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Quantitative determination of the number of active surface sites and the turnover frequencies for methanol oxidation over metal oxide catalysts

I. Fundamentals of the methanol chemisorption technique and application to monolayer supported molybdenum oxide catalysts

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Abstract

A detailed study of the methanol chemisorption and oxidation processes on oxide surfaces allowed the development of a method to quantify the number of surface active sites (N_s) of metal oxide catalysts. In situ infrared analysis during methanol adsorption showed that molecular methanol and surface methoxy species are co-adsorbed on an oxide surface at room temperature, but only surface methoxy species are formed at 100°C. Thermal stability and products of decomposition of the adsorbed species were determined with temperature programmed reaction spectroscopy (TPRS) experiments. Controlled adsorption with methanol doses resulted in a stable monolayer of surface methoxy species on the oxide surfaces. The stoichiometry of methanol chemisorption resulted in one surface methoxy adsorbed per three Mo atoms for polymerized surface molybdenum oxide structures, regardless of surface molybdenum oxide coordination. The activity of the catalysts per surface active sites (turnover frequencies — TOF) was calculated in order to quantitatively compare the reactivity of a series of monolayer supported molybdenum oxide catalysts. The TOF value trends reflect the influence of the bridging Mo–O–Support bond and the electronegativity of the metal cation of the oxide support. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methanol chemisorption; Molybdenum oxide catalyst; Surface active sites; Turnover frequency; Methanol oxidation; TPRS

1. Introduction

Several approaches have previously been proposed to quantify the number of surface active sites on metal oxide catalysts. Oxygen chemisorption at high temperature (250–350°C) is the earliest method proposed to determine vanadium (V^{3+}, V^{4+}) sites on bulk V_2O_5 and supported vanadium oxide catalysts [1,2]. Later studies suggested that low temperature oxygen chemisorption (LTOC) was a more suitable method to determine the active surface area of molybdenum and vanadium oxide containing catalysts. The LTOC

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method is performed at −78°C on a surface that was reduced at 500°C in a flow of hydrogen [3–6]. A method based on a reaction occurring on the oxide surface was developed by Murakami and coworkers [7,8] to quantify the surface V=O species on bulk V_2O_5 and supported vanadium oxide catalysts. The technique involves a reaction of known stoichiometry, between NO and NH_3 on a V=O site to produce N_2. However, recent studies demonstrated that the reaction of NO and NH_3 on vanadia/titania catalysts is an acid–base and redox process, and both Brønsted acid sites V–OH and V=O groups are involved in adsorption and activation of ammonia [9,10].

Despite the efforts to develop a method to quantify the number of active surface sites on metal oxides, all these studies possessed a certain degree of inaccuracy due to: (1) the number of active sites is determined with a different probe molecule than the actual reactant, (2) the oxide catalysts are treated with H_2 and the reduction stoichiometry of the catalyst is usually not known, (3) the chemisorption and reduction temperatures are far removed from the actual reaction conditions, and (4) both surface and bulk sites are involved in the measurements.

The present study reports on a novel chemisorption method that employs the dissociative adsorption of methanol to surface methoxy intermediates in order to quantitatively determine the number of surface active sites on metal oxide catalysts. This study was inspired by the pioneering work of methanol adsorption and selective oxidation on MoO_3 and $Fe_2(MoO_4)_3$ catalysts published by Sleight and coworkers [11–13]. The group performed adsorption and temperature programmed reaction/adsorption studies in order to elucidate the methanol oxidation mechanism and the nature of surface intermediates. The major contribution of their work was the determination of the number of surface active sites through the quantification of methanol molecules adsorbed at room temperature. The aim of the present work is to improve the methanol chemisorption approach to quantify the number of surface active sites and apply the technique to model supported molybdenum oxide catalysts. Knowledge of the number of surface active sites will enable the calculation of the activity per site (turnover frequency — TOF) during oxidation reactions. Therefore, the catalytic behavior of the different metal oxides will, for the first time, be compared on the same basis. In addition, the methanol oxidation product distribution at low conversions reflects the nature of the surface active sites since redox sites yields H_2CO, acid sites yield CH_3OCH_3 and basic sites yield CO_2 [14]. Thus, methanol is a “smart” chemical probe molecule that can provide fundamental information about the number of surface active sites, the TOF values and the distribution of different types of surface sites of metal oxide catalysts.

2. Experimental

2.1. Catalyst synthesis

Methanol adsorption and temperature programmed reaction spectroscopy (TPRS) studies were performed on monolayer supported molybdenum oxide on TiO_2, Al_2O_3, ZrO_2, SiO_2, MnO, NiO, Nb_2O_5 and Cr_2O_3. These materials were prepared by the incipient-wetness impregnation method of the oxide supports with an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). A detailed description of the synthesis was published before [15].

2.2. Catalyst characterization

The catalysts were characterized by BET surface area, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and X-ray absorption near edge spectroscopy (XANES). Experimental details about the various characterization instruments can be found in prior publications [15,16]. The combination of characterization techniques provided detailed information about the surface structure/composition of the monolayer supported molybdenum oxide catalysts.

2.3. Infrared spectroscopy

The nature of the surface species generated during methanol adsorption on the monolayer supported molybdenum oxide catalysts was studied by in situ infrared spectroscopy. The experiments were performed with a BioRad FTS-40A FTIR Spectrometer. The equipment and analysis procedure has been described in detail in Ref. [17].

2.4. Adsorption and temperature programmed reaction spectroscopy

Adsorption–desorption studies were performed using a high vacuum microbalance/temperature-programmed reaction apparatus coupled with a mass spectrometer. This instrumentation has been previously described [13]. The experiments were carried out with the following procedure: the catalyst (∼10 mg in powder form) was placed in the sample pan of a microbalance (Cahn R.G. — UHV), where it was pretreated by heating to 400°C at 1×10^{-8} Torr followed by oxidation at the same temperature in 10 Torr of oxygen. Chemisorption was performed by exposing the pretreated sample to 10, 10^2, 10^3 and 10^4 mTorr of methanol vapor for ∼16 min. The amount of adsorbed methanol was measured gravimetrically as the stable weight after pumping out at room temperature up to 10^{-8} Torr. Adsorption experiments were performed at 23 and 100°C. After saturation of the surface was reached, the sample was heated up to 400°C and the effluent gases were continuously monitored with a quadrupole mass spectrometer (UTI 100).

2.5. Methanol chemisorption and oxidation

The experimental conditions required to quantify the number of surface active sites via methanol chemisorption were determined over a wide range of temperature and methanol partial pressure in a Cahn TGA microbalance (Model TG-131) coupled with a PC for temperature and weight monitoring. The system allowed a controlled flow of high purity gases: air for pretreatment, helium and a mixture of methanol in helium for adsorption experiments. A detailed flow diagram of the system is presented in Fig. 1. Adsorption experiments were carried out with a mixture of 2000 ppm of methanol in He.

The methanol oxidation steady state kinetics were obtained in a fix-bed catalytic reactor under differential conditions and product formation was determined with an on-line gas chromatograph (HP 5840) equipped with TCD and FID detectors and two columns: capillary column (CP-sil 5CB) for methylal, dimethyl ether, methyl formate and methanol analysis and a packed column (Carboxene-1000) for CO, CO_2, O_2, formaldehyde and methanol analysis [16].

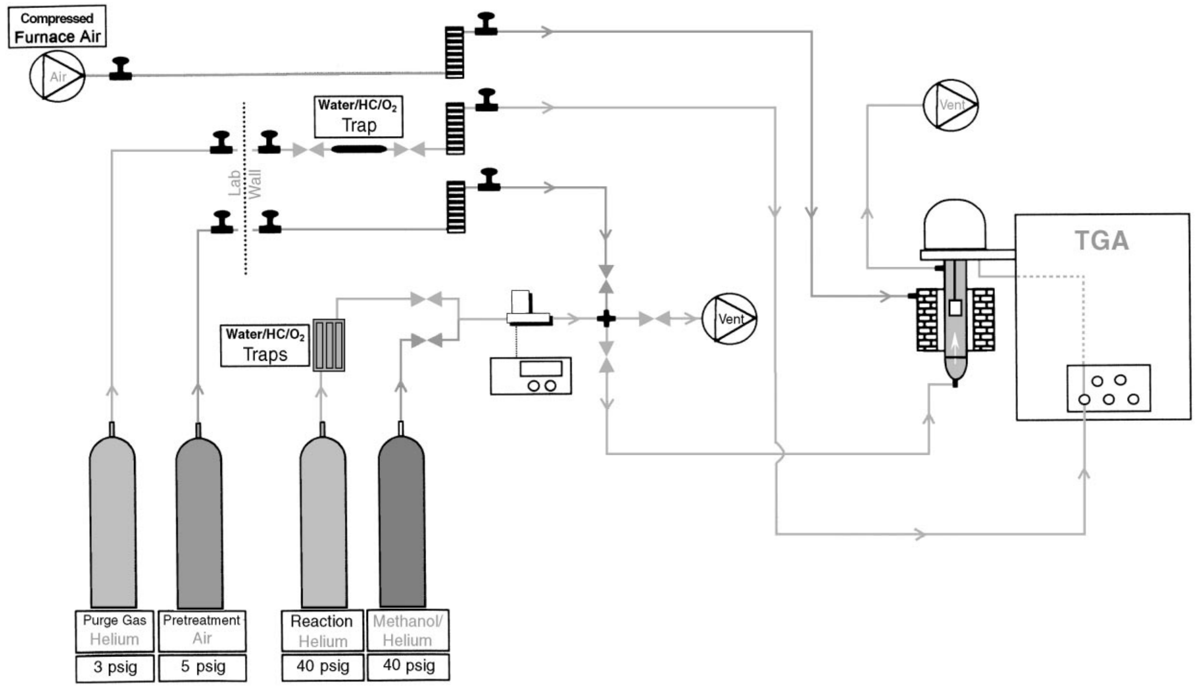

Fig. 1. Microbalance and gas flow system for methanol chemisorption experiments.

The following operating parameters were used in order to maintain methanol conversion below 10%: sample weight, ~20 mg, reaction temperature, 250°C; flow rate, 100 cm^3 (NTP) min^{-1} and feed gas composition methanol/oxygen/helium, 6/13/81 mol%.

3. Results and discussion

3.1. The methanol adsorption process: effect of temperature and partial pressure

Previous studies demonstrated that methanol chemisorption on MoO_3 at room temperature results in a combination of molecular and dissociative adsorption mechanisms [18]. The first mechanism can be considered as a physical adsorption since the methanol molecules adsorb intact on the surface. Dissociative adsorption is a chemisorption process that involves the formation of metal–methoxy (M–OCH_3) groups. Further infrared studies carried out by Groff indicated that at 100°C, undissociated methanol species are volatile while the surface methoxy groups remain intact on the MoO_3 surface [18]. More recently, similar conclusions were obtained by infrared analysis of monolayer supported vanadium oxide catalysts [19]. The infrared spectra of methanol adsorbed on monolayer supported molybdenum oxide on Al_2O_3 (18% MoO_3/Al_2O_3) at 30 and 100°C, are presented in Fig. 2. Methanol adsorbed on an oxide surface at low temperature generates two bands in the C–H stretching region (2700–3000 cm^{-1}). The bands at 2845 and 2955 cm^{-1} are assigned to the symmetric bend ($2\delta_s$) of the CH_3 unit in adsorbed surface methoxy species and the symmetric stretch (ν_s) of the CH_3 unit in the intact methanol molecule, respectively [18]. Upon heating the sample to 100°C, the band at 2845 cm^{-1} does not change, however, the signal at 2955 cm^{-1} decreases in intensity and splits into two new bands at 2949 and 2965 cm^{-1} (assigned to the symmetric (ν_s) and asymmetric stretch (ν_{as}) of the CH_3 unit in adsorbed methoxy species) [19].

More information about the nature and stability of the species formed during methanol adsorption is obtained from TPRS experiments. Controlled methanol adsorption on 18% MoO_3/Al_2O_3 catalyst was performed upon exposure to different methanol partial pressures until saturation of the surface was reached. Fig. 3 shows methanol adsorption at 23 and 100°C, as a function of the exposure in Langmuir units (1L = 10^{-6} Torr s). The chemisorption isotherms fit the Langmuir adsorption model, as already reported for bulk MoO_3 [20]. Regardless of the temperature, the surface of the catalyst is saturated when it is exposed to methanol partial pressures above 1000 mTorr. The difference in methanol uptake with the temperature of

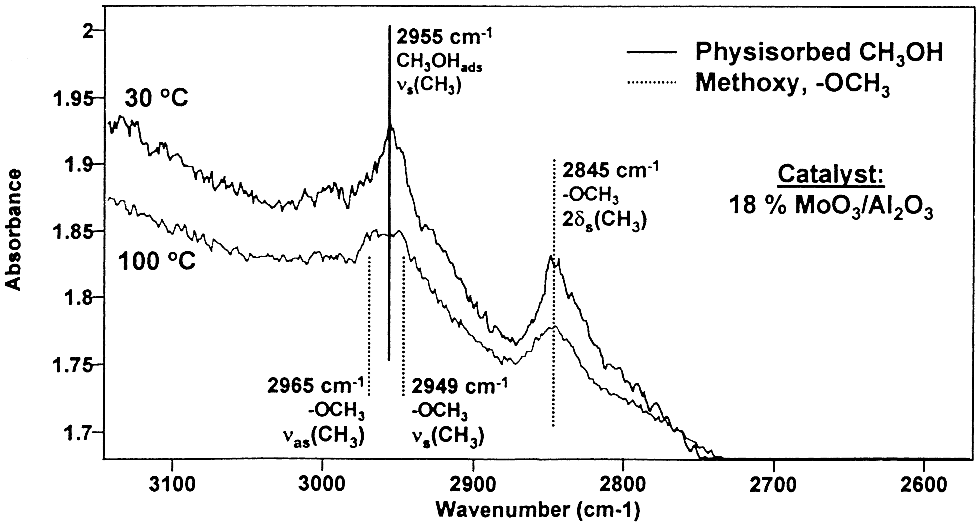

Fig. 2. In situ IR spectra of methanol adsorbed on 18% MoO_3/Al_2O_3 catalysts at 23 and 100°C.

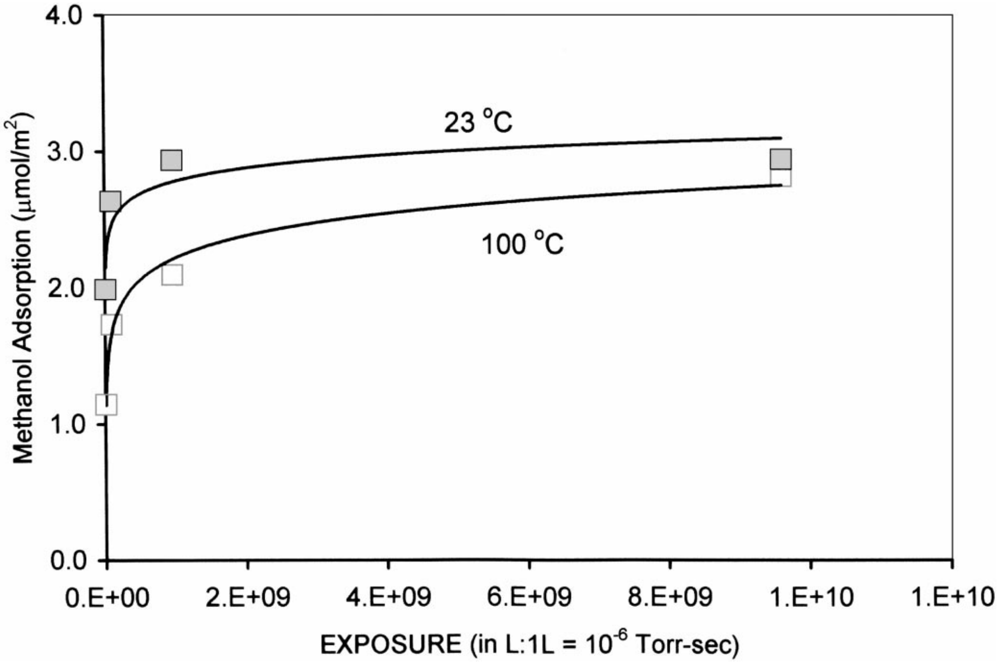

Fig. 3. Weight gains of 18% MoO_3/Al_2O_3 catalyst exposed to increasing partial pressures of methanol at 23 and 100°C.

the adsorption is related to the nature of the species involved in the process. The values of micromols of methanol adsorbed at different partial pressures assumes molecular methanol regardless of the temperature of adsorption. However, according to the IR analysis, methanol adsorbs as surface methoxy species at 100°C. Moreover, previous studies by Farneth et al. [12] demonstrated that water is also desorbed from the surface during the adsorption process. At low temperature, methanol is mainly molecularly physisorbed, therefore, methanol molecular weight should be considered, in order to calculate molar adsorption from the weight gain value. At high temperature, 78% of the weight increment corresponds to surface methoxy species and 22% to water molecules (considering 2 CH_3O/H_2O molar ratio). Thus, the true molar adsorption is somewhat higher than the values shown in Fig. 3. The difference in the nature of the adsorbed species is also concluded from the desorption profiles from the 18% MoO_3/Al_2O_3 catalyst shown in Figs. 4 and 5. The products and desorption temperatures (T_{max}) after saturation of the surface with methanol at 23°C are similar to the results previously reported in the literature for bulk MoO_3(Fig. 4) [12]. The first desorption peak starting at 50°C ($T_{max} \sim 100°C$) is due to pure methanol ($m/e = 32$). The shape and broadness of the signal can be ascribed to the presence of physisorbed (molecular methanol) and chemisorbed (methoxy –CH_3O) species on the catalyst surface that resulted in CH_3OH formation. Formaldehyde ($m/e = 30$) desorbs as a broad signal with $T_{max} \sim 250°C$. The signal with $m/e = 28$ corresponds to a cracking product of methanol and formaldehyde in the mass spectrometer. Both surface methoxy formation and decomposition generate water that is desorbed all along the spectra. Free acid sites of the alumina supports (not covered with surface molybdenum oxide species) lead to methanol dehydration–condensation and formation of a small amount of dimethyl ether.

The TPRS product spectra of methanol adsorbed at 100 and 23°C are similar, however, some important differences in the T_{max} and shape of methanol signal, as well as the area of the CH_2O peak, can be observed (Fig. 5). Methanol begins to desorb at 100°C and the peak maximum is shifted to 150°C, which is associated with a higher stability of the species formed from methanol adsorbed at 100°C. According to the literature, surface methoxy species are able to

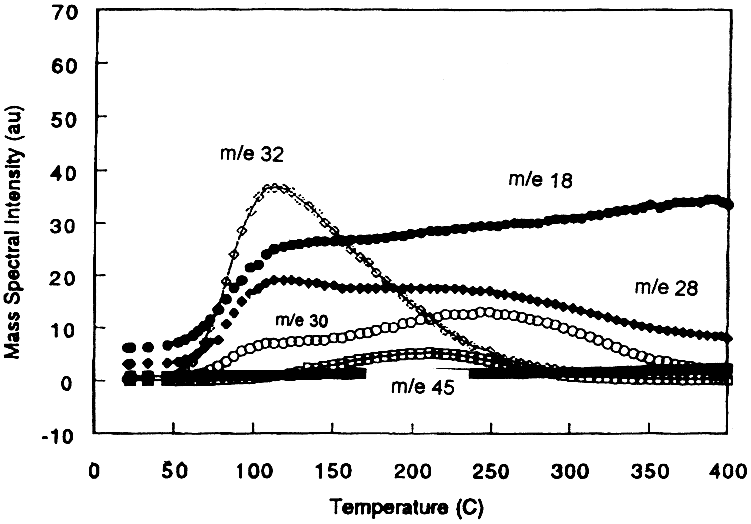

Fig. 4. Temperature-programmed desorption spectra of methanol adsorbed on 18% MoO_3/Al_2O_3 catalyst at 23°C: methanol ($m/e = 32$), formaldehyde ($m/e = 30$), water ($m/e = 18$), dimethyl ether ($m/e = 45$) and product of methanol and formaldehyde cracking in the mass spectrometer ($m/e = 28$).

recombine with adsorbed hydrogen atoms ($OCH_{3ads} + H_{ads} \rightarrow CH_3OH$) and desorb as molecular methanol at the temperature of the experiment [12]. The T_{max} of formaldehyde is not modified compared with methanol chemisorbed at low temperature, however, the integral of the signal is considerably greater in the TPRS of methanol chemisorbed at 100°C. Formaldehyde is produced only through the reaction of surface methoxy species, therefore, the result indicates that the formation of alkoxy species is favored when methanol is adsorbed at high temperature, in agreement with the infrared studies.

Infrared and TPRS experiments clearly show that the formation of surface methoxy species is greatly

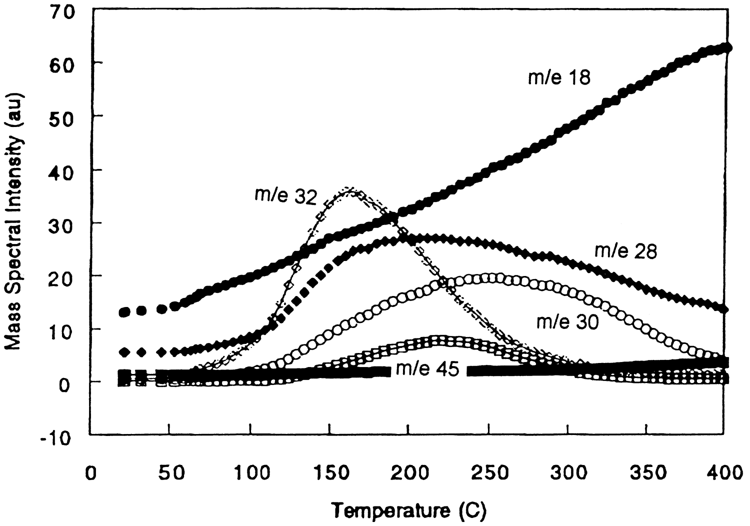

Fig. 5. Temperature-programmed desorption spectra for methanol adsorbed on 18% MoO_3/Al_2O_3 catalyst at 100°C. Products as in Fig. 4.

influenced by the temperature of methanol adsorption. Adsorption at low temperature involves physisorption of non-reacting molecular methanol in a larger amount relative to the surface methoxy species. However, methanol adsorption at 100°C generates only surface M–OCH_3 intermediates, avoiding further reaction to selective oxidation products. In addition, the partial pressure of methanol in contact with the oxide surface also needs to be adjusted in order to saturate the surface of the catalyst with surface methoxy species.

3.2. Quantification of active sites on monolayer supported molybdenum oxide catalysts

Surface methoxy groups are the intermediate species in the production of partially oxygenated reaction products (formaldehyde, methyl formate, methylal, etc.) during methanol selective oxidation on catalysts containing transition metal oxides (vanadium, molybdenum, etc.). Therefore, knowledge of the amount of surface methoxy species formed during methanol chemisorption is the key for the determination of the number of surface active sites available for methanol selective oxidation. The results described in the previous section demonstrated that an oxide surface in contact with 1000 mTorr of methanol vapor at 100°C is suitable to be covered with a stable monolayer of surface methoxy groups. The technique was applied to a series of monolayer supported molybdenum oxide catalyst in order to establish the number of surface active sites per surface area unit (N_s). The number of surface methoxy species was calculated from the weight gain of the catalysts under the required conditions for maximum surface methoxy production, subtracting the contribution of the water molecules that are formed and desorbed during methanol chemisorption process. In the particular case of 5% MoO_3/SiO_2 catalyst, molybdenum does not form a complete monolayer on the silica support therefore the weight gain of the catalyst after exposure to methanol vapor is due to methoxy species adsorbed on surface molybdenum species and the bare silica support. Kinetic experiments and in situ Raman studies during methanol reaction over a series of transition metal oxides supported on silica demonstrated that Si–OCH_3 species are very stable and remain on the surface up to 300°C [21]. In contrast, TPRS experiments show that Mo–OCH_3 species readily react and desorb at that temperature. These evidences indicate that the amount of methoxy species adsorbed only on the support can be quantified after heating the catalyst at 300°C to remove Mo–OCH_3 species. The amount of surface methoxy species of 5% MoO_3/SiO_2 catalyst was determined subtracting the weight of the catalyst after heating to the total weight gain of the sample after methanol chemisorption.

Table 1 shows the surface molybdenum oxide molecular structures (surface structure of molybdenum oxide on MnO, NiO and Cr_2O_3 have not been determined yet); surface concentration of Mo atoms; surface methoxy concentration expressed as the number of accessible surface active sites per surface area unit (N_s), and the concentration of surface methoxy species adsorbed per surface molybdenum atom.

The surface Mo coverages employed in the present investigation correspond to about a monolayer of surface Mo oxide species ($\sim$7 μmol of Mo per m^2). At monolayer surface coverage, the active phase is 100% dispersed on the oxide supports, avoiding bulk MoO_3 formation and minimizing the adsorption of methanol on exposed oxide support sites. Previous studies, by in situ XANES and Raman spectroscopy, determined that the surface structure of the supported molybdenum oxide depends on the oxide support [15]. At monolayer surface coverage and dehydrated conditions, the surface molybdenum oxide species are polymerized, octahedrally coordinated on Nb_2O_5 and TiO_2 and possess a mixture of octahedral and tetrahedral coordinations on ZrO_2 and Al_2O_3. Silica is not completely covered with molybdenum due to the low density and reactivity of the silica surface hydroxyls, which accounts for the low Mo surface density and the isolation of the surface molybdenum species on the silica support. The amount of surface active sites, N_s, does not depend on the surface molybdenum oxide coordination and is lower than the surface Mo density. Furthermore, surface methoxy chemisorption stoichiometry is $\sim 1\,CH_3O_{ads}$ per 3–4 Mo_s for a polymerized molybdenum oxide structure and $\sim 1\,CH_3O_{ads}$ per Mo_s for isolated molybdenum oxide species. These results reflects the presence of lateral interactions in the surface methoxy overlayer and demonstrate that, even when every exposed Mo atom could be an active redox site, not all of them are simultaneously available under reaction conditions.

Methanol oxidation over these supported molybdenum oxide catalysts primarily yielded redox products.

Table 1
Surface molybdenum oxide structures and methanol chemisorption data (O_h: octahedral coordination; T_d: tetrahedral coordination; polym.: polymerized)

Catalyst	Mo molecular structure [22]	Mo surface density [22] (μmol/m^2)	N_s (μmol methoxy/m^2)	Methoxy adsorbed per Mo atom
3% MoO_3/ZrO_2	$O_h + T_d$ (polym.)	5.31	1.25	0.24
6% MoO_3/Nb_2O_5	O_h (polym.)	7.64	2.10	0.28
6% MoO_3/TiO_2	O_h (polym.)	7.64	3.07	0.40
2% MoO_3/MnO	Not determined	7.50	1.14	0.15
3% MoO_3/Cr_2O_3	Not determined	7.42	2.87	0.39
18% MoO_3/Al_2O_3	$O_h + T_d$ (polym.)	6.97	2.78	0.40
4% MoO_3/NiO	Not determined	7.32	1.47	0.20
5% MoO_3/SiO_2	T_d (isolated)	0.70	0.95	1.35

The surface molybdenum oxide species catalyze the selective oxidation of methanol to formaldehyde as the primary product; and methyl formate, dimethyl ether and dimethoxy methane in smaller amounts (see Table 2). The presence of exposed alumina Lewis acid sites for the 18% MoO_3/Al_2O_3sample lead to a high production of dimethyl ether as was observed before in the TPRS experiments. The methanol oxidation TOF were calculated by determining the production rate of redox products at 250°C and normalizing the rate to the number of surface sites available for adsorption of CH_3O_{ads}, and the resulting TOF values are presented in Table 2. The specific activities of the catalysts do not correlate with either the concentration of available surface active sites N_s or with surface molybdenum oxide structure. However, there is a definite dependence of the TOF values with the specific oxide support.

3.3. *Methanol selective oxidation over monolayer supported molybdenum oxide catalysts: structure–reactivity relationship*

The variation of catalytic activity of supported molybdenum oxide catalysts does not correlate with either the number of surface active sites N_s or with surface Mo oxide molecular structure at monolayer coverage (see Fig. 6a and Tables 1 and 2). In fact, methanol adsorption is insensitive to the surface oxide Mo coordination since there is no preferential adsorption on tetrahedral or octahedrally coordinated surface molybdenum oxide sites. Nevertheless, the chemisorption stoichiometry is greatly modified by polymerized or isolated surface molybdenum oxide species. Previous studies reported a slight increase of catalytic activity with increasing surface Mo density, suggesting that polymerized surface molybdenum

Table 2
Reactivity of monolayer molybdenum oxide supported catalysts

Catalyst	Activity[a] (μmol/m^2 s)	TOF[b] (s^{-1})	Selectivity (%)[c]				
			FA	MF	DMM	DME	CO_x
3% MoO_3/ZrO_2	0.58	0.47	82	8	10	–	–
6% MoO_3/Nb_2O_5	0.39	0.14	60	–	16	24	–
6% MoO_3/TiO_2	0.68	0.18	73	7	6	14	–
2% MoO_3/MnO	0.50	0.44	85	15	–	–	–
3% MoO_3/Cr_2O_3	0.25	0.08	83	8	9	–	–
18% MoO_3/Al_2O_3	0.23	0.04	42	3	4	51	–
4% MoO_3/NiO	0.07	0.04	76	–	6	18	–
5% MoO_3/SiO_2	0.006	0.003	–	–	49	51	–

[a] Activity based on overall methanol conversion.

[b] TOF based on methanol partial oxidation products (FA, MF and DMM). Reaction temperature: 250°C.

[c] FA: formaldehyde; MF: methyl formate; DMM: dimethoxy methane; DME: dimethyl ether and CO_x: $CO + CO_2$.

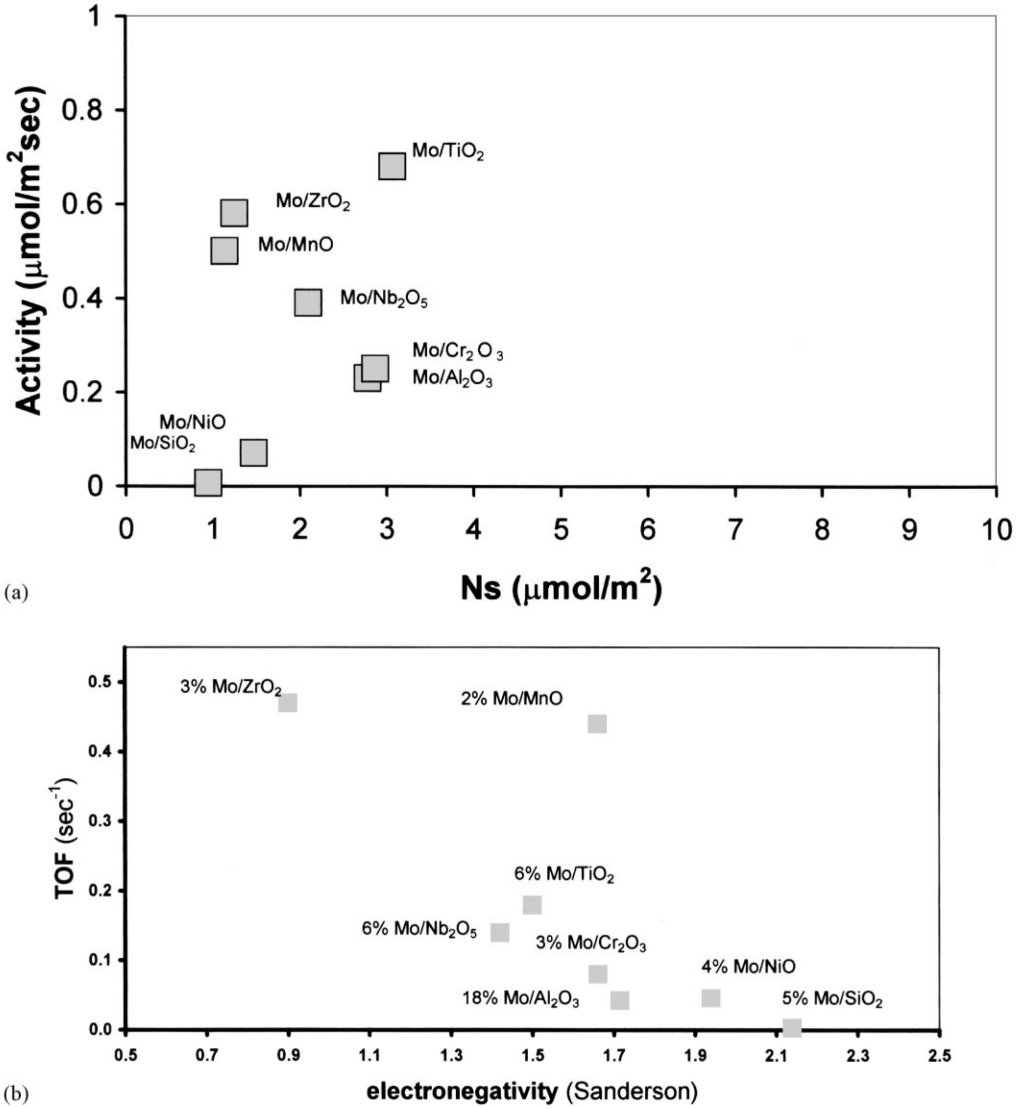

Fig. 6. (a) Activity towards methanol reaction at 250°C versus number of surface active sites (N_s) of monolayer supported molybdenum oxide catalysts. (b) Specific activity (TOF) towards methanol selective oxidation at 250°C versus electronegativity of the oxide support of monolayer supported molybdenum oxide catalysts.

oxide species are slightly more active than the isolated, MoO_4 species that preferentially exist at low coverage [22]. In the case of surface molybdenum oxide supported on SiO_2, that contains only isolated Mo species, one surface methoxy is adsorbed per Mo atom, therefore, all the available surface active sites are covered, but polymerized structures are able to only adsorb one CH_3O over three sites. This ensemble of sites may be more suitable to rapidly adsorb the H-atom from the surface methoxy decomposition to produce the formaldehyde product.

The selective oxidation of methanol over transition metal oxides catalysts involves the formation of surface methoxy species, cleavage of the C–H bond of the surface CH_3O species to produce formaldehyde and the desorption of products. These steps (adsorption–reaction–desorption) are reflected in the specific activity parameter (TOF). The quantification of the true concentration of the surface active sites on monolayer supported molybdenum oxide catalysts, through controlled chemisorption of methanol on the oxide surface, allowed the normalization of the reaction rate per surface active site. The specific activity is independent of Mo structure, but again molybdenum oxide supported on SiO_2 possesses the lowest TOF value. The strongest correlation of the TOF appears with the nature of the oxide support. The specific activity of the catalysts increases according to the following trend: $ZrO_2 > MnO > TiO_2 > Nb_2O_5 > Cr_2O_3 > Al_2O_3 \sim NiO > SiO_2$, which also coincides with increasing electronegativity values of the metal cations of the oxide supports (see Fig. 6b). These observations are in agreement with previously published investigations that suggest that Mo(V)–O–Support bond controls the activity of monolayer molybdenum and vanadium supported catalysts [17,22]. The electronegativity of the metal cation of the oxide support controls the electron density of the active site and, consequently, would modify the adsorption, reaction and desorption rates. The origin of the support effect on the methanol selective oxidation has been extensively studied on supported vanadium catalysts [17]. The investigations demonstrated that both the adsorption equilibrium and the rate of surface methoxy decomposition are sensitive to the specific metal oxide support. Calculations of the adsorption equilibrium constant, K_{ads}, showed a $\sim$ 6 times increase for vanadia on oxide supports of $Al < Ti < Zr < Ce$, whereas the methoxy surface decomposition rate constant, k_{rds} (rds = rate-determining step) showed a $\sim$ 22 times increase in value over the same catalysts.

Methanol interaction with the monolayer surface molybdenum oxide supported catalysts and bulk MoO_3 are surprisingly alike. The following similarities can be concluded between this work and published investigations on methanol adsorption on bulk MoO_3: (1) M–OCH_3 species are produced during methanol adsorption at 100°C; (2) only these species are intermediates in methanol selective oxidation; (3) methanol, formaldehyde and water desorb during TPRS experiments; (4) formaldehyde desorbs at $\sim$ 200°C, and (5) the amount of surface methoxy species, determined with the integrated intensity of the CH_2O TPD peak, that saturates the bulk MoO_3 surface is 1.16 μmol/m^2, which is of the same order for N_s of supported molybdenum oxide catalysts [11–13]. These observations indicate that methanol chemisorption is also a suitable method to quantify surface active sites on bulk molybdenum oxide based catalysts. Moreover, the comparison of methanol interactions between “model” monolayer supported molybdenum oxide catalysts and bulk metal oxide catalysts is of interest in the study of the surface structure of bulk metal oxide catalysts since no spectroscopic method is available to directly describe the outer surface layer of bulk metal oxide catalytic systems.

4. Conclusions

This study demonstrates that is possible to cover a metal oxide surface with a stable monolayer of surface methoxy species when a supported molybdenum oxide catalyst at 100°C is in contact with 1000 mTorr of methanol. Surface methoxy species are the intermediates species during methanol selective oxidation to formaldehyde and, hence, the number of surface active sites (N_s) can be directly determined if the amount of CH_3O_s is measured. The knowledge of N_s is the key factor in determining the catalytic activity per surface active site (TOF), which enables comparison of the reactivity of different catalytic systems under the same basis.

Methanol chemisorption on a series of monolayer supported molybdenum oxide catalysts is independent of the Mo oxide surface coordination. However, methanol adsorption shows a strong steric effect: methanol forms one surface methoxy per 3 Mo atoms on polymerized surface molybdenum oxide species and one surface methoxy per Mo atom on isolated surface molybdenum oxide species. This effect can be attributed to repulsive interactions between surface alkoxy groups bound to adjacent surface molybdenum oxide sites.

Monolayer molybdenum oxide catalysts show a great variation of reactivity depending upon the nature of the specific oxide support. TOF values diminish with increasing electronegativity of the metal cation of the oxide support, indicating that the molybdenum–oxygen–support (Mo–O–S) bond is controlling the methanol selective oxidation process.

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