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

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Supporting information

Synthesis of γ-Al$_2$O$_3$ sol gel support

In this procedure, aluminum tri-*sec*-butoxide (50 mL) was dissolved in 2-butanol (80 mL) under stirring at 358 K. Then, aluminum alkoxide complexation was performed by addition of 35 mL of butan-1,3-diol before subsequent hydrolysis using 35 mL of water. After addition of water, the stirring was kept during 1 h at 358 K before keeping the solution under static conditions at room temperature during 1 h more. The powder obtained after evaporation in a rotary evaporator was dried overnight at 373 K before subsequent calcination at 773 K under air for 4 h (temperature increase rate = 0.6 K.min^{-1}).

Preparation of AR01

AR01, which is a bulk catalyst of general formula Mo$_{12}$V$_3$W$_{1.2}$Cu$_{1.2}$Sb$_{0.5}$O$_x$, is prepared as follows: 1.63 g of ammonium paratungstate are added to 60 mL of distilled water previously heated at 368 K. Once the tungsten precursor is dissolved, 11.0 g of ammonium heptamolybdate and 1.82 g of ammonium metavanadate, and then antimony acetate, are then successively added under stirring to the solution. 'Solution I' is thus obtained. 'Solution II' is then obtained by adding 1.56 g of copper sulfate to 10 mL of distilled water. When copper precursor is dissolved, Solution II is slowly added to Solution I under stirring. The obtained slurry is then dried at 373 K, calcined at 663 K for 5 h under air flow (temperature increase rate = 1 K.min^{-1}), and cooled to room temperature in the same atmosphere. AR01 composition was checked by ICP. The difference between the measured composition and the theoretical one did not exceed 5 %.

Preparation of Re/Al$_2$O$_3$ and Re/TiO$_2$

Anatase-TiO$_2$ (Sachtleben-HOMKAT K03) and γ-Al$_2$O$_3$ (prepared by sol-gel procedure described in a section of the present ESI) supported Re samples (7.4 wt.% Re on TiO$_2$ and 20 wt.% Re on γ-Al$_2$O$_3$) are prepared by grinding the support with metallic Re at room temperature before calcination at 673 K in O$_2$ for 6 h. Prior to use, the samples were activated at 623 K for 1 h under pure O$_2$ flow.

Catalytic test procedure

Catalytic activities for the methanol oxidation reaction were evaluated in a fixed-bed reactor. Before test, AR01 was activated 1 h at 613 K (temperature increase rate = 10 K.min^{-1}). Reaction feed was composed of x Vol.% CH$_3$OH (where x = 5, 7.5, 19, 28, 38) and 8.5 Vol.% O$_2$ in helium. GHSV was adjusted at 22000 mL.h^{-1}.g^{-1}. Reactants and products were analyzed using an on-line gas microchromatograph (SRA3000) equipped with two columns (Q plot, Molecular sieves) and two TCDs. Carbon balance was comprised between 95 % and 105 %, which was considered as satisfactory.

Table S1 Effect of the activation atmosphere on the catalytic performances of AR01. Test conditions: 7.5 Vol.% CH_3OH; 8.5 Vol.% O_2 in He; total flow rate of 54.4 mL.min^{-1} (GHSV = 22000 mL.h^{-1}.g^{-1}); temperature of 553 K.

Activation conditions			Conversion/ %	Selectivity/ mol.%					
Flow rate/ mL.min^{-1}	O_2/ Vol.%	He/ Vol.%		DMM	F	DME	CO	CO_2	MF
20	100	0	68.3	90.1	4.3	3.9	Trace	0	1.7
20	20	80	63.0	89.2	4.0	3.2	1.8	0	1.7
20	0	100	56.8	82.7	8.5	4.8	1.8	Trace	2.2
None			34.9	2.0	77.6	10.1	5.3	0	5.1
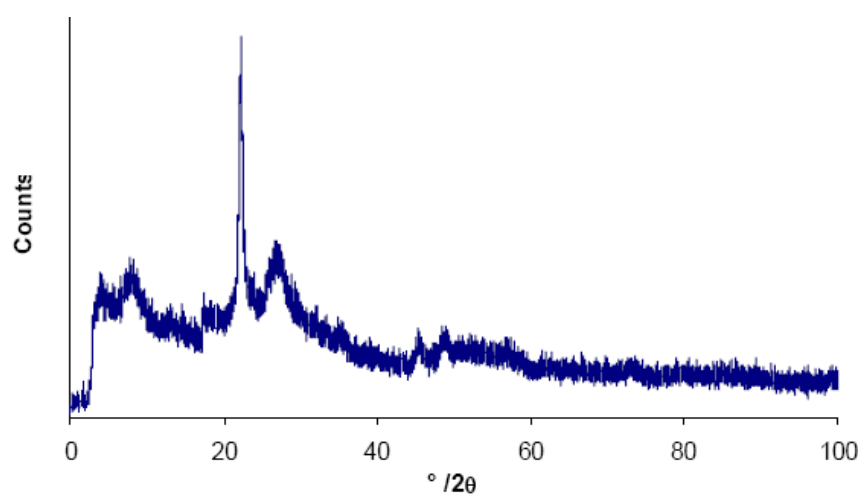
Fig. S1 XRD diffractogram of AR01. AR01 is essentially amorphous and the peak near $2\theta = 22°$ is attributed to octahedral MoO_6 entities stacking.
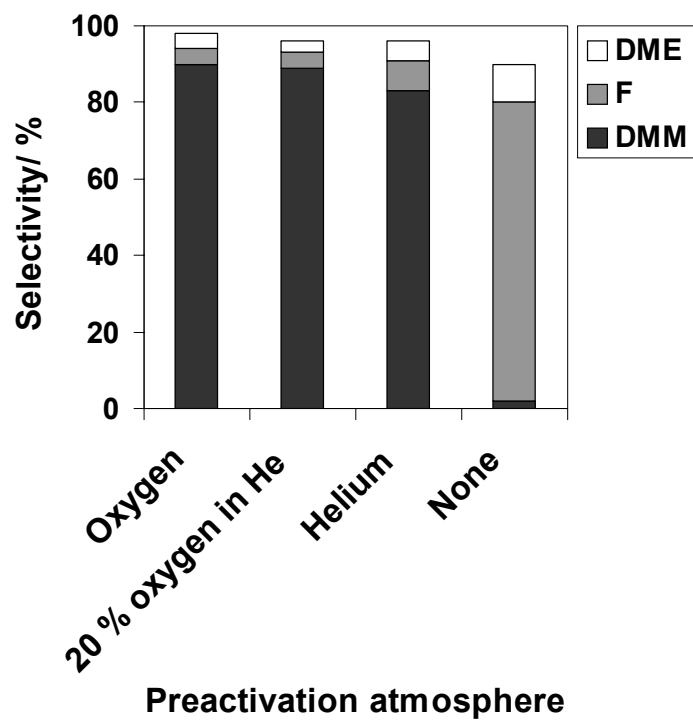
Fig. S2 Effect of the activation atmosphere on the selectivity of AR01. Test conditions: 7.5 Vol.% CH_3OH; 8.5 Vol.% O_2 in He; total flow rate of 54.4 mL.min^{-1} (GHSV = 22000 mL.h^{-1}.g^{-1}); temperature of 553 K.

Table S2 Effect of the methanol partial pressure in the feed on the catalytic performances of AR01 at 553 K.

Feed composition/Vol.%			Conversion/	Selectivity/ mol.%						$P_{DMM}{}^a$	$P_{DMM+F+DME}{}^a$
CH$_3$OH	O$_2$	He	%	DMM	F	DME	CO	CO$_2$	MF	10^{-5}.mol.min^{-1}.g^{-1}	
5.0	8.5	86.5	78.2	88.4	6.0	3.8	0	0	1.8	51	57
7.5	8.5	84.0	63.0	89.2	4.0	3.2	1.8	0	1.7	63	68
19.0	8.5	72.5	39.7	86.4	4.0	6.0	1.8	0	1.8	97	108
28.0	8.5	63.5	40.5	74.7	13.6	8.1	1.4	0	2.2	126	163
38.0	8.5	53.5	25.1	71.6	14.5	9.0	2.2	0	2.6	102	135

[a] P = Productivity defined as the number of moles of CH$_3$OH converted in DMM (or DMM+DME+F) per minute and per gram of catalyst. For example, P_{DMM} is calculated using the following formula:

$$P_{DMM} = \frac{Q_{CH3OH}(L.min^{-1})}{24.4(L.mol^{-1})} \cdot \frac{X(\%).S(\%)}{10000} \cdot \frac{1}{m_{cata}(g)}$$