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Catalytic oxidation of methanol on Mo/Al_2O_3 catalyst: An EPR and Raman/infrared operando spectroscopies study

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Abstract

The oxidation of methanol has been studied on Mo/Al_2O_3 catalyst in absence and presence of oxygen. Quasi-simultaneous IR and Raman spectroscopies were used to follow the evolution of the active phase and adsorbed species on the catalyst under reaction conditions.

An increase of reduced Mo species on the active phase is observed by Raman spectroscopy in parallel with a deactivation of the redox properties of the catalyst. Complementary EPR experiments show the transformation of Mo^{VI} to Mo^{V} and its accumulation in absence of oxygen. Selectivity toward oxidation products is drastically affected by the accumulation of Mo^{V} species on the active phase. Oxygen addition to the reaction mixture leads to a decrease of the amount of Mo^{V} and a partial restoration of the oxidative properties of the catalyst.

Keywords: Raman spectroscopy; Methanol; Redox

1. Introduction

Analysis techniques such as XPS and HREELS are generally used to characterize the surface state of heterogeneous catalysts but they cannot be used under working conditions. Infrared and Raman vibrational spectroscopy represent an attractive alternative as they can be applied to probe the catalyst under reaction or operando conditions [1]. The combination of Raman and IR spectroscopies can then give a better insight into catalytic systems under steady state conditions enabling to obtain information on the nature of the adsorbed species, the nature of the active phase and on the nature of their interaction. The oxidation state of active sites can also be characterized using bulk analysis techniques such as EPR to obtain data on an atomic scale [2].

Molybdenum oxide based catalysts are used industrially for the partial oxidation of hydrocarbons and alcohols such as methanol. The partial oxidation of methanol is of great interest for industrial applications [3] but is also a probe reaction to test the catalytic properties of new preparations [4]. Indeed, numerous studies have shown that methanol oxidation is very sensitive to the nature of active sites and can be used to study the acidic and oxidation properties of catalytic surfaces [4–6]. The possible pathways for the reaction of methanol on a bulk or supported metal oxide catalyst are summarized in Scheme 1.

The oxidative–reductive processes lead to oxidized species such as formaldehyde (F), formic acid (FA) and carbon oxides (CO_x) whereas acid–base functions mainly lead to the dehydration product (dimethylether, DME). Successive dehydrations of oxidation products can yield dimethoxymethane (DMM) or methyl formate (MF) [4]. Hence, the distribution of the reaction products gives indications on the functionalities present on the catalyst surface. Moreover, oxidation of methanol is well adapted for spectroscopic studies [7,8] and has been described on various materials [9,10].

We have focused the present study on the characterization of the active phase and adsorbed species with Raman/infrared and

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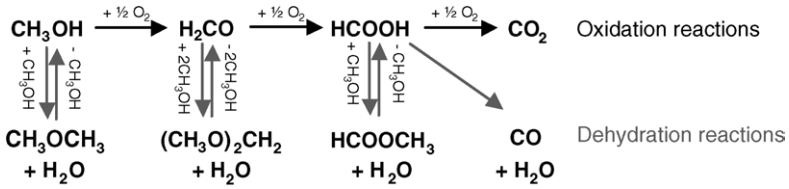

Scheme 1. Reaction pathways in methanol transformation on MoO_3 catalysts [4].

EPR spectroscopies during the oxidation reaction of methanol on a well-designed polymolybdate deposited on γ-alumina.

2. Experimental

Aluminium oxide was prepared by sol–gel procedure mixing aluminium sec-butoxide (Fluka, ≥95%) and 2-butanol at 85 °C. Water was added in a molar ratio of $1Al/6C_4H_9OH/10H_2O$, giving a gel that was dried at 120 °C overnight and then calcined at 500 °C for 4 h. The specific surface area (SSA) of the obtained alumina is ca. 500 m^2/g. The catalyst samples were prepared by incipient wetness impregnation of this alumina support with ammonium heptamolybdate solution ($Mo_7O_{24}(NH_4)_5{\cdot}4H_2O$, Fluka, ≥99%), the amount of added heptamolybdate being adjusted for the preparation of a catalyst with 20 wt.% of Mo. After drying overnight at 100 °C, the sample was calcined in air at 500 °C for 3 h with a ramp rate of 40 °C h^{-1}. Such a preparation leads to a coverage of 2.5 molybdenum atoms per square nanometers, which means that roughly 1/3 of the alumina surface is covered by the molybdate phase based on an area of 0.15 nm^2/Mo that is the area of one MoO_3 unit in bulk MoO_3 [11].

Infrared and Raman spectrum were collected on exactly the same spot with a LabRAM IR (Jobin Yvon Horiba) spectrometer described elsewhere [12]. This technology allows the quasi-simultaneous examination of one sample area by both techniques without any manipulation of the sample, thus both spectra are recorded in exactly the same conditions. Raman spectra were recorded with an excitation radiation at 632.8 nm (resolution 2 cm^{-1}) and infrared spectra were collected using a MCT detector with 256 scans (resolution 4 cm^{-1}). The sample was crushed and placed into the IR/Raman reactor equipped with a ZnSe window. The reaction mixture (He/CH_3OH or O_2/CH_3OH) is then introduced and passes through the sample (as in a fixed-bed reactor). Methanol partial pressure in the gas feed was adjusted to 4 kPa by the mean of a saturator followed by a condenser cooled to 0 °C. The ratio $W/F^0_{CH_3OH}$ was set to 0.030 h kg/mol. Both saturator and reactor can be bypassed by four-port valves. Gas lines between the saturator and the GC were heated to 80 °C. The effluent gas mixture was analyzed by an online μ-gas chromatograph (SRA) equipped with Poraplot Q and 5A molecular sieve columns.

Alternatively, the IR/Raman reactor has been replaced by a specially designed fixed-bed reactor dedicated to the EPR measurements in the same reaction conditions (Fig. 1). This cell consists of a U-tube containing a filter where the catalyst is located. The reactive mixture goes through the catalyst from the bottom and the products are then analyzed by the μ-gas chromatograph.

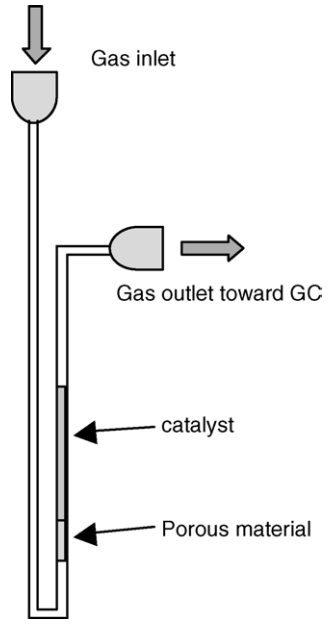

Fig. 1. Cell dedicated to the EPR experiments.

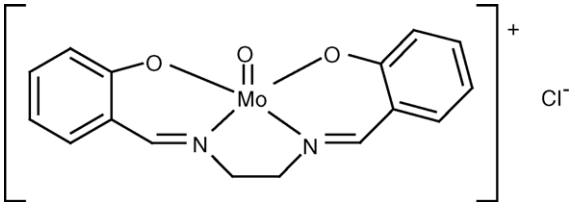

Fig. 2. Structure of the reference compound used for spin quantification in the EPR experiments (oxo-molybdenum *N*,*N*′-bis-(salicylidene)ethylenediamine).

The EPR spectra were collected with an X-Band BRUKER ELEXYS E580 spectrometer operating at 100 kHz modulation frequency and 2 G modulation amplitude. Microwave power was set to 1 mW. The spin quantification for Mo(V) species was performed using a synthesized oxo-molybdenum-*N*,*N*′-bis-(salicylidene)ethylenediamine [13] in a dual EPR cavity at room temperature (Fig. 2).

3. Results and discussion

The Raman spectrum of the supported Mo/Al_2O_3 catalyst, reported in Fig. 3a, exhibits the features of the surface

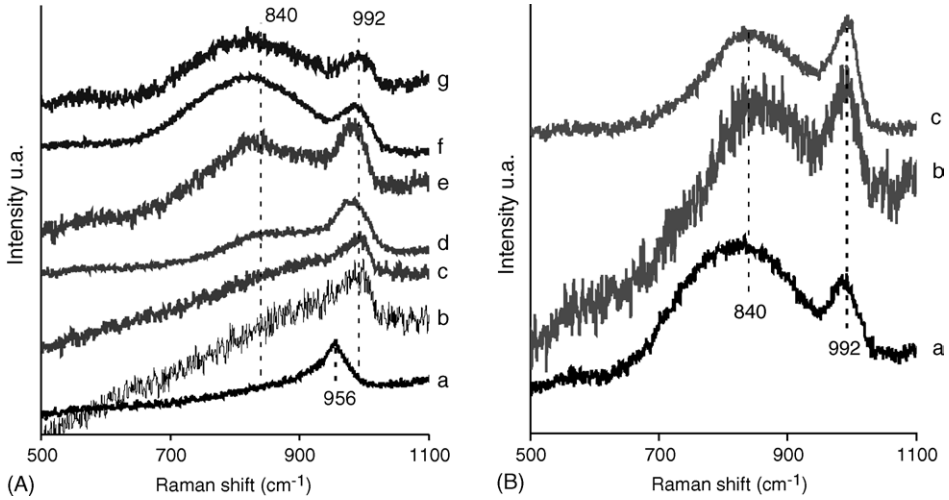

Fig. 3. (A) Raman spectrum of Mo/Al_2O_3 catalyst: (a) fresh catalyst; (b) activated catalyst, under methanol in absence of oxygen; (c) 150 °C, t = 0 min; (d) 150 °C, t = 15 min; (e) 150 °C, t = 60 min; (f) 200 °C, t = 30 min; (g) 200 °C, t = 60 min. (B) Raman spectrum of Mo/Al_2O_3 catalyst under methanol in absence of oxygen: (a) 250 °C, t = 20 min, under methanol in the presence of oxygen; (b) 250 °C, t = 15 min; (c) 250 °C, t = 45 min.

polymolybdate phase [14] with a main line at 956 cm^{-1} characteristic of the MoO_{2t} groups (where t stand for terminal). Prior to reaction, the catalyst was activated under O_2 at 350 °C during 2 h. The dehydration process is clearly evidenced on the Raman spectrum b (Fig. 3A) by the shift of the line at 956–992 cm^{-1}, value characteristic of the Mo=O_t stretching mode of the dehydrated polymolybdate phase [14]. It is noteworthy that no bulk MoO_3 was evidenced on the catalyst at any moment of the preparation and reaction. The dehydration was also evidenced in the infrared spectrum (not shown here) by the disappearance of the bands around 1635 cm^{-1} characteristic of water adsorbed on the support and by a shift of ν(OH) bands of hydroxyl groups due to the dehydration of the alumina.

Then, Raman (Fig. 3) and infrared (Fig. 4) spectra recorded during the methanol oxidation reaction were collected at different temperatures under catalytic conditions.

In absence of oxygen at 150 °C, only a small amount of methanol (13%) is converted and only DME is produced (Table 1). In the meantime, infrared bands at 2946 and 2840 cm^{-1} were observed which are due to the antisymmetric C–H stretch (ν_{as}) and to the symmetric C–H stretch (ν_s) of adsorbed OCH_3, respectively, along with a band at 1446 cm^{-1} assigned to the C–H bending modes [15,16] (Fig. 4). These bands indicate a dissociative adsorption of methanol into methoxy species on either the molybdate phase or the alumina support. Groff [15] reported bands located at 2925, 2825 and 1440 cm^{-1} that were found to be characteristic of methoxy species adsorbed on polycrystalline MoO_3. Alternatively, the dissociation of methanol on a pure alumina surface leads to the appearance of a shoulder at 2970 and bands at 2955, 2844 cm^{-1} (CH_3 stretchings) and 1472, 1458 cm^{-1} (CH_3 bendings) [16]. The comparison of our results with the published data suggests that the methoxy species are adsorbed essentially on the alumina support and that the methoxy species on the molybdate phase react rapidly or spill over the support. Moreover, the coverage of the polymolybdate phase (1/3) suggests that

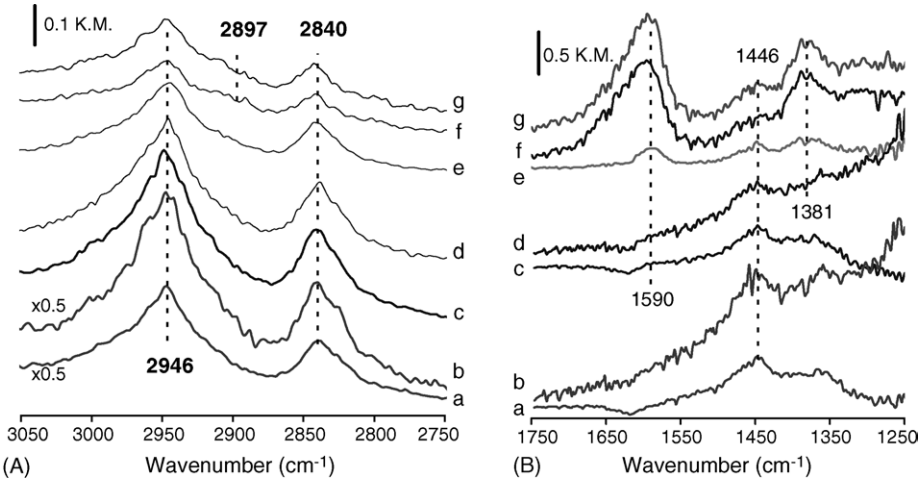

Fig. 4. Infrared spectrum of Mo/Al_2O_3 catalyst under methanol in absence of oxygen: (a) 150 °C, t = 15 min; (b) 150 °C, t = 60 min; (c) 200 °C, t = 30 min; (d) 200 °C, t = 60 min; (e) 250 °C, t = 15 min, under methanol in the presence of oxygen; (f) 250 °C, t = 30 min; (g) 250 °C t = 60 min.

Table 1
Activity and selectivities measurements obtained during IR/Raman operando experiments on Mo/Al_2O_3

Catalyst	T (°C)	Time at T (min)	Mixture	Conversion (%)	S_{DME}	S_{H_2CO}	S_{CO_x}	S_{MF}	S_{DMM}
Mo/Al_2O_3	150	10	CH_3OH/He	13	100	–	–	–	–
	150	60	CH_3OH/He	13	100	–	–	–	–
	200	10	CH_3OH/He	66	57	36	–	7	–
	200	60	CH_3OH/He	44	100	–	–	–	–
	250	10	CH_3OH/He	86	99	–	1	–	–
	250	50	CH_3OH/O_2	93	40	52	8	–	–
Al_2O_3	250	30	CH_3OH/He	88	100	–	–	–	–
	250	50	CH_3OH/O_2	88	99	–	1	–	–

methoxy species accumulated on the support will dominate the infrared spectra in that range of wavenumber.

During the increase of the temperature, the decrease in intensity of the aforementioned stretching bands is observed, in agreement with the increase of the methanol conversion up to 86% at 250 °C. Raman spectra (Fig. 3) of the catalyst show the progressive development, with the time of stream, of a new line at ca. 840 cm^{-1} in parallel with a decrease of the intensity of the line at 992 cm^{-1}. This Raman line at 840 cm^{-1} has already been reported in similar experimental conditions [17]. The relative intensity of the 840 cm^{-1} line increases with time at low temperature, while at higher temperature, it stabilizes much faster and does not significantly change with time. In parallel, at 200 °C, products from the oxidation reaction of methanol are evidenced (F and MF) but a fast deactivation of the oxidative function is observed with the time of stream, although methanol conversion is continuing yielding only DME. As mentioned earlier, at 250 °C in the absence of oxygen, the intensity of the Raman line at 840 cm^{-1} increase much faster. The deactivation of the oxidative function is so fast that oxidation products cannot be detected and mainly DME is detected even at the beginning of the experiment. The influence of oxygen was then followed by exchanging helium by oxygen in the reaction mixture. As shown by Raman spectroscopy on Fig. 3B, the presence of oxygen in the reactive mixture induces an increase in the relative intensity of the terminal $Mo{=}O_t$ Raman line characteristic of the dehydrated polymolybdate phase. This suggests that the initial phase is partially regenerated. In the mean time, the methanol conversion increases up to 93% as well as the selectivity of the reaction to formaldehyde indicating that the oxidative functions are partly restored by oxygen. In parallel, the band at 1590 and 1381 cm^{-1} in the infrared spectra assigned to ν_{as}(COO) and ν_s(COO) as well as the one at 2897 cm^{-1} assigned to ν(CH) in HCOO indicate the formation of HCOO-species at the surface of the catalyst (Fig. 4B). The second major product, DME, is mainly produced by reaction of methanol on γ-alumina by a dehydration process. Indeed, it has been checked that in the same conditions on a bare γ-alumina (in presence or absence of oxygen) the reaction only yields DME (Table 1).

The concordance of the appearance of the line at 840 cm^{-1} and the deactivation of oxido-reductive function raises questions on the exact nature of the species responsible of this line. For comparison, the evolution upon reduction of a fresh Mo/Al_2O_3 catalyst has been followed by Raman spectroscopy. The Raman spectra are reported on Fig. 5. They show a similar development of a band at ca. 840 cm^{-1} upon reduction during 2 h under H_2 at 250 °C while the relative intensity of the line at 995 cm^{-1} decreases. Furthermore, exchanging the hydrogen by deuterium clearly shows an isotopic shift of the band at 840–770 cm^{-1}. This specific line can therefore be assigned to a reduced Mo–OH group [18].

All these data suggest that methanol reacts with the active phase to give oxidation products until all accessible centres are reduced. The reduced sites can be identified by the broad Raman line at 840 cm^{-1}. When the number of available oxidized sites decreases, the percentage of oxidation product decreases down to zero and the selectivity towards dehydration products (mainly DME) increases.

The question of the oxidation state of the reduced molybdenum centres cannot be addressed by vibrational spectroscopy, so we then turned to EPR measurements. Operando EPR was performed under the same catalytic conditions as those used for Raman and infrared studies in order to precise the

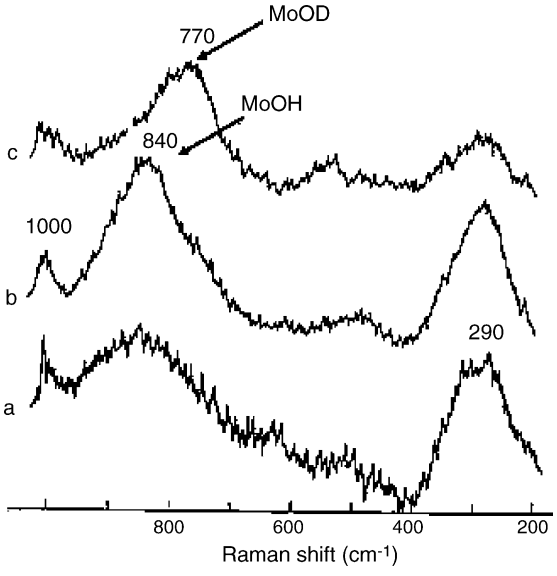

Fig. 5. Raman spectra of Mo/Al_2O_3 after reduction under H_2: (a) at 150 °C, (b) H_2 at 250 °C and (c) D_2 at 250 °C.

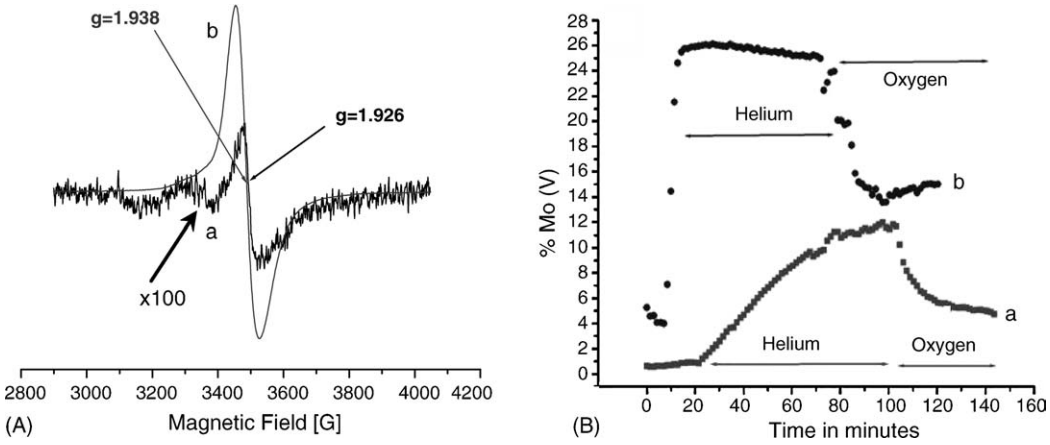

Fig. 6. (A) EPR spectra of the activated catalyst (100×) (a) and of the catalyst during reaction (b). (B) Evolution of the quantity of Mo^V as determined by EPR spectroscopy under He/CH_3OH and O_2/CH_3OH at 200 °C (a) and 300 °C (b).

atomic nature of reduced centre. The results are presented in Fig. 6. After activation under O_2 at 350 °C and prior to reaction, the very low amount of Mo^V detected at $g = 1.926$ suggests that the oxidation state of molybdenum centres is mainly VI. Under the reactive mixture, the presence of Mo^V oxo-molybdenum entities was then identified at $g = 1.938$, the Mo^V signal consisting of a single isotropic line. The spin quantification using EPR spectroscopy with a high accuracy is not straightforward. It has been performed using a pure Mo^V (oxo-molybdenum-*N*,*N*′-bis-(salicylidene)ethylenediamine). However, the signal of the reference compound drops with increasing the temperature following the Curie law and the quantification has to be done at room temperature. When the maximum of Mo^V species is reached during the methanol conversion the sample is cooled down to room temperature and the spectra of sample and reference are measured in a dual mode cavity. This allows to determine the factor between the signal intensity and the amount of Mo^V at a given temperature and to deduce the amount of Mo^V present in the sample at a given temperature whatever the time on stream. As the whole procedure is performed in the catalytic cell without any exposure to air, we can be quite confident that Mo^V is not reoxidized. The deduced amount of Mo^V species and its evolution versus the time on stream under a He/CH_3OH and O_2/CH_3OH gas mixture at 200 and 300 °C is reported in Fig. 6B.

As soon as the gas mixture (He/CH_3OH) was introduced an increase of the Mo^V quantity at different rates depending on the temperature, was observed. The amount of Mo^V reaches a plateau after several minutes. The height of the plateau depends on the temperature: it corresponds to 12% at 200 °C and 26% at 300 °C of the total molybdenum atoms presents in the sample.

The EPR results can be related with the catalytic tests showing that if the plateau of Mo^V is reached the selectivity to formaldehyde drops to zero and methanol conversion produces exclusively DME by reaction on alumina. All the redox functions have been reduced and the sites need to be regenerated. In order to reoxidize the Mo sites, helium has to be replaced by oxygen in the gas mixture. This results in a pronounced decrease of the amount of Mo^V. The amount of Mo^V is divided by two as shown in Fig. 6B. The oxidative sites are partially regenerated as evidenced by the presence of formaldehyde in the effluent gas mixture. These experiments have clearly evidenced the accumulation of a Mo^V species during the course of methanol oxidation. As the oxidation occurs, reduced centres are formed that need to be reoxidized by molecular oxygen present in the gas feed. If there is no oxygen in the gas phase, reoxidation of the active centres cannot take place and the oxidative function of the catalyst becomes inactive.

Methanol oxidation to formaldehyde is, however, a two electrons process and one would expect an evolution of Mo^{VI} to Mo^{IV} during the reaction. The presence of large amount of Mo^V implies that at least two molybdenum atoms are required for the reaction to take place (two Mo^{VI} centres being reduced into two Mo^V). We can then conclude that the redox function of oxo-molybdenum species deposited on alumina is efficient only if a polymolybdate phase is present. According to this interpretation monomeric molybdenum centres on alumina should not be active in selective oxidation. Indeed a simple catalytic test of methanol reaction on a 4 wt.% Mo deposited on alumina with the same method shows that, in the presence of oxygen, no oxidation products are formed. Such a low content of molybdenum leads to monomeric molybdate species as evidenced by the Raman line at 920 cm^{-1} (spectrum not reported here). It is then possible to assume that the oxidation properties of an oxo-molybdate phase are due to the ability of Mo^{VI} to be reduced to Mo^V and that, in the case of methanol oxidation, this implies the cooperation of two molybdenum centres.

4. Conclusion

During the reaction of transformation of methanol on polymolybdate supported on γ-alumina, the active centres induced in redox processes have been identified with operando Raman and EPR spectroscopies. During the same time, the methanol conversion has been followed. The formation and the accumulation of reduced Mo^V centres in parallel with Mo–OH

species in absence of oxygen in the reaction mixture lead to a strong deactivation towards oxidation products (mainly F and MF). In the presence of oxygen, a partial regeneration of the active centres leads mainly to formaldehyde and the conversion of methanol increases up to 93% at 250 °C. The important amount of Mo^{V} appearing during the course of the reaction shows that a polymolybdate phase is at the origin of the redox process.

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