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Quantitative Determination of the Number of Surface Active Sites and the Turnover Frequencies for Methanol Oxidation over Metal Oxide Catalysts: Application to Bulk Metal Molybdates and Pure Metal Oxide Catalysts

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The present work investigates the number and nature of the surface active sites and the catalytic activity of bulk metal molybdates and bulk metal oxides on methanol selective oxidation. Bulk metal molybdates were synthesized by coprecipitation and characterized by laser Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and specific surface area analysis. The number of surface active sites (*N*s) was determined by measuring the amount of methoxy species produced by methanol chemisorption on the catalysts at 100°C. The specific activity values (TOFs) were calculated by normalizing the reaction rate by the number of surface active sites. The significant differences in catalytic behavior of bulk metal molybdates and bulk metal oxides, and the surface molybdenum enrichment observed on metal molybdates, gave evidences that the surface of bulk metal molybdates may be composed only by molybdenum oxide species in a two-dimensional overlayer. It was not possible to establish the structure of surface molybdenum oxide species; however, it can be concluded that the structure of surface active sites species of bulk metal molybdates and monolayer supported oxide catalysts are different according to the dispersion of the Ns values of these systems. This work shows, for the first time in the literature, that bulk metal molybdates and monolayer supported molybdenum oxide catalysts possess similar activity and TOF in methanol selective oxidation. The number of active surface sites and the specific activity toward selective oxidation products (TOF redox), CO_2 (TOF basic), and dimethyl ether (TOF acid) of bulk metal oxides were also determined. In contrast to bulk metal molybdates, most bulk metal oxides catalyze the total combustion of methanol even at low methanol conversion. © 2001 Academic Press

Key Words: **methanol chemisorption; metal molybdates; surface active sites; turnover frequency; methanol oxidation; selective oxidation; bulk catalysts; supported catalysts; metal oxides.**

1. INTRODUCTION

The present investigation focuses on the quantification of the number of surface active sites and methanol selective oxidation over metal molybdate and bulk metal oxide catalysts. Previous studies established the fundamentals of the methanol chemisorption technique to determine the number of surface active sites for methanol selective oxidation on monolayer supported molybdenum and vanadium oxide catalysts (1–3). Spectroscopic analysis (infrared and temperature programmed reaction spectroscopy) of methanol adsorbed on monolayer supported molybdenum and vanadium catalysts under several temperatures and alcohol partial pressures showed that methanol is molecularly physisorbed at room temperature and dissociatively chemisorbed as methoxy -OCH_3 species at higher temperatures. At 100°C and 2000 ppm of methanol vapor in the gas phase it is possible to cover the surface of an oxide with a stable monolayer of surface methoxy species. Surface methoxy is the intermediate species in the formation of methanol selective oxidation products (formaldehyde, methyl formate and dimethoxymethane) and, therefore, the amount of these species can be taken as the number of surface active sites. The calculation of the catalytic activity per active site (per methoxy) that is, the turnover frequency TOF of monolayer molybdenum oxide supported on Al_2O_3, TiO_2, ZrO_2, SiO_2, MnO, NiO, Nb_2O_5, and Cr_2O_3 allowed the comparison of the reactivity of this series of catalytic systems (1–3). The present work extends the use of the methanol chemisorption technique to bulk metal molybdate and bulk metal oxides catalysts. The interest in metal molybdates and MoO_3–metal molybdate mixtures began in 1926 when the high efficiency of the $MoO_3/Fe_2(MoO_4)_3$ system to produce formaldehyde from methanol in excess of oxygen was discovered (4). During the following years, much research was devoted to understanding the catalytic behavior and the nature of the active sites of molybdenum-based catalytic systems.

Sleight *et al.* performed spectroscopic studies on methanol adsorbed on pure MoO_3 and $MoO_3/Fe_2(MoO_4)_3$ that combined with the reaction mechanism gave more insights on the number of active sites and the nature of

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surface intermediates (5–7). The authors demonstrated that methanol is adsorbed as undissociated molecules and methoxy species only on a fully oxidized surface. Surface methoxy species are the intermediate species for formaldehyde production and the breaking of the carbon–hydrogen bond is the rate-limiting step in the reaction of surface methoxy groups over molybdates. This group observed that MoO_3 was 2–4 times less active toward methanol oxidation than $Fe_2(MoO_4)_3$ when normalized by the number of methanol adsorbed at room temperature. The observation that methanol does not dissociatively chemisorb on coordinatively saturated Mo ions (coordination number of 6), which are the predominant sites on orthorhombic MoO_3, suggested that the activity of iron molybdate was related to the fact that all surface molybdenum atoms in the pseudocubic $Fe_2(MoO_4)_3$ have a coordination number less than 6. Further kinetic studies of methanol selective oxidation to formaldehyde over ferric and ferrous molybdate, bismuth, chromium, aluminum, and heteropoly molybdates, demonstrated that a wide range of metal molybdates are active and selective on the process and that the same mechanism of methanol adsorption and reaction is accomplished (8).

An interesting, if not the only *in situ* electron microscopy study during methanol reaction over $Fe_2(MoO_4)_3$, MoO_3, and $MoO_3/Fe_2(MoO_4)_3$ was performed by Gai *et al.* (9). The experiments on ferric molybdate showed that under *in situ* reaction conditions using CH_3OH, $CH_3OH–O_2$, and H_2 environments, the catalyst is reduced to ferrous molybdate ($FeMoO_4$), α-Fe_2O_3, and metallic Fe. The extent of the reduction is limited and the activity and selectivity of the catalyst are prolonged in the presence of gaseous oxygen. Experiments on MoO_3 using $CH_3OH–O_2$ showed the presence of suboxides and regions of ordered oxygen vacancies. *In situ* experiments carried out on iron molybdate–MoO_3 physical mixtures showed that the same changes described for the individual components are produced in the mixture under reaction conditions.

Kinetics studies performed by Mann *et al.* and more recently by Ivanov *et al.* indicated that a mixture of MoO_3 and $MnMoO_4$ possess activity and selectivity similar to $MoO_3/Fe_2(MoO_4)_3$ in methanol selective oxidation to formaldehyde (10a, 10b, 11). $Fe_2(MoO_4)_3/Cr_2(MoO_4)_3/MoO_3$ mixture has also been proposed as suitable catalytic system to oxidize methanol to formaldehyde (12). The spectroscopic analysis of the catalyst before and after reaction showed the modification of the composition due to the interaction with methanol.

Wachs *et al.* physically and chemically characterized a series of bismuth molybdates (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, γ-Bi_2MoO_6, γ'-Bi_2MoO_6, $Bi_{38}Mo_7O_{78}$, etc.) by means of methanol reaction and spectroscopic analysis (13). Bismuth molybdates are selective to formaldehyde (58–98% at low methanol conversions) regardless of Mo coordination or surface Bi/Mo concentration. The authors demonstrated that only well crystallized bismuth–molybdenum phases are selective catalysts toward methanol reaction. The analysis of the near surface region by means of XPS spectroscopy showed a comparable surface and bulk molybdenum concentration before reaction with methanol.

The system $SnO_2–MoO_3$ was found to be active in methanol selective oxidation to formaldehyde and methyl formate (14). Weng *et al.* suggested the formation of $SnMoO_2/MoO_3$ when the mixture is calcined at 873 K. More recently, Rivarola *et al.* suggested a synergetic effect between the oxides that enhance the catalytic activity of the mixture based on the observation of the lower activity of the individual oxides (15). This effect would be the origin of Mo^{5+} sites that would improve the redox capacity of the mixture. According to spectroscopic analysis, no new compounds or modification of the surface composition are produced when the mixture is calcined at 353 K or under reaction conditions. Pure bulk metal oxides and mixtures of oxides have also received attention in methanol oxidation literature. Spectroscopic studies of adsorbed methanol and temperature programmed desorption analysis demonstrated that surface methoxy and formate species are generated upon exposure of metal oxides (Al_2O_3, ZrO_2, TiO_2, NiO, Fe_2O_3, ZnO, CuO, Cu_2O, Cr_2O_3, CeO_2, Bi_2O_3, Co_3O_4, Mn_2O_3) to methanol vapor. The product distribution of methanol reaction depends on the redox and/or acid–base nature of the surface active sites; however, most pure metal oxides produce CO_x above 200°C due to the decomposition of surface formate species.

Wachs *et al.* performed *in situ* Raman spectroscopy and steady state kinetic measurements of methanol selective oxidation over Al_2O_3, TiO_2, ZrO_2, Nb_2O_5, and supported molybdenum oxide catalysts (16). The bare oxide supports possess low activity toward methanol selective oxidation at 230°C. Dehydration of methanol to dimethyl ether and CO/CO_2 generation were the major products of reaction. Similarly, methanol dehydrogenates to CO, CO_2, and H_2 over Cr_2O_3 at 300°C (17). In addition, dimethyl ether and water are produced on acid sites of chromium oxide.

In contrast, Fe_2O_3 and copper-based oxides possess selective oxidation activity. Murakami *et al.* demonstrated that hematite catalyzed the production of small amounts of formaldehyde, methyl formate, and carbon monoxide at 225°C and low conversions (18).

Methanol reaction on copper was the subject of several investigations since metallic copper and metallic silver were the former industrial catalysts used to produce formaldehyde on a large scale. Studies of methanol chemisorption on copper(110)-oriented single crystal surfaces covered with chemisorbed oxygen and CuO powder showed that methanol interacts with adsorbed oxygen to form surface CH_3O species that decompose to formaldehyde and H_2 slightly above room temperature (19, 20).

Methanol steady state kinetics of methanol reaction over Bi_2O_3 showed the production of CO_2 due to the basicity of the oxide (13). Wachs *et al.* performed methanol reaction under differential conditions over a series of bulk Bi_2O_3 with different specific surface areas. The authors detected combustion products (CO_2, CO) as major products and formaldehyde in minor amounts regardless of the specific surface area or the calcination temperature of the oxide. Similarly, CeO_2, Co_3O_4, ZnO, and NiO catalyzed methanol combustion over a wide range of temperatures and methanol conversions (21–24).

The present work applies methanol chemisorption to quantify the number of surface active sites and presents a reliable comparison of the catalytic activities per active site (turnover frequencies) of bulk metal molybdates, monolayer molybdenum oxide catalysts, and metal oxides with the aim of obtaining insights into the catalytic behavior of supported and bulk molybdate catalytic systems. This work also deals with one of the fundamental questions of catalysis: the true surface composition of bulk catalysts and its difference with bulk composition. The nature of the surface of metal molybdates will be mapped comparing the products distribution of methanol reaction over MoO_3 and pure bulk metal oxides.

2. EXPERIMENTAL

2.1. Catalysts Synthesis

$Fe_2(MoO_4)_3$, $NiMoO_4$, $CoMoO_4$, $MnMoO_4$, and $Bi_2Mo_3O_{12}$ were synthesized by coprecipitation from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Alpha Aesar Products, 99.9%) and the corresponding metal nitrate [$Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$ Alpha Aesar Products, 99.9%] or chloride ($MnCl_2 \cdot 3H_2O$, Alpha Aesar Products, 99.9%) (25–29). A solution of ammonium heptamolybdate was added dropwise to the metal nitrate /chloride solution under stirring. The mixture was maintained at 80°C and pH 6.0 (pH 1.75 for $Fe_2(MoO_4)_3$) by adding HNO_3 (1 M solution) or NH_4Cl (1 M solution) as needed. After aging for 3 h, the precipitate was filtered, washed with distilled water, and dried at 100°C overnight. The precursor was calcined at 500°C for 4 h.

$CuMoO_4$, $Zr(MoO_4)_2$, $Cr_2(MoO_4)_3$, $ZnMoO_4$, $Ce_8Mo_{12}O_{49}$, and $Al_2(MoO_4)_3$ were synthesized through an organic route from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Alpha Aesar Products, 99.9%), the corresponding metal nitrate [$Cu(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $(NH_4)_2Ce(NO_3)_6$, $Al(NO_3)_3 \cdot 9H_2O$ Alpha Aesar Products, 99.9%] or chloride($ZrCl_4$, Alpha Aesar Products, 99.9%) and citric acid [$HOC(COOH)(CH_2COOH)_2 \cdot H_2O$ Alfa Aesar 99.9%] (30).

Fifteen grams of the metal containing chemical (nitrate/chloride) were dissolved in 200 ml of distilled water to which 20 g of citric acid was added and stirred to dissolve. The required amount of ammonium heptamolybdate was dissolved in 200 ml of distilled water and the solution was added to the metal–citric-acid solution. The mixture was dried in a steambath until a glassy texture was observed. The precursor was further dried in a vacuum oven at 70°C overnight, grounded, and calcined at 500°C for 24 h. The precursors of $Al_2(MoO_4)_3$ and $Zr(MoO_4)_2$ were calcined at 600 and 700°C, respectively, in order to obtain crystalline materials.

Molybdenum trioxide was synthesized by thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Alfa Aesar 99.9%) at 300°C for 14 h. Bulk metal oxides studied in the present work are commercial high purity chemicals (Alfa Aesar Puratronic 99.99%).

2.2. Catalyst Characterization

2.2.1. Laser Raman spectroscopy. The purity of bulk metal molybdate phases was determined by Raman spectroscopy. The spectra were obtained under ambient conditions with an Ar^+ ion laser (Spectra Physics Model 2020-50, excitation line 514.5 nm) delivering 15–40 mW of incident radiation. The powdered solid (aprox. 100–200 mg) was pressed into a thin wafer about 1 mm thick that was mounted onto a spinning sample holder and rotated at 2000 rpm to avoid local heating effects. The scattered radiation from the sample was directed into a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research OMA III optical multichanneled analyzer (Model 1463) equipped with an intensified photodiode array detector cooled to 243 K. The spectral resolution and reproducibility are 2 cm^{-1}.

2.2.2. Specific surface area. The BET surface areas of the samples were determined by N_2 adsorption at 77 K on a Quantasorb surface area analyzer (Quantachrome Corporation, Model OS-9).

2.2.3. X-ray photoelectron spectroscopy. The near-surface composition of bulk metal molybdates was investigated using X-ray photoelectron spectroscopy (XPS). The analysis was performed in a Model DS800 XPS surface analysis system (Kratos Analytical Plc, Manchester, UK) that operates with an X-ray beam of predominantly $MgK\alpha$ or $AlK\alpha$ X-rays and a base pressure of 5×10^{-9} Torr. The specimens for XPS analysis were prepared by pressing the catalyst powder between a stainless steel holder and a polished single crystal silicon wafer.

2.2.4. X-ray diffraction. X-ray diffraction spectra of chromium, cerium, aluminum, and zirconium molybdates were obtained with a Philips XRD-3720 equipment with an XRG-3100 X-ray generator ($CuK\alpha$, 1.54060–1.54439 Å). Data acquisition and processing was performed with a DEC (Digital Equipment Corporation) Microvax 3100 computer system. The operating conditions were: voltage, 45 kV; current, 30 mA; peak angle range, 2.00–90.02°; sample time, 30.00 s/deg.

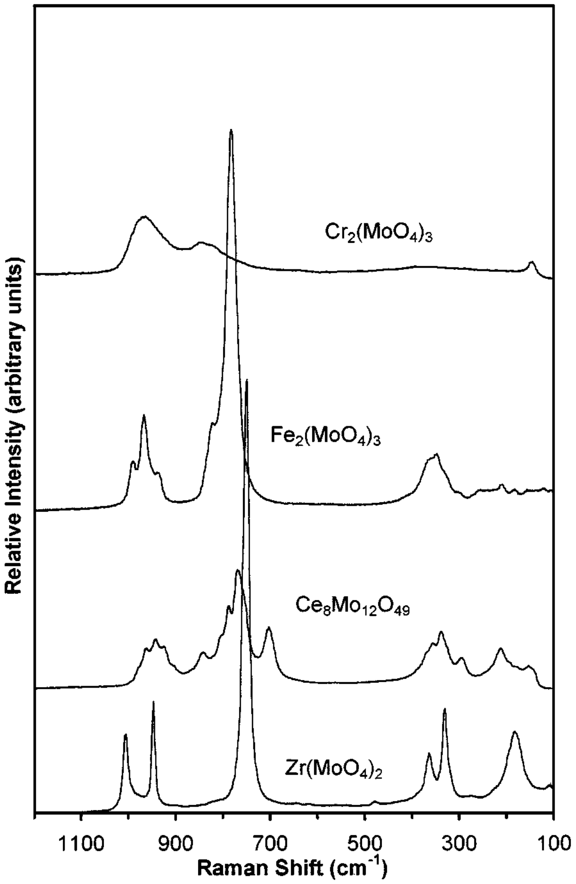

FIG. 1. Raman spectra of bulk metal molybdates.

2.3. *Methanol Chemisorption and Oxidation*

The number of surface active sites was quantified by methanol chemisorption. The catalysts were exposed to a mixture of 2000 ppm of methanol vapor in He at 100°C and the weight change was determined with 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 and the methanol chemisorption technique has been previously published (3).

Methanol oxidation steady state kinetics was obtained in a fixed-bed catalytic reactor under differential conditions. The following operating parameters were used in order to maintain methanol conversion below 10% for methanol reaction over metal molybdates: sample weight, ~10 mg; reaction temperature, 380°C; flow rate, 100 cm^3 (NTP) min^{-1}; and feed gas composition methanol/oxygen/helium, 6/13/81 mol%. The activity of bulk metal oxides varies greatly between the different systems; therefore, the reaction temperature was adjusted for each individual metal oxide to reach a low methanol conversion. The following are the temperatures for methanol oxidation over bulk metal oxides: CeO_2, 380°C; MnO, 300°C; Cr_2O_3, 290°C; NiO, 300°C; CoO, 270°C; CuO, 330°C; Fe_2O_3, 300°C and ZnO, 380°C. Bi_2O_3 is active at temperatures above 450°C.

Methanol conversion and the amount of products were quantified 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.

3. RESULTS

3.1. *Bulk and Surface Characterization of Metal Molybdates*

The purity of MoO_3 and bulk metal molybdates was determined by Raman spectroscopy. Figures 1–3 show the spectra of bulk metal molybdates. Pure MoO_3 possess three intense Raman signals at 996, 819, 668 cm^{-1} and smaller bands at 380, 339, 291, 246, 161, and 131 cm^{-1} that have been well documented in the literature for orthorhombic crystalline alpha-MoO_3 (data not shown). Bulk metal

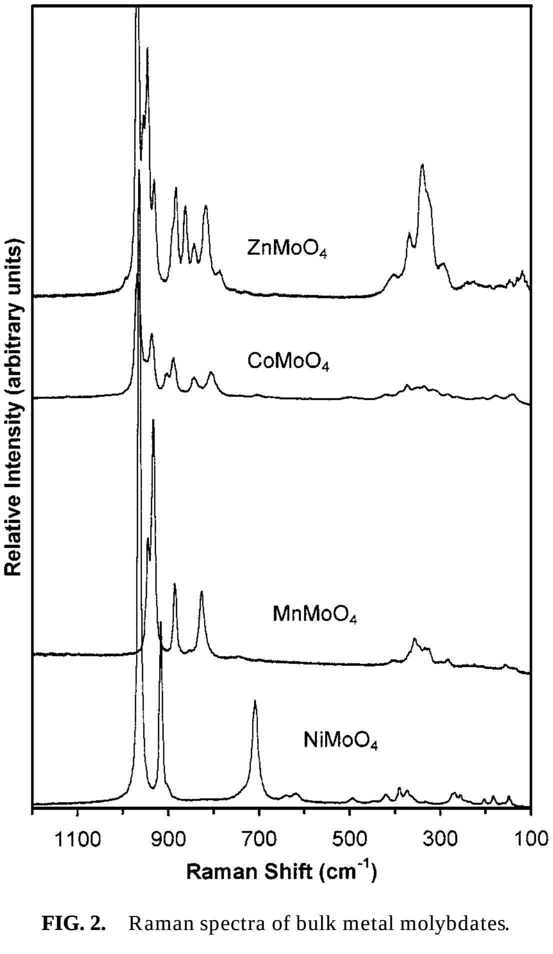

FIG. 2. Raman spectra of bulk metal molybdates.

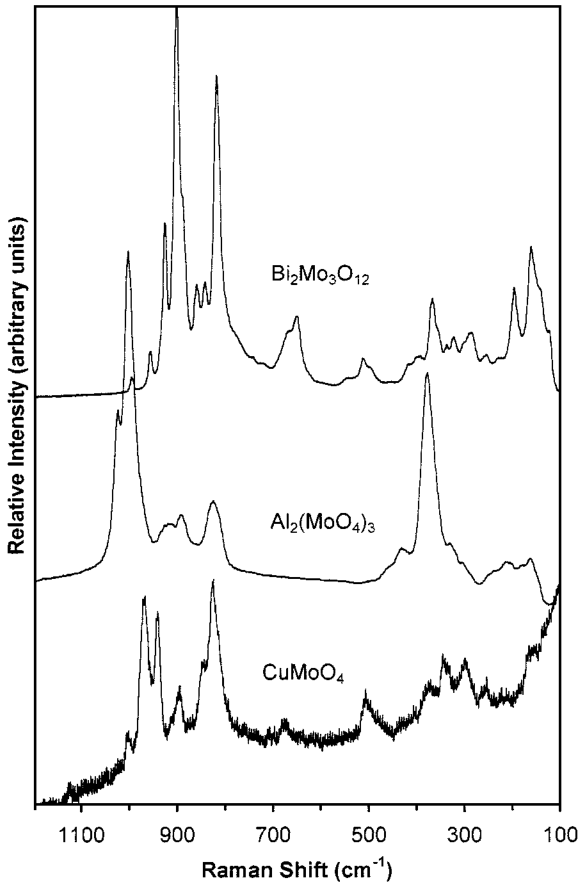

FIG. 3. Raman spectra of bulk metal molybdates.

molybdate phases are free of excess molybdenum since no MoO_3 Raman signals were detected. Additionally, pure CuO, Cu_2O, NiO, ZnO, Cr_2O_3, CeO_2, and MnO metal oxides were analyzed by Raman spectroscopy. Table 1 presents the Raman bands obtained for those systems and the signals of iron oxides, ZrO_2, Al_2O_3, and bismuth oxides from literature references (31–33). The absence of Raman bands belonging to bulk metal oxides in metal molybdates spectra ensures that no segregation of bulk metal oxides occurs during calcination. Raman spectra of $MnMoO_4$, $NiMoO_4$, $CoMoO_4$, α-$Bi_2Mo_3O_{12}$, and $Fe_2(MoO_4)_3$ coincides with the signals previously reported in the literature (26, 27, 29, 33, 34). The structures of chromium, cerium, aluminum, and zirconium molybdates were primarily analyzed by X-ray diffraction since no Raman spectra are available in the literature. XRD spectra presented in Fig. 4 belong to the following structures: $Cr_2(MoO_4)_3$, $Ce_8Mo_{12}O_{49}$, $Al_2(MoO_4)_3$, and $Zr(MoO_4)_2$ (35). Zinc and copper molybdates were identified with commercial $ZnMoO_4$ and $CuMoO_4$ (Alfa Aesar 99.9%). No new signals or other modifications in the Raman spectra of metal molybdates were observed after reaction with methanol.

Figure 5 shows surface molybdenum/metal ratio of metal molybdates before and after reaction with methanol. Although Raman analysis demonstrated that metal molybdates do not segregate bulk MoO_3 or metal oxides, the surface of these systems is generally nonstoichiometric due to enrichment in molybdenum. Surface molybdenum concentration increased after exposure to methanol under reaction conditions. These results were further confirmed comparing the activity and selectivity on the methanol oxidation reaction over metal molybdates with pure MoO_3 and metal oxides, which are presented below.

3.2. Surface Active Sites Quantification and Turnover Frequency in Methanol Selective Oxidation

The number of surface active sites present in bulk metal molybdates, pure MoO_3, and metal oxides was determined by covering the surface with a stable monolayer of chemisorbed methoxy species (1–3). Previous studies established that the maximum surface methoxy coverage is reached exposing the samples at 100°C to an atmosphere of 2000 ppm of methanol in helium. The amount of surface methoxy species can be calculated with the weight change of the catalyst monitored with a microbalance.

The quantification of the amount of methoxy species that can be formed on the catalyst surface allows the calculation of the catalytic activity per surface active site and the direct comparison of the activity of different systems. The specific catalytic activity (turnover frequency TOF) toward methanol selective oxidation was calculated by determining the production rate of redox products (formaldehyde, methyl formate, and dimethoxymethane) normalized per surface site. Table 2 presents the specific surface area, surface density of active sites expressed as the amount of

TABLE 1

Raman Bands of Pure Bulk Metal Oxides

Metal oxide	Raman bands (intensity) [cm^{-1}]
CuO	123 (s), 158 (m), 294 (m), 462 (w), 632 (w)
Cu_2O	122 (m), 154 (m), 219 (s), 633 (s)
NiO	502 (s)
ZnO	109 (m), 329 (m), 377 (m), 433 (s), 1171 (s)
Cr_2O_3	550 (s), 600 (s)
CeO_2	450 (s)
MnO	648 (m)
Fe_3O_4[a]	662 (s), 532 (w)
γ-Fe_2O_3[a]	676 (s), 468 (w), 390 (w), 124 (s)
α-Fe_2O_3[a]	605 (m), 493 (w), 403 (m), 289 (s), 221 (s), 127 (m)
ZrO_2[b]	180 (s), 190 (m), 220 (w), 300 (w), 330 (m), 350 (m), 385 (m), 470 (s), 530 (w), 550 (w), 610 (m), 625 (s).
Al_2O_3[b]	no Raman bands in the 100–1100 cm^{-1} region
α-Bi_2O_3[c]	451 (m), 410 (w), 319 (m), 298 (m), 213 (m), 175 (w)
β-Bi_2O_3[c]	450 (w), 307 (m), 294 (s), 147 (vs)
δ-Bi_2O_3[c]	570 (m)

Note. s, strong; m, medium; w, weak.

[a] Data from Ref. (31).

[b] Data from Ref. (32).

[c] Data from Ref. (33).

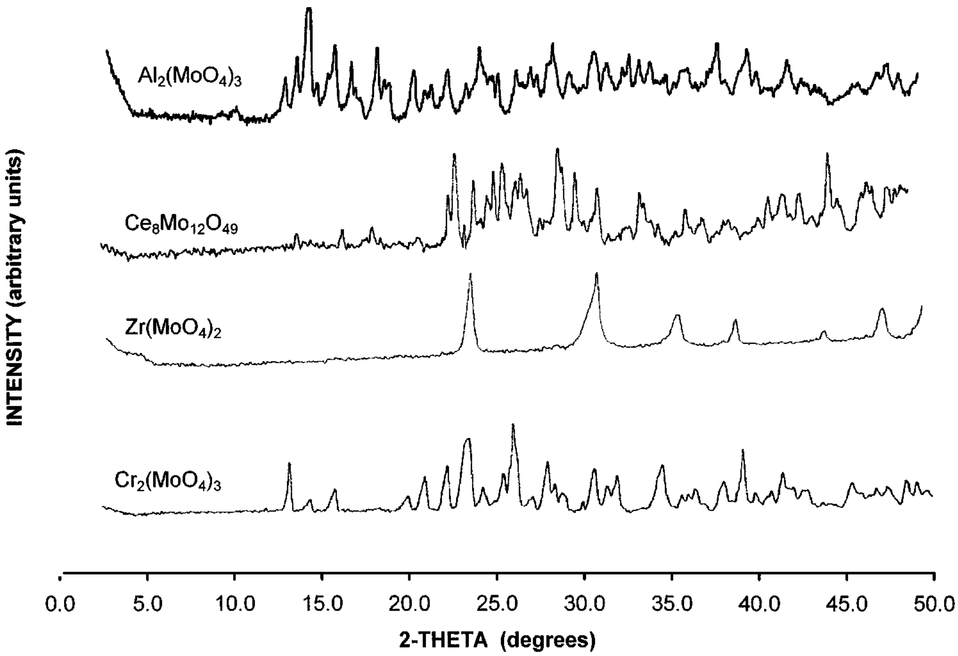

FIG. 4. X-ray diffraction spectra of $Cr_2(MoO_4)_3$, $Ce_8Mo_{12}O_{49}$, $A_{12}(MoO_4)_3$, and $Zr(MoO_4)_2$.

methoxy species per surface area (Ns), reaction rate, TOF, and selectivity of bulk metal molybdates. Surface active site density of copper and bismuth molybdates are probably subject to error due to the low surface area determined with the BET method; however, this parameter does not influence TOF values.

Bulk metal molybdates are active in methanol reaction at 380°C and highly selective toward formaldehyde. Dimethyl ether was also detected while no carbon oxides were produced under low methanol conversion reaction conditions. Further experiments performed on $NiMoO_4$ and $Fe_2(MoO_4)_3$ suggest that the specific activities and the surface active sites density of bulk metal molybdates are independent of the specific surface area; however, the selectivity toward formaldehyde varies slightly with surface area (Table 3).

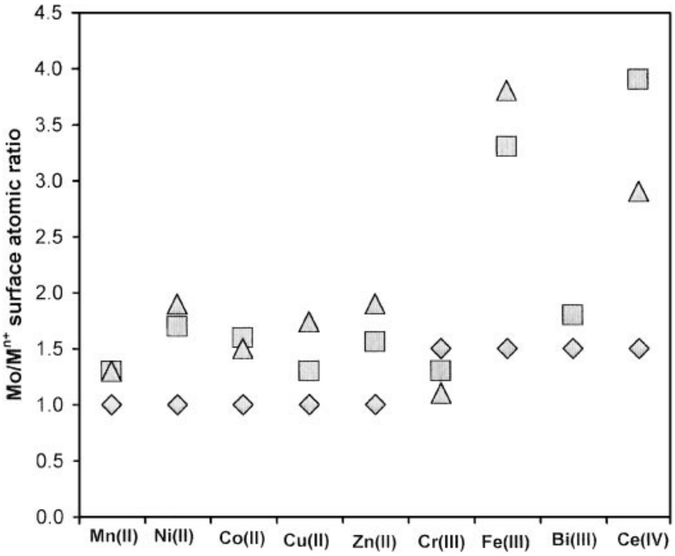

FIG. 5. Surface molybdenum/metal atomic ratio of bulk metal molybdates: (◆) theoretical ratio and experimental values obtained (■) before and (▲) after reaction with methanol.

The amount of surface active sites and the reactivity for methanol selective oxidation of pure bulk metal oxides was also studied. The significant differences between the catalytic behavior of metal molybdates and metal oxides in methanol reaction are a key factor in uncovering the true surface composition of bulk molybdates. Table 4 shows the specific surface area, surface density of active sites (Ns), turnover frequencies, and selectivity of pure bulk metal oxides at low methanol conversion. Again, the low surface areas of MnO, CoO, CuO, and Bi_2O_3 could be affecting the surface active sites density values; however, the specific activity TOF is independent of this parameter.

The number of surface active sites, specific activities, and selectivity values of ZrO_2 and Al_2O_3 have been taken from literature references (16, 36). The activity of bulk metal oxides was determined at different temperatures (typically 300°C) in order to maintain low methanol conversion values (see Section 2.3). It is expected that secondary reactions do not affect the main reaction at low methanol conversion and, therefore, the distribution of products reflects the nature of the surface active sites.

Metal oxides possess high catalytic activity and selectivity toward total combustion of methanol even at low conversion, with the exception of cerium, copper, and

TABLE 2

Surface Active Sites and Reactivity of Bulk Metal Molybdates and MoO_3 Catalysts toward Methanol Selective Oxidation

Catalyst	S_{BET} [m^2/g]	Ns [$\mu mol/m^2$]	Reaction rate[a] [$\mu mol/m^2$ sec]	TOF[b] [s^{-1}]	Selectivity [%][c] FA	DME	DMM
$Zr(MoO_4)_2$	31.3	1.0	36.0	24.8	62.1	34.4	3.1
$Ce_8Mo_{12}O_{49}$	4.0	12.0	46.5	3.3	86.5	13.5	—
$MnMoO_4$	1.9	3.1	20.6	6.6	99.8	—	—
$Cr_2(MoO_4)_3$	1.7	12.6	43.1	3.1	91.0	9.0	—
$Al_2(MoO_4)_3$	2.8	5.0	9.4	1.8	26.1	73.9	—
$NiMoO_4$	9.5	2.8	2.6	0.9	100.0	—	—
$CoMoO_4$	5.5	4.1	4.4	0.9	88.2	11.8	—
$CuMoO_4$	0.8	23.9	24.7	1.1	100.0	—	—
$Fe_2(MoO_4)_3$	9.6	4.2	9.6	1.4	61.0	39.0	—
$ZnMoO_4$	2.1	15.7	18.2	1.0	87.4	12.6	—
$Bi_2Mo_3O_{12}$	0.2	16.5	23.4	1.4	100.0	—	—
MoO_3	5.0	0.7	4.4	5.3	84.1	15.9	—

[a] Activity based on overall methanol conversion at 380°C.

[b] Turnover frequency based on methanol partial oxidation products (formaldehyde and dimethoxy methane); Reaction temp., 380°C.

[c] Selectivity toward formaldehyde (FA), dimethyl ether (DME), and dimethoxy methane (DMM) at 380°C.

bismuth oxides that produce only formaldehyde and Al_2O_3 that catalyzes the dehydration of methanol to dimethyl ether. Further experiments of methanol reaction over MnO, Cr_2O_3, NiO, CoO, Fe_2O_3, and CuO at 380°C (Bi_2O_3 is inactive below 450°C) showed that CO_2 is the major product of reaction.

4. DISCUSSION

4.1. *Surface Composition and Catalytic Activity of Bulk Metal Molybdates*

One of the fundamental questions of all catalytic studies about bulk compounds is the true surface composition and its difference from the bulk composition. Regularly it is assumed that the properties of the bulk reflect the state of the surface. X-ray photoelectron spectroscopy is a valuable tool that measures the concentration of atoms in a near surface region of a sample. The photoelectrons that escape from the solid, and are subsequently detected during the analysis, originate from a narrow mean free path of 10–20 Å for kinetic energies in the 15–1000 eV range (37). In contrast, a reactive molecule only interacts with the exterior surface of a catalyst and may be more reliable for the determination of the true surface composition of a catalyst than a spectroscopic technique. Methanol is a chemical probe molecule that can provide fundamental information about the number of surface active sites and the distribution of different types of surface sites of metal oxide catalysts. The methanol oxidation product distribution reflects the nature of the surface active sites since redox, acid, and basic sites yield formaldehyde (HCHO), dimethyl ether (CH_3OCH_3), or CO_2, respectively (38). Bulk metal molybdates and MoO_3 catalyze methanol selective oxidation toward formaldehyde and dehydration to dimethyl

TABLE 3

Surface Active Sites and Reactivity of $NiMoO_4$ and $Fe_2(MoO_4)_3$ Catalysts with Varying Surface Areas

Catalyst	Synthesis method	S_{BET} [m^2/g]	Ns [$\mu mol/m^2$]	Reaction rate[a] [$\mu mol/m^2$ sec]	TOF[b] [s^{-1}]	Selectivity[c] [%]
$NiMoO_4$	inorganic	9.5	2.8	2.6	0.9	100.0
	inorganic	15.6	3.3	8.6	2.3	87.0
$Fe_2(MoO_4)_3$	organic	1.5	6.7	26.7	2.3	58.0
	inorganic	3.9	8.3	23.3	1.8	64.9
	inorganic	9.6	4.2	9.6	1.4	61.0

[a] Activity based on overall methanol conversion at 380°C.

[b] Turnover frequency based on methanol selective oxidation products (formaldehyde and dimethoxy methane); Reaction temp., 380°C.

[c] Selectivity toward methanol selective oxidation products at 380°C.

TABLE 4

Surface Active Sites and Reactivity of Bulk Metal Oxides toward Methanol Selective Oxidation at Low Conversion

Oxide (reaction temp.)	S_{BET} [m^2/g]	Ns [μmol/m^2]	TOF[a] [s^{-1}]	Selectivity [%]					
				FA	CO_2	CO	DME	DMM	MF
ZrO_2[b] (230°C)	39.0	1.1	0.1	—	14.0	—	trace	—	86.0
CeO_2 (380°C)	2.4	4.8	1.3	100.0	—	—	—	—	—
MnO (300°C)	0.8	1.6	31.0	79.5	20.5	—	—	—	—
Cr_2O_3 (290°C)	3.0	12.4	7.1	35.7	59.6	4.7	—	—	—
Al_2O_3[b] (300°C)	180.0	5.6	0.0	—	—	—	100.0	—	—
NiO (300°C)	1.1	4.4	6.4	82.6	17.4	—	—	—	—
CoO (270°C)	0.4	2.2	24.7	61.2	34.2	—	—	—	4.7
CuO (330°C)	0.3	7.0	15.9	100.0	—	—	—	—	—
Fe_2O_3 (300°C)	21.4	3.2	3.3	57.9	—	—	36.4	1.2	4.5
ZnO (380°C)	5.3	0.3	18.2	32.7	31.5	22.9	—	—	12.8
Bi_2O_3 (450°C)	0.2	2.0	24.7	100.0	—	—	—	—	—

[a] Turnover frequency based on methanol partial oxidation products (formaldehyde, methyl formate and dimethoxy methane).

[b] Ns, reaction rate (for TOF calculation) and selectivity values from Refs. (16, 36).

ether due to the presence of surface redox and acid sites, respectively. In contrast, the basic nature of the surface active sites of ZrO_2, MnO, Cr_2O_3, NiO CoO, and ZnO catalyze the total combustion of methanol to CO_2 even at low methanol conversion (see Tables 2 and 4). This observation suggests that the activity toward methanol selective oxidation of zirconium, manganese, chromium, nickel, cobalt, and zinc molybdates is attributed to the presence of surface molybdenum oxide species. The catalytic behavior at low methanol conversion of CeO_2, CuO, Fe_2O_3, and the corresponding bulk metal molybdates ($Ce_8Mo_{12}O_{40}$, $CuMoO_4$, and $Fe_2(MoO_4)_3$) is alike. The presence of the metals on the surface of these bulk metal molybdates cannot be discarded even though the XPS analysis showed a surface enrichment of molybdenum (see Fig. 5). In the particular case of $Al_2(MoO_4)_3$ the presence of aluminum on the surface is undoubted considering the selectivity to dimethyl ether of the catalyst and Al_2O_3. Finally, the high selectivity of $Bi_2Mo_3O_{12}$ toward formaldehyde at 380°C, could be only attributed to surface molybdenum oxide species since Bi_2O_3 is inactive at that temperature.

The great difference between the specific activity values (TOFs) of bulk metal oxides and metal molybdates is also marked. In general, metal oxides are more active in methanol reaction and less selective toward partial oxidation products than MoO_3 and bulk metal molybdates.

The differences in catalytic behavior between MoO_3 and metal oxides and XPS results suggest that the surface of metal molybdates is composed mainly of molybdenum atoms. Moreover, the Raman spectra of metal molybdates do not show MoO_3 or new compounds after reaction, which indicates that molybdenum is covering the catalyst's surface probably in a single two-dimensional overlayer.

Studies of thermal- and reaction-induced spreading of MoO_3 and V_2O_5 over metal oxides demonstrated that molybdenum and vanadium spontaneously migrate at 400–500°C and react with methanol forming a volatile metal–methoxy complex at 200–250°C (39). This property of molybdenum species suggests that the surface molybdenum enrichment of bulk metal molybdates is produced during calcination at 500°C and is increased due to the reaction environment (6% methanol/oxygen–helium at 380°C). The thermal treatment of the precursors and the nature of the reactant play an important role in the formation of the catalyst surface. Many publications stress the influence of certain parameters of the synthesis process like pH, temperature or atomic ratio of the components on the catalytic properties of mixed oxides; however, the present work shows that those parameters influence the bulk homogeneity rather than the surface of the metal molybdate catalysts (40). For example, Tables 2 and 3 show that the synthesis in inorganic (i.e., $NiMoO_4$, $MnMoO_4$, $Fe_2(MoO_4)_3$, $CoMoO_4$, $Bi_2Mo_3O_{12}$) or organic media (the rest of molybdate series) does not influence the specific surface area or the surface composition of metal molybdates.

Finally, it is important to notice that the turnover frequency of most metal molybdates are similar or even higher than the TOF value of $Fe_2(MoO_4)_3$, which is known to be one of the components of the catalytic system used to produce formaldehyde on an industrial scale. Moreover, with the exception of zirconium and aluminum molybdates, all the metal molybdates investigated are more selective toward formaldehyde than iron molybdate.

4.2. Comparison of Methanol Selective Oxidation over Bulk Metal Molybdates and Monolayer Supported Molybdenum Catalysts

The catalytic activity of bulk and supported catalysts has been a matter of controversy in the catalytic field. The higher catalytic activity of supported than bulk catalysts has been reported in the literature; however, this conclusion

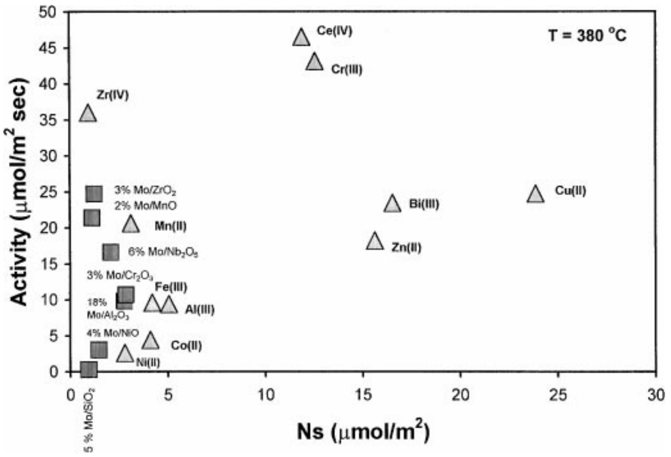

FIG. 6. Comparison of reaction rate and surface active sites density (Ns) of (▲) bulk metal molybdates and (■) monolayer molybdenum oxide supported catalysts.

was made on the basis of conversion of reactant to products instead of specific activities due to the uncertainty regarding the number of surface active sites of bulk catalysts (41–43). The present work overcomes this problem since methanol chemisorption enables the quantification of surface active sites of bulk metal molybdates and the calculation of the activity per surface active site. Previous work established the density of surface active sites by methanol chemisorption technique and the turnover frequencies in methanol selective oxidation of monolayer molybdenum supported on TiO_2, Al_2O_3, Nb_2O_5, NiO, MnO, ZrO_2, Cr_2O_3, and SiO_2 (3). In order to compare the catalytic activity of bulk metal molybdates and monolayer molybdenum oxide supported catalysts, the reaction rate and TOF values of supported catalysts were extrapolated to 380°C considering that the activation energy for methanol reaction over supported molybdenum oxide catalysts is typically 20 kcal/mol (44).

Figure 6 compares reaction rate and surface active sites density, Ns. The surface active sites density of both systems shows quite a different behavior. Monolayer molybdenum supported catalysts possess relatively constant Ns values. Previous studies determined that the amount of surface active sites of monolayer supported molybdenum catalysts is influenced by polymerized or isolated molybdenum species rather than the surface molybdenum coordination (octahedral or tetrahedral) (3). Surface active site density of some bulk metal molybdates are higher than molybdenum supported catalysts and do not correlate with the surface composition or the nature of the metal cation. The dispersion observed in Ns values is probably related with the surface structure of the molybdenum oxide species. Unfortunately, this is a difficult issue to clarify since no spectroscopic technique is capable of revealing the surface structure of the active sites of bulk catalysts. The activity of supported molybdenum oxide catalysts is independent of Ns at monolayer surface coverage; however, the activity of bulk molybdate catalysts appears to be somewhat dependent of Ns. Nevertheless, activity values are similar for both systems.

Figure 7 compares the turnover frequencies toward selective oxidation products of monolayer molybdenum supported catalysts and bulk metal molybdates with the same components, such as, $Zr(MoO_4)_2$ and 3% MoO_3/ZrO_2, $MnMoO_4$ and 2% MoO_3/MnO, $NiMoO_4$ and 4% MoO_3/NiO, $Al_2(MoO_4)_3$ and 18% MoO_3/Al_2O_3 and $Cr_2(MoO_4)_3$ and 3% MoO_3/Cr_2O_3. The surprising similarity of the turnover frequency of bulk and supported molybdenum based catalysts gives further proof that the surface composition of these systems is alike although it is not possible to conclude about the surface molybdenum oxide structures.

4.3. *Reactivity of Pure Bulk Metal Oxides*

In line with typical catalytic research performed on bulk metal oxide systems, the studies of the reactivity of metal oxides is focused on reactant conversion and products selectivity. Kinetic experiments are typically performed mainly at high temperatures and high conversion due to the application of metal oxides in the catalytic abatement of air pollutants. In the 1960s, some efforts were devoted to establishing regularity in the catalytic behavior of pure metal oxides in hydrocarbon oxidation (45–47). Correlations between the catalytic activity and electronegativity, heat of formation, and acid–base property of the oxides were reported. The present work will review those observations considering the catalytic activity per active surface site, TOF, of the metal oxides.

Table 5 shows redox, basic and acid TOFs at low methanol conversion, heat of formation, and electronegativity of

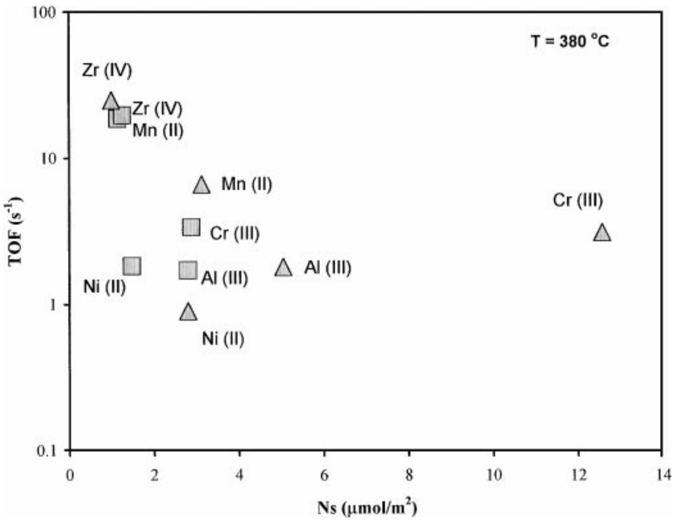

FIG. 7. Comparison of specific activity (TOFs) and surface active sites density (Ns) of (▲) bulk metal molybdates and (■) monolayer molybdenum oxide supported catalysts.

TABLE 5

Redox, Basic, and Acid Turnover Frequency Values of Bulk Metal Oxides toward Methanol Reaction

Oxide	ΔH_0/O atom[a] [Kcal/mol]	Electronegative M–O bond[b]	TOF $[s^{-1}]$ REDOX[c]	BASIC[d]	ACID[e]
CoO	−57.5	1.69	24.7	12.8	—
MnO	−92.0	1.99	31.0	8.0	—
Cr_2O_3	−89.6	1.99	7.1	11.9	—
CuO	−38.5	1.67	15.9	—	—
NiO	−58.4	1.71	6.4	1.5	—
Fe_2O_3	−66.2	1.45	3.2	—	1.9
ZnO	−83.4	1.43	18.2	12.6	—
CeO_2	−122.7	2.65	1.3	—	—

[a] Heat of formation per oxygen atom of the oxide.

[b] Difference of electronegativities (Sanderson) between oxygen and metal atoms.

[c] Turnover frequency based on methanol partial oxidation products (formaldehyde, methyl formate, and dimethoxy methane).

[d] Turnover frequency based on CO_2 production.

[e] Turnover frequency based on dimethyl ether production.

the metal–oxygen bond of a series of pure metal oxides. Turnover frequency toward methanol selective products (formaldehyde, methyl formate, and dimethoxy methane) indicates the redox capacity, TOF toward CO_2 reflects the basic character and the TOF toward dimethyl ether indicates the acid character of the surface active sites.

Moro-Oka *et al.* reported an increment of the catalytic activity of metal oxides toward hydrocarbon oxidation with the decrease of the metal–oxygen bond strength, which was quantified with the heat of formation of the oxide per oxygen atom (45). The present work does not find a correlation between the redox or basic TOF with the strength of the M–O bond of the oxides. These results demonstrate that the rate determining step of methanol oxidation over metal oxides does not involve the breaking of a surface metal–oxygen bond. The electronegativity of the metal–oxygen bond was also found to be responsible for alcohol dehydrogenation activity of metal oxide catalysts (46). Again no influence of the electronegativity on TOF values was observed in the present work.

Metal oxides can be divided into three groups according to the surface electron density (48, 49). The first group comprises the oxides characterized by a high concentration of centers that can supply electrons to adsorbed oxygen molecules generating electron-rich species such as O^-. These oxides possess p-type semiconductivity due to the presence of transition metal cations in the valence state with low ionization potential, such as CoO, MnO, Cr_2O_3, and NiO. The second group is characterized by a low concentration of electron donor centers, which adsorb oxygen as species O_2^- less rich in electrons. These are semiconducting oxides of the n-type, such as ZnO and Fe_2O_3. The third group involves MoO_3, WO_3, Nb_2O_5, transition metal molybdates and tungstates that possess oxygen atoms in the form of well-defined oxyanions. The oxides of the first two groups activate and adsorb oxygen in the form of highly active ionic radicals that can be considered as electrophilic reactants. In the case of olefins, such electrophilic species are responsible for the degradation of the carbon skeleton and total oxidation. The compounds of the third group do not activate oxygen at the surface and practically no chemisorption of oxygen is detected on nonreduced catalysts. In conclusion, the high activity of CoO, MnO, Cr_2O_3, and NiO (probably CuO could also be considered although the semiconductor type is not known) toward methanol reaction, mainly total oxidation, could be attributed to the presence of highly reactive surface oxygen radicals. The above-mentioned properties of these oxides suggest that there should be a correlation between TOF values and the ionization potential or the electron donor capacity of metal oxides surface, which would depend on the distribution of oxidation states of surface cations. This fundamental study does not go further on metal oxides reactivity, but it is important to stress that methanol chemisorption and specific activity values made it possible to reexamine previous theories on metal oxides and are the key to understand the catalytic behavior of these systems.

5. CONCLUSION

This study demonstrated that methanol is a selective chemical probe for the quantification and determination of the nature of surface active sites of metal molybdates and bulk metal oxides. The determination of the density of surface active sites enables the calculation of the catalytic activity per active site TOF, which allows a reliable comparison of the catalytic behavior of bulk catalysts. These measurements revealed that the surface of bulk metal molybdates is primarily composed of molybdenum species approaching a surface two-dimensional layer (a monolayer) of molybdenum oxide species.

The comparison of catalytic activity and TOF of bulk metal molybdates and monolayer molybdenum oxide supported catalysts demonstrated that both systems possess similar activity and selectivity in methanol selective oxidation. The higher surface active sites density of bulk metal molybdates than supported molybdenum catalysts suggests that these systems possess different surface molybdenum structures. Bulk metal oxides showed that they are active toward total oxidation rather than methanol selective oxidation compared with bulk metal molybdates and monolayer supported molybdenum catalysts. The specific activity of the bulk metal oxides does not correlate with parameters such as electronegativity or heat of formation, which have been used to explain the catalytic behavior of these systems in the past.

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