas, usually obtained from methane or coal. Recently, production of so-called 'biomethanol' has started in new units that process biomass-derived syngas. Methanol can now be considered as a sustainable platform molecule, with perspectives of downstream chemical applications.

1,1-Dimethoxymethane (DMM) is a chemically stable compound with various possible uses (solvent, fuel additive . . .). For example, the selective oxidation of DMM into formaldehyde (F) enables the preparation of concentrated F solutions.[1] High volume applications have recently been patented: polyoxymethylenedimethylether (POMM) synthesised from DMM can be blended with diesel fuels,[2] or can advantageously replace methanol in fuel cells with lower toxicity and higher efficiency.[3] POMM is also an embalming agent that is much safer for an embalmer's health compared to F.[4]

On an industrial scale, DMM is produced by catalytic distillation.[5] Acetalization is performed in the liquid phase by the reaction of methanol with F issued from methanol oxidation.[6] Obviously, realizing the direct conversion of methanol into DMM would enable the elaboration of a more economical one step process. This direct reaction is strongly sensitive to the nature of the catalytically-active sites.[7] Consecutive redox and acid-catalyzed pathways (Scheme 1) can give different products, and the difficulty in selectively obtaining DMM explains the scarcity of the literature on this subject. Nevertheless, promising results have been reported over supported Re oxide and Re-based mixed oxides,[8] and over bulk or supported molybdenum catalysts.[9] Variations of V-TiO_2-based formulations recently gave rather good DMM productivities (at max. 0.33 ± 0.03 kg_{DMM} h^{-1} kg_{cat}^{-1}).[10] However, the highest DMM productivity, before the present paper, was obtained in our team on a $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}O_x$ (AR01) formulation working under optimized conditions.[11]



Scheme 1 Methanol oxidation pathways (adapted from ref. 7).

FeMo formulations are industrially used to produce F[12,13] using reactant feeds with low concentrations of methanol (< 7.5 mol%). A conversion of 99% is observed with a selectivity for F of 94%, while DMM is formed in very small quantities. However, we found that when in contact with a high methanol concentration, the FeMo catalyst exhibited a remarkably high DMM productivity.

In this work, we compare the performance of an industrial FeMo catalyst [(MoO_3–$Fe_2(MoO_4)_3$)] provided by Arkema, of which the preparation method and the main characteristics are described elsewhere,[14] with that of AR01.[11,15] A 6.9 wt% Re/TiO_2 formulation (ReTi) was tested as a reference, as it has also previously exhibited interesting performances, but with drawbacks such as a high price due to its rarity and to Re depletion under the reaction conditions.[11] The ReTi catalyst was obtained by grinding anatase-TiO_2 (Sachtleben-HOMKAT F01) and metallic Re at room temperature before calcining at 673 K in O_2 for 6 h.[16] The 6.9 wt% Re loading was confirmed by inductively coupled plasma (ICP) elemental analysis. The FeMo catalyst and AR01 exhibited much lower specific surface areas (< 10 m^2 g^{-1}) than ReTi (101 m^2 g^{-1}). We also synthesized an

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† Electronic Supplementary Information (ESI) available: Preparation of the FeMo catalyst, composition of the FeMo catalysts, DSC, XRD, conversion curves, performances with time on stream, influence of GHSV. See DOI: 10.1039/c0gc00194e

Table 1 Comparison between the catalytic performances of ReTi, AR01 and FeMo at 553 K

			Selectivity/equiv. carbon (mol%)				
Catalyst	Feed[a]	Conversion (%)	DMM	F	DME	MF	$CO + CO_2$
ReTi	P	65	74	1	11.9	7	6.1
AR01	P	57	89.2	3.3	5.1	1.2	1.2
FeMo	P	59.9	2.8	87.6	7.3	1.7	0.6
ReTi	R	20.2	79.6	0.1	9.6	9.5	1.2
AR01	R	18.1	67.8	13.2	15	31	0.9
FeMo	R	55.7	89.7	4.2	5.3	0.7	0.1

[a] Conditions: P = poor feed; R = rich feed.

FeMo catalyst (see the preparation procedure in the ESI†).[14] We verified the reproducibility of the catalytic performances, which were in the very reasonable range of ±3% compared to those of industrial FeMo due to slight differences in composition (ESI†, Table S1). Furthermore, differential scanning calorimetry (DSC) analysis evidenced a small exothermal peak close to 648 K, and two more intense peaks close to 668 and 683 K, respectively (ESI†, Fig. S1). The presence of three phases was confirmed by XRD analysis (ESI†, Fig. S2): $Fe_2(MoO_4)_3$, MoO_3 and β-$Fe_2(MoO_4)_3$. XRD recorded at a temperature close to 673 K further confirmed the formation of crystallographic phases (ESI†, Fig. S3).

The performances of the catalysts were evaluated at atmospheric pressure in a fixed bed reactor. Two different feed compositions were selected outside of the flammability zone (between 7.5 and 40% methanol in air):[17] the 'poor feed' with $CH_3OH/O_2/He$ = 7.5/8.5/84 and the 'rich feed' with $CH_3OH/O_2/He$ = 40/13/47 (mol%). Gas hour space velocity (GHSV) was adjusted to 22 NL h^{-1} g_{cat}^{-1}. The reactants, namely oxygen and methanol, and the products, namely dimethylether (DME), F, DMM, methyl formate (MF), CO and CO_2, were analyzed using an online gas micro chromatograph (SRA3000) equipped with two columns (plot U and molecular sieves) and two thermal conductivity detectors (TCDs). The total carbon balance was, in any case, over 95%, which was satisfactory. Prior to use, AR01 and ReTi were activated at 623 K for 1 h in an oxygen flow, while FeMo was used without pre-treatment, as in its conventional use to yield F.

In poor feed conditions, all the catalysts exhibited quite similar conversions, within a ±5% range (Table 1; Fig. S4†). The conversion obviously increased with temperature to reach *ca.* 60% at 553 K, irrespective of the sample (Fig. S4†). Meanwhile, in rich feed conditions, the conversion of ReTi and AR01 drastically decreased (less than 20%) but remained at the same level as that observed in poor feed conditions over the FeMo catalyst (Fig. S4†). The selectivities for the reactions performed at 553 K are reported in Table 1. In poor feed conditions, the FeMo catalyst is, as expected, selective for F (87.6%) with a very low selectivity for DMM (2.8%), while ReTi and AR01 are selective for DMM (74 and 89.2%, respectively). In rich feed conditions, the DMM selectivity observed over ReTi and AR01 remains high (79.6 and 67.8%, respectively) and the FeMo catalyst, which was selective for F in poor feed conditions, becomes very selective for DMM (*ca.* 90%) with an almost unaltered conversion (59.9%—poor *vs.* 55.7%—rich).

The productivity of the catalysts in DMM is reported in Fig. 1. The FeMo catalyst is completely atypical compared to ReTi and AR01. ReTi and AR01 show similar DMM productivities, with maximum values in rich feed conditions at 553 K of *ca.* 1.5 and 1.0 kg_{DMM} h^{-1} kg_{cat}^{-1}, respectively. In contrast, over the FeMo catalyst, while in poor feed conditions the DMM productivity did not exceed 0.05 kg_{DMM} h^{-1} kg_{cat}^{-1}, a remarkable increase was observed when using rich feed conditions, with DMM productivities ranging from 2.2 kg_{DMM} h^{-1} kg_{cat}^{-1} at 523 K to the remarkable value of 4.6 kg_{DMM} h^{-1} kg_{cat}^{-1} at 553 K; this is by far the highest value ever reported in the literature. The versatile behaviour of the FeMo catalyst is illustrated in Fig. 2, with a F productivity much larger than that of AR01 and ReTi. Furthermore, the performance of the FeMo catalyst was stable with time on stream, which is well in line with its actual industrial use for producing F. An example of a long-term experiment is given in the ESI (Fig. S5).† In addition, Fig. S6 (ESI†) confirms that the GHSV of 22 NL h^{-1} g_{cat}^{-1} is optimal for the FeMo formulation.

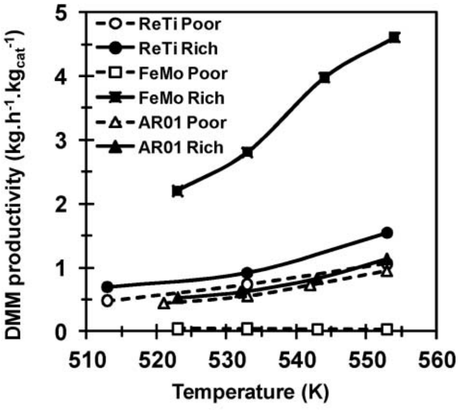

Fig. 1 DMM productivity over the various catalysts as a function of temperature with poor (open symbols) and rich (filled symbols) feeds.

We calculated the apparent activation energy of the reaction (E_a, Table 2) using Arrhenius plots. In poor feed conditions, the three catalysts exhibited similar E_a values of *ca.* 41 kJ mol^{-1}, which corresponds to the value previously reported for the conversion of methanol into F.[18,19] However, while the main product over FeMo is F, it is DMM over ReTi and AR01. This can be explained if we consider that the limiting step of the reaction is the oxidation step of methanol into F. Then, provided proper acid sites are present on the catalyst, F can further be

Table 2 Activation energy (E_a) calculated for the various catalysts working in the poor and the rich feed conditions

Catalyst	Feed[a]	E_a/kJ mol^{-1}	Major product
ReTi	P	40.8	DMM
AR01	P	41.7	DMM
FeMo	P	40.8	F
ReTi	R	26.2	DMM
AR01	R	33.5	DMM
FeMo	R	45.7	DMM

[a] Conditions: P = poor feed; R = rich feed.

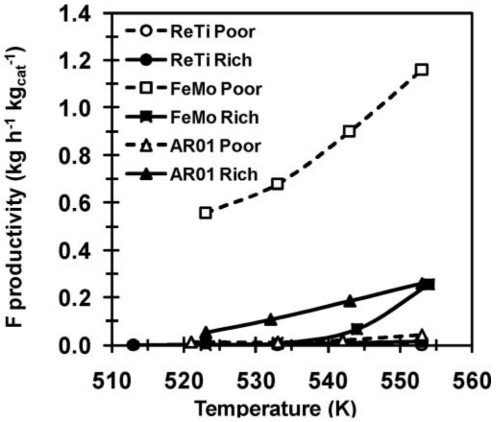

Fig. 2 Formaldehyde productivity over the various catalysts as a function of temperature with poor (open symbols) and rich (filled symbols) feeds.

easily converted into DMM, which seems to be the case over AR01 and ReTi.

In rich feed conditions, E_a is lower for ReTi and AR01, with respective values of 26.2 and 33.5 kJ mol^{-1}, while the main product is still DMM. This can be explained if the mechanism is not the same for the two feed conditions, as evoked by Edwards[18] Density functional theory (DFT) calculations are currently in progress in our lab to support this hypothesis of a dual mechanism. In contrast, the E_a observed over FeMo placed in rich feed conditions increased to 45.7 kJ mol^{-1}, with DMM as the main product instead of F in the poor feed conditions. The reason for this atypical behaviour is not yet elucidated but might originate from (1) the development of specific acid sites over FeMo in the rich feed conditions and/or (2) a F desorption rate lower than the formation/desorption rate of DMM in the presence of high methanol partial pressures. The acidity of FeMo catalysts, which is required in addition to redox properties to yield DMM, has previously been characterized *ex situ*.[14,20] Surface acidity is linked with the presence of Mo^{VI} entities, and the over-stoichiometry in Mo seems to have an effect on the acid sites' quantity/strength. However, the acidic behaviour of this catalyst in real working conditions still needs further investigation. The catalytic results in the present paper strongly suggest that acidity could be drastically different, according to the operating conditions (rich feed *vs.* poor feed).

Further, XRD experiments were performed using a D8 Advance apparatus (Brüker AXS) equipped with a controlled temperature/atmosphere chamber. The FeMo catalyst was analyzed in the presence of methanol and oxygen. When exposing the catalyst to the reactants' atmosphere, we observed a shift of peaks, corresponding to an elongation of the *b* parameter of the MoO_3 cell. Furthermore, Raman spectroscopy performed under Operando conditions using the FeMo catalyst in poor and rich feed conditions showed in both cases a concomitant and progressive decrease with time on stream in the intensity of the Raman bands corresponding to MoO_3 and $Fe_2(MoO_4)_3$.

The mechanism of the reaction in conventional conditions, *i.e.*, poor feed, is still a matter of debate, even if several groups have studied this reaction over various types of solids. The unusual behaviour described in this paper—when using experimental conditions radically different from the usual ones—raises further questions.

Conclusion

According to our discovery, DMM, a valuable product, can be readily and sustainably produced in existing infrastructures dedicated to methanol conversion into formaldehyde over the same FeMo catalysts with air as a dilutent/oxidant by using high methanol partial pressures instead of the low partial pressures conventionally used for formaldehyde production.

Acknowledgements

The authors gratefully acknowledge Arkema as well as the CE for its financial support through contract number MIRG-CT-2007-046383. The authors also want to thank Mr O. Gardoll, Mrs N. Djelal and Mrs L. Burylo from UCCS for their precious technical help.

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