Amorphous oxide as a novel efficient catalyst for direct selective oxidation of methanol to dimethoxymethane†

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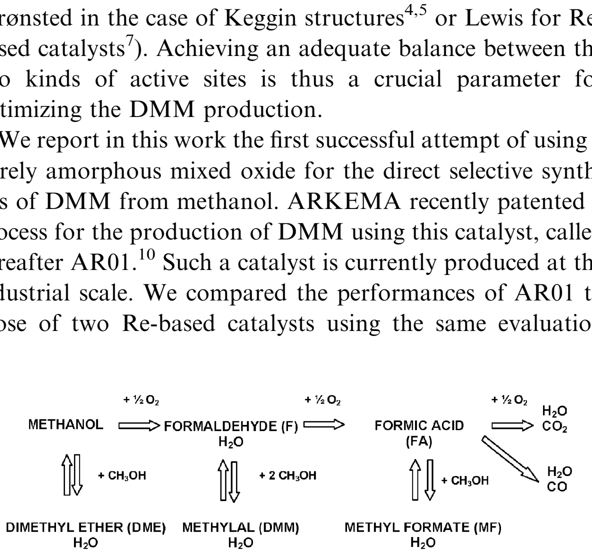
We report for the first time the use of an amorphous oxide catalyst for the selective oxidation of methanol in the gas phase, leading at 553 K to the production of dimethoxymethane with a selectivity as high as 90% at high methanol conversion (68%).

During the 20 past years numerous efforts have been devoted to the development of selective catalysts for the partial oxidation of methanol, with important industrial applications as a target. It is now well admitted that this reaction is strongly sensitive to the nature of the active sites.[1] Different products can be obtained as shown in Scheme 1. Redox sites enable the production of partially oxidized species [formaldehyde (F), formic acid (FA)] or totally oxidized species (CO and CO_2). Acidic sites enable condensation reactions, which can give dimethyl ether (DME), dimethoxymethane [or 'methylal' (DMM)] and methyl formate (MF). As proposed by Tatibouët *et al.*,[1] this dual behavior enables probing of structural (cristallographic plane reactivity) and chemical (acid–base and redox) properties of oxide catalysts.

Among the aforementioned products, DMM is especially interesting for industrial applications, since it is suitable as a fuel additive with a high chemical stability. Industrially, DMM is conventionally produced through catalytic distillation by acetalization of methanol and formaldehyde.[2] Hagen and Spangler extensively described the use of DMM for polyoxymethylenedialkyl ether synthesis.[3] Gas phase DMM production patents are rare because of the difficulty of obtaining high DMM yields in a one-step gas-phase methanol-selective oxidation procedure. In the academic literature, many authors reported attempts to use molybdenum-based catalysts for this reaction. In studies reporting the use of bulk and supported 12-molybdophosphoric acid catalysts,[4] it was shown that β-MoO_3 was the active phase for direct formation of DMM. High DMM selectivity (S_{DMM}; up to 55%) was obtained at low conversion (<20%). Liu *et al.*[5] obtained high DMM production rates over bulk and supported $H_{3+n}V_nMo_{12-n}PO_{40}$ Keggin structures. Partial incorporation of vanadium in the Keggin structure (n = 1, 2) yielded the highest DMM selectivities: S_{DMM} = 58.1% at a methanol conversion of 68.2% over 9.2 wt% $H_4PVMo_{11}O_{40}$ supported on SiO_2. The same authors further used a different catalytic system, namely RuO_2 supported on TiO_2, Al_2O_3 and TiO_2–Al_2O_3. Lower performances were obtained with a maximum DMM selectivity of 66.8% at a methanol conversion of only 20% (4.4 wt% Ru/Al_2O_3).[6] Promising results were obtained by the Iwasawa's group[7] who observed high DMM yields over Re oxide and Re-based mixed oxides supported on various oxide supports (TiO_2, V_2O_5, ZrO_2, α-Fe_2O_3, γ-Fe_2O_3, α-Al_2O_3...). The maximum DMM selectivity varied between 60% (Re/SiO_2) and 90–93% (Re/α-Al_2O_3, V_2O_5, ZrO_2) for a methanol conversion comprised of between 15% (Re/SiO_2, α-Al_2O_3, α-Fe_2O_3) and 60% (Re/TiO_2). These catalysts were patented[8] but the low thermal stability of Re at intermediate reaction temperatures (>573 K) and its prohibitive cost unfortunately limit their industrial perspectives. Recently, Fu *et al.*[9] reported excellent results over $Ti(SO_4)_2$-modified V_2O_5/TiO_2 catalysts with DMM selectivities of 89–92% for 48–60% methanol conversions. Irrespective of the catalytic system, all the studies suggest a dual mechanism involving redox and acidic sites (Brønsted in the case of Keggin structures[4,5] or Lewis for Re-based catalysts[7]). Achieving an adequate balance between the two kinds of active sites is thus a crucial parameter for optimizing the DMM production.

We report in this work the first successful attempt of using a purely amorphous mixed oxide for the direct selective synthesis of DMM from methanol. ARKEMA recently patented a process for the production of DMM using this catalyst, called hereafter AR01.[10] Such a catalyst is currently produced at the industrial scale. We compared the performances of AR01 to those of two Re-based catalysts using the same evaluation



Scheme 1 Reaction pathways for the reaction of catalytic partial oxidation of methanol (adapted from ref. 1).

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procedure. AR01 is a bulk catalyst of general formula $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}O_x$ obtained by a simple coprecipitation method. The synthesis procedure of AR01, as well as those of the reference catalysts (a sol–gel γ-Al_2O_3[11] and a TiO_2 supported Re catalyst[12]), are described in the ESI file.† The three catalysts have been tested for the selective oxidation of methanol. A full description of the catalytic test procedure is given in the ESI file.†

Due to the simple straightforward coprecipitation method used for its synthesis, AR01 unsurprisingly exhibits a low specific surface area ($< 10\ m^2\ g^{-1}$). Moreover, because of the intermediate/low calcination temperature (613 K), AR01 is amorphous, which was confirmed by XRD analysis (Fig. S1†).

Optimal preactivation conditions were determined for the lab-scale test. Especially, we found that the oxygen content in the preactivation feed played an important role on the catalytic performances of AR01 (Table S1 and Fig. S2†). The best result was obtained for preactivation under pure O_2 with a DMM selectivity of 90.1% at a methanol conversion of 68.3% (Table S1†), which is the best result ever reported in the literature. Lowering the O_2 percentage in the preactivation feed led to a slight decrease in both DMM selectivity and methanol conversion (Table S1 and Fig. S2†), which however kept high levels. A test performed on a non-activated catalyst led to an unacceptable decrease in DMM selectivity (S_{DMM} = 2.0%). For further experiments, a 20 vol% O_2 in He preactivation feed was retained, because it simulates air flowing, which is preferred for practical applications, while maintaining very high catalytic performances, close to those obtained over the catalyst preactivated in pure oxygen.

Table 1 compares the catalytic performances of AR01 with those of the two Re-based catalysts. The γ-Al_2O_3-supported Re catalyst yielded mainly DME due to the acidobasic function of the support. The performances of the Re catalyst supported TiO_2 catalyst were better than that of AR01 at low reaction temperatures (Re/TiO_2: 473 K; Conversion = 10.3%, S_{DMM} = 86.3%; AR01: 473 K; Conversion = 8.3%, S_{DMM} = 85.9%). The slightly higher activity at low temperature of the Re samples can be attributed, as proposed by Iwasawa's group,[7] to a high reactivity (*i.e.*, high reducibility) of Re-oxide species, which enables lower temperature methanol oxidation when compared to AR01. Nevertheless, increase in temperature irreversibly damaged the Re/TiO_2 catalyst by volatilization of Re oxo-species. Over 513 K, we observed the condensation of a green solid at the outlet of the reactor (cold point), which was identified as Re_2O_7. This is a well known issue when using Re based solids.[13] Further, it should be noted that the given Re amounts in the catalysts (*i.e.*, 7.4 wt% and 20 wt%) corresponds to the quantities of Re used during their preparation. However, the calcination procedure, followed by the necessary preactivation procedure and the subsequent catalytic test progressively depleted the Re content of the catalysts, especially when operating at high temperatures, which considerably altered the expected performances when increasing temperature. On the other hand, over AR01 it was possible to increase the methanol conversion to 63% while maintaining the DMM selectivity at a high value of 89.2% at 553 K (Table 1). All the other possible reaction products (F, DME, MF, and CO_x; Scheme 1) were also formed in low amount. With the increase in temperature, we observed an increase in the selectivity of oxidation products (F and CO_x). At the same time, a decrease in the selectivity in DME and MF (condensation products) was observed. This trend can be explained assuming a slight increase in the quantity of active redox site, and/or the deactivation of a part of the acidic sites when increasing the working temperature. Nevertheless, redox sites present on the surface of AR01 are not too strong because they clearly favor partial oxidation rather than complete oxidation (S_{CO_x} remained low and the CO always represented more than 95% of the CO_x). Further, the amorphous character of AR01 is an important parameter. Methanol conversion to DMM needs cooperative work of two types of sites (acid ones and redox ones). Inadequate catalyst treatment leads to phase segregation and improper sites distribution on the surface with a strong detrimental effect on DMM selectivity. With properly handled amorphous AR01, DMM selectivity was not altered up to 553 K (Table 1).

These catalytic results obtained over AR01 are clearly superior to those claimed by Liu *et al.* who obtained their highest selectivities in DMM in the range of 50–60% for conversions in the range of 60–68% over $H_{3+n}PV_nMo_{12-n}O_{40}$ supported SiO_2 samples.[5] In contrast to our results on AR01, these authors observed a drastic decrease in DMM selectivity when increasing the reaction temperature. While over the $H_5PV_2Mo_{10}O_{40}/SiO_2$ catalyst a methanol conversion of 39.9% with a DMM selectivity of 61.8% was obtained at 453 K, at 513 K the methanol conversion slightly increased to 42.4% but meanwhile the DMM selectivity dropped at 32.7%. Note that the same authors found a maximum DMM selectivity over a supported Ru catalyst (4.4 wt%Ru/Al_2O_3) of

Table 1 Comparison between the catalytic performances of AR01 and two rhenium reference samples[a]

				Selectivity (mol%)				
Sample	$S_{BET}/m^2\ g^{-1}$	Temperature/K	Methanol conversion (%)	DMM	F	DME	MF	$CO + CO_2$
AR01	<10	473	8.3	85.9	Trace	6.1	8.0	0
		523	31.3	89.7	1.1	5.3	3.1	0.7
		553	63	89.2	4.0	3.2	1.7	1.8
7.4 wt%Re/TiO_2[b]	101	473	10.3	86.3	0	12	1.7	0
		533	52.1	78	4.3	7.7	5.4	4.6
20 wt%Re/γ-Al_2O_3[b]	398	473	11.6	33	0	64.2	2.8	0
		513	29.5	27.8	0	65.6	4.1	2.5

[a] 7.5 vol% CH_3OH; 8.5 vol% O_2 in He; Total flow rate of 54.4 mL min^{-1} (GHSV = 22 000 mL $h^{-1}\ g^{-1}$). [b] 7.5 vol% CH_3OH; 15.0 vol% O_2 in He; Total flow rate of 64.3 mL min^{-1} (GHSV = 26 000 mL $h^{-1}\ g^{-1}$).

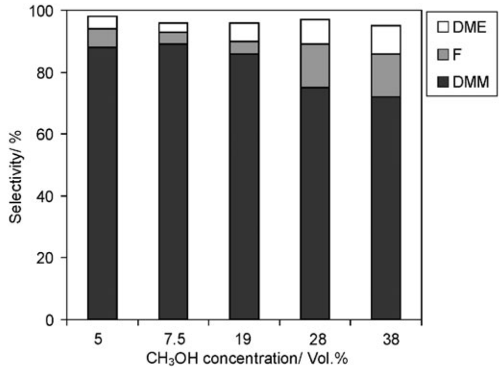

Fig. 1 Effect of the methanol partial pressure in the feed on the catalytic performances of AR01 at 553 K.

66.8% at a methanol conversion of ~20%.[6] Superior DMM selectivity (93.7% at 21.5% methanol conversion over 10 wt% Re on V_2O_5) was only found by the Iwasawa's group.[7] Unfortunatly, no information on the influence of temperature on S_{DMM} was given.

The performances of AR01 preactivated in air flow are substantially similar to those recently claimed by Fu *et al.*[9] over a V_2O_5/TiO_2–$Ti(SO_4)_2$ catalysts with DMM selectivities of 89–92% for 48–60% methanol conversions at 433 K. However, preactivation of AR01 in pure oxygen led to even better performances with DMM selectivities of 90% for a methanol conversion of 68% at 553 K. Note that this reaction is exothermic. Design of an energy efficient industrial process involves heat recovery through high pressure steam utilization as an energy carrier, which can be optimized if the process temperature is sufficiently high. This is enabled by the use of AR01, which can work at higher temperatures while maintaining very high S_{DMM} (*i.e.*, 90%).

We then studied the effect of methanol partial pressure on the performances of AR01. With the increase in methanol partial pressure, methanol conversion progressively decreased from 78.2% for 5 vol% CH_3OH to 25.1% for 38 vol% CH_3OH (Table S2†). The DMM selectivity only moderately decreased with the increase in methanol partial pressure but always remained larger than 70% (Fig. 1). As a result, DMM productivity increased with a maximum of 126×10^{-5} mol $\min^{-1}$ g^{-1} at a methanol concentration of 28 vol% (Table S1†), which is much larger than the largest one obtained by Fu *et al.*,[9] *i.e.*, 21.8×10^{-5} mol $\min^{-1}$ g^{-1} (calculated by applying to their numerical results the formula given as a footnote in Table S2†). Note that the observed decrease in DMM selectivity led to an increase in the selectivities in F and DME, which are valuable compounds. The sum of the DMM, F, and DME selectivities remained around 95%, irrespective of the methanol concentration (Fig. 1), which is thus satisfactory.

The last point concerns the stability of the AR01 sample, which is critical when one considers industrial perspectives. As aforementioned, Re-based catalysts performances are hindered by metal loss occurring over ~513 K, which makes them unusable for practical applications. In contrast, AR01 was found to be stable with time on stream for said high processing temperatures. After 28 h of reaction at 553 K (preactivation in simulated air; 5 vol% CH_3OH–8.5 vol% O_2 in He at a GHSV of 22 000 mL h^{-1} g^{-1}), we observed only a slight decrease in methanol conversion of less than 5 points, which occurred in the first 4 h of the run. Then, conversion remained stable. This lag time thus corresponded to the time required for catalyst stabilization. In contrast, no change in DMM selectivity was observed ($S_{\mathrm{DMM}} \sim 90 \pm 2\%$).

In summary, the amorphous $Mo_{12}V_3W_{1.2}Cu_{1.2}Sb_{0.5}O_x$ (AR01) sample synthesized by a simple straightforward co-precipitation procedure exhibits both high activity and high selectivity in DMM. Results clearly showed superior performances when considering practical industrial applications among all the references already published in the field of the one-step gas-phase methanol oxidation in DMM. Moreover, it was clearly established that the catalyst can work in a wide range of reaction temperatures and methanol concentrations without any drastic loss in DMM selectivity, which is interesting considering possible parameters fluctuation in real operating conditions.

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