

Quantitative determination of the number of surface active sites and the turnover frequency for methanol oxidation over bulk metal vanadates

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Abstract

The present work investigates the number and nature of the surface active sites, selectivity and turnover frequency towards methanol selective oxidation of a series of bulk metal vanadates. The catalysts were synthesized through an organic route and characterized by laser Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and specific surface area analysis (BET). The number of surface active sites (N_s) was determined by measuring the concentration of surface methoxy species adsorbed on the catalysts exposed to an atmosphere of 2000 ppm of methanol in helium at 100 °C. The specific activity values (TOFs) were calculated by normalizing the methanol oxidation reaction rate by the number of surface active sites probed by methanol chemisorption. The comparison of the methanol oxidation products distribution from bulk metal vanadates, pure V_2O_5 and corresponding metal oxides (NiO, MnO, etc.) strongly suggests that the metal vanadate catalysts consist of only surface vanadium oxide sites. The comparison of the TOF values demonstrated that bulk metal vanadates possess similar activity to monolayer vanadium oxide supported catalysts and are more active than bulk metal molybdates for methanol selective oxidation. Moreover, bulk metal vanadates are as active and selective as the commercial $MoO_3/Fe_2(MoO_4)_3$ catalysts at high methanol conversion.

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1. Introduction

The chemisorption of chemical probe molecules is a well-known method to characterize the surface

properties of catalytic materials. Recently, methanol chemisorption was shown to be a reliable method to determine the number of surface active sites of metal oxide catalysts [1–4]. Wachs et al. demonstrated that methanol chemisorbs as a stable monolayer of surface methoxy species on an oxide surface exposed to an atmosphere of 2000 ppm of methanol in He at 100 °C. Surface methoxy species, $CH_3O_{(ads)}$, are

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also the reaction intermediates in the selective oxidation/dehydration of methanol and, therefore, the quantification of the amount of surface methoxy species allows the quantitative determination of the density of surface active sites for methanol selective oxidation. The number of chemisorbed surface methoxy species can be determined both gravimetrically and through in situ infrared spectroscopy. Both methods were successfully applied to a series of monolayer supported catalysts (oxides of molybdenum, vanadium, chromium, tungsten), bulk metal molybdates and bulk metal oxides [1–6].

Knowledge of the surface active site density also allows for the calculation of the catalytic activity per active site (turnover frequency (TOF) or specific activity) and a reliable comparison of the catalytic activity of different materials. The determination of the active surface site density and specific activity of monolayer molybdenum oxide supported catalysts and bulk metal molybdates demonstrated for the first time in the literature that both systems possess similar surface compositions and activity towards methanol selective oxidation [5]. The present investigation extends the novel methanol chemisorption technique to bulk metal vanadates and compares the TOF values of these systems with monolayer vanadium oxide supported and bulk metal molybdates catalysts for methanol selective oxidation.

Bulk metal vanadates are active catalysts in the selective oxidation of methanol to formaldehyde at high conversions. Recent investigations established that metal vanadates possess a higher activity and stability than the $\text{MoO}_3/\text{Fe}_2(\text{MoO}_4)_3$ mixture commercially employed in the industrial production of formaldehyde via methanol oxidation [7].

The most studied topic concerning bulk metal vanadates in recent years has been the oxidative dehydrogenation of propane to propylene over bulk magnesium vanadate phases (pyro-vanadate $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$, meta-vanadate $\text{Mg}_3\text{V}_2\text{O}_8$ and ortho-vanadate $\beta\text{-MgV}_2\text{O}_6$). The higher catalytic activity and selectivity observed on magnesium pyro-vanadate phase was attributed to the lability of its surface O^{2-} ions [8,9]. Au et al. [10] reported that rare earth ortho-vanadates such as SmVO_4 , LaVO_4 and YVO_4 are as active as magnesium vanadate in ODH of propane.

Owen and Kung [11] demonstrated that magnesium, zinc, chromium, nickel, copper and iron

ortho-vanadates are active in the ODH of butane. The selectivity towards butenes and butadiene correlated with the reducibility of the cation in aqueous media, but ODH is a vapor–solid process rather than an aqueous process.

Mixtures of bulk metal vanadates with chlorides have also been applied as catalysts in soot combustion. Saracco et al. [12,13] found that copper and potassium vanadates along with cesium, rubidium or potassium chloride catalyze the combustion of amorphous carbon at 382 °C (the non-catalyzed reaction takes place at 617 °C).

Although, several scientific studies established that bulk metal vanadates are active catalysts in selective oxidation reactions, there are no reported investigations that have determined the number of surface active sites and the specific catalytic activity (TOF) values.

2. Experimental

2.1. Synthesis

$\text{Mg}_2(\text{VO}_4)_2$, NbVO_5 , CrVO_4 , FeVO_4 , $\text{Ni}_3(\text{VO}_4)_2$, $\text{Co}_3(\text{VO}_4)_2$, $\text{Mn}_3(\text{VO}_4)_2$, AlVO_4 , AgVO_3 , $\text{Cu}_3(\text{VO}_4)_2$ and $\text{Zn}_3(\text{VO}_4)_2$ were synthesized through an organic route from NH_4VO_3 (Alpha Aesar Products, 99.9%), the corresponding metal nitrates ($\text{Mg}_3(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Alfa Aesar or J.T. Baker, 99.9%) or chlorides ($\text{MnCl}_2 \cdot 3\text{H}_2\text{O}$ and NbCl_5 ; Alfa Aesar, 99.9%) and citric acid ($\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$; Alfa Aesar, 99.9%). The details of the synthesis are under patent revision [7].

2.2. Characterization

2.2.1. Laser Raman spectroscopy

The phase purity of the bulk metal vanadate phases was determined by Raman spectroscopy because of its ultra-sensitivity to metal oxide microcrystalline phases (especially below 40 Å that are XRD amorphous). 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 (approximately 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 Micromeritics Accusorb surface area analyzer.

2.2.3. X-ray photoelectron spectroscopy

The near-surface composition of the bulk metal vanadates was investigated using XPS. The analysis was performed in a model DS800XPS surface analysis system (Kratos Analytical Plc, Manchester, UK) that operates with an X-ray beam of either Mg $\text{K}\alpha$ or Al $\text{K}\alpha$ X-rays and a base pressure of 5×10^{-19} Torr. The details of the technique have been published previously [5].

2.2.4. X-ray diffraction

X-ray diffraction (XRD) spectra were measured with a Philips PW 1390 that operates with Cu $\text{K}\alpha$ radiation and a Ni filter. The details of the technique have been published previously [14].

2.3. Determination of the number of surface active sites (N_s) through methanol chemisorption

The number of surface active sites was quantified by methanol chemisorption by exposure to a mixture of 2000 ppm of methanol vapor in He at 100°C that generated a stable monolayer of surface methoxy species. The amount of adsorbed surface methoxy species was determined gravimetrically in the present investigation. A detailed flow diagram of the equipment and the chemisorption technique has been previously published [1].

2.4. Methanol oxidation

Methanol oxidation steady-state kinetics were obtained in a fix-bed catalytic reactor under differential

reaction conditions (methanol conversion $\leq 10\%$) as well as high methanol conversion. The following operating parameters were used in order to maintain methanol conversion below 10% for methanol reaction over metal vanadates: sample weight, ~ 10 mg; reaction temperature, 300°C ; flow rate, 100 cm^3 (NTP) min^{-1} and feed gas composition methanol/oxygen/helium, 6/13/81 mol%.

The experiments at high methanol conversion were performed under the following operating conditions: sample weight, 30–200 mg; reaction temperature, 300°C ; flow rate, 100 cm^3 (NTP) min^{-1} and feed gas composition methanol/oxygen/helium, 6/13/81 mol%. The catalysts were tested for 24 h. at high methanol conversion in order to determine their stability under reaction conditions.

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 and discussion

3.1. Bulk phase analysis of metal vanadates

Bulk metal vanadates were synthesized through an organic route that was applied successfully to obtain a series of bulk metal molybdates in previous publication [5]. The literature also shows that bulk vanadates of rare earth elements and magnesium vanadates are suitable to be obtained with that method [8,10]. The present work extends the application of the organic route synthesis to the preparation of manganese, cobalt, niobium and aluminum ortho-vanadates, and silver meta-vanadate (the ortho-vanadate phase is unstable and decomposes at 400°C). The Raman analyses of the samples are presented in Fig. 1. The spectra of $\text{Mg}_3(\text{VO}_4)_2$, $\text{Ni}_3(\text{VO}_4)_2$, $\text{Cu}_3(\text{VO}_4)_2$, $\text{Zn}_3(\text{VO}_4)_2$, CrVO_4 , $\text{Mn}_3(\text{VO}_4)_2$ and FeVO_4 are in agreement with those reported in the literature for pure bulk metal ortho-vanadate compounds [11]. The structures of NbVO_5 , $\text{Co}_3(\text{VO}_4)_2$, AlVO_4 and $\beta\text{-AgVO}_3$ were further analyzed with XRD diffraction since

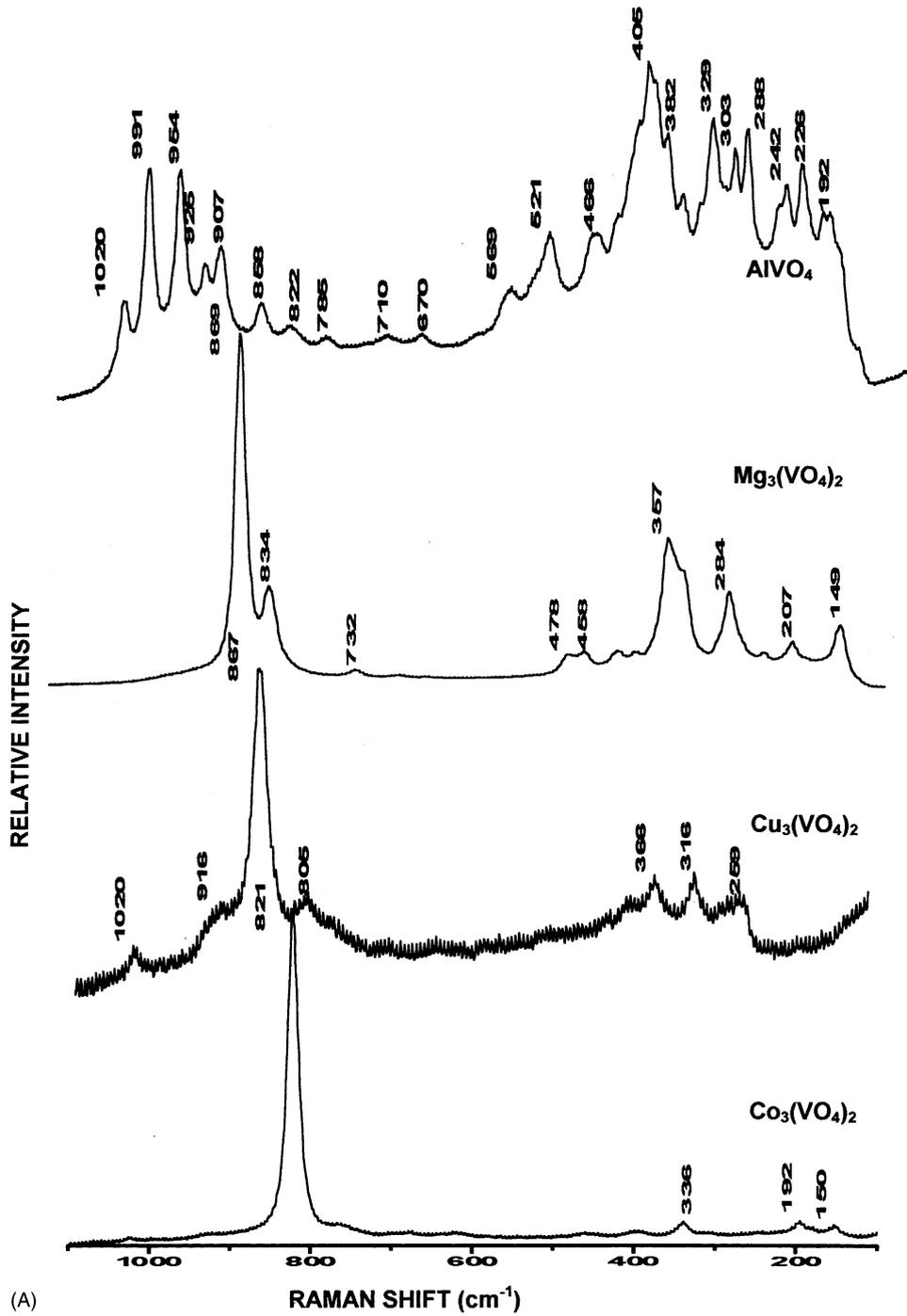
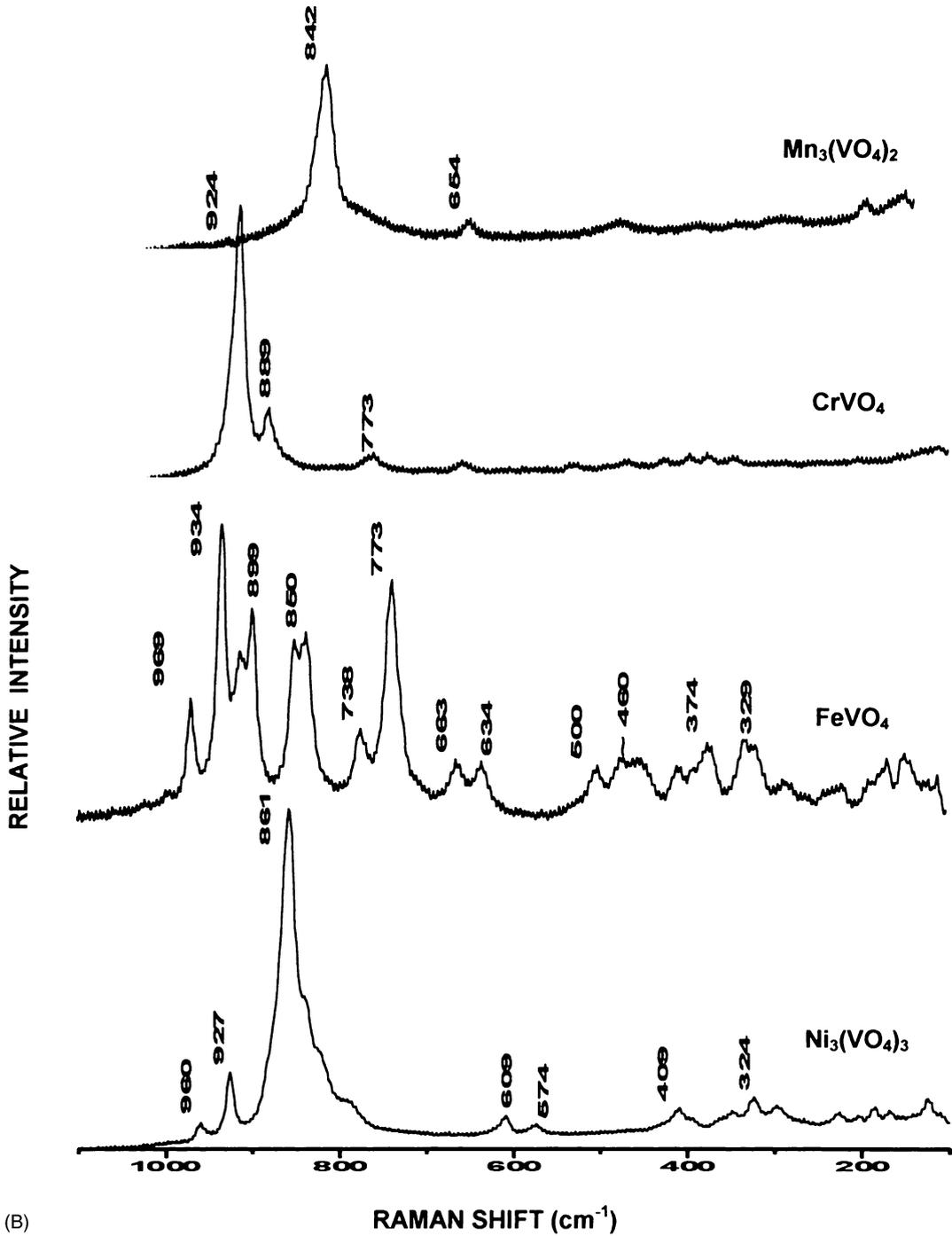
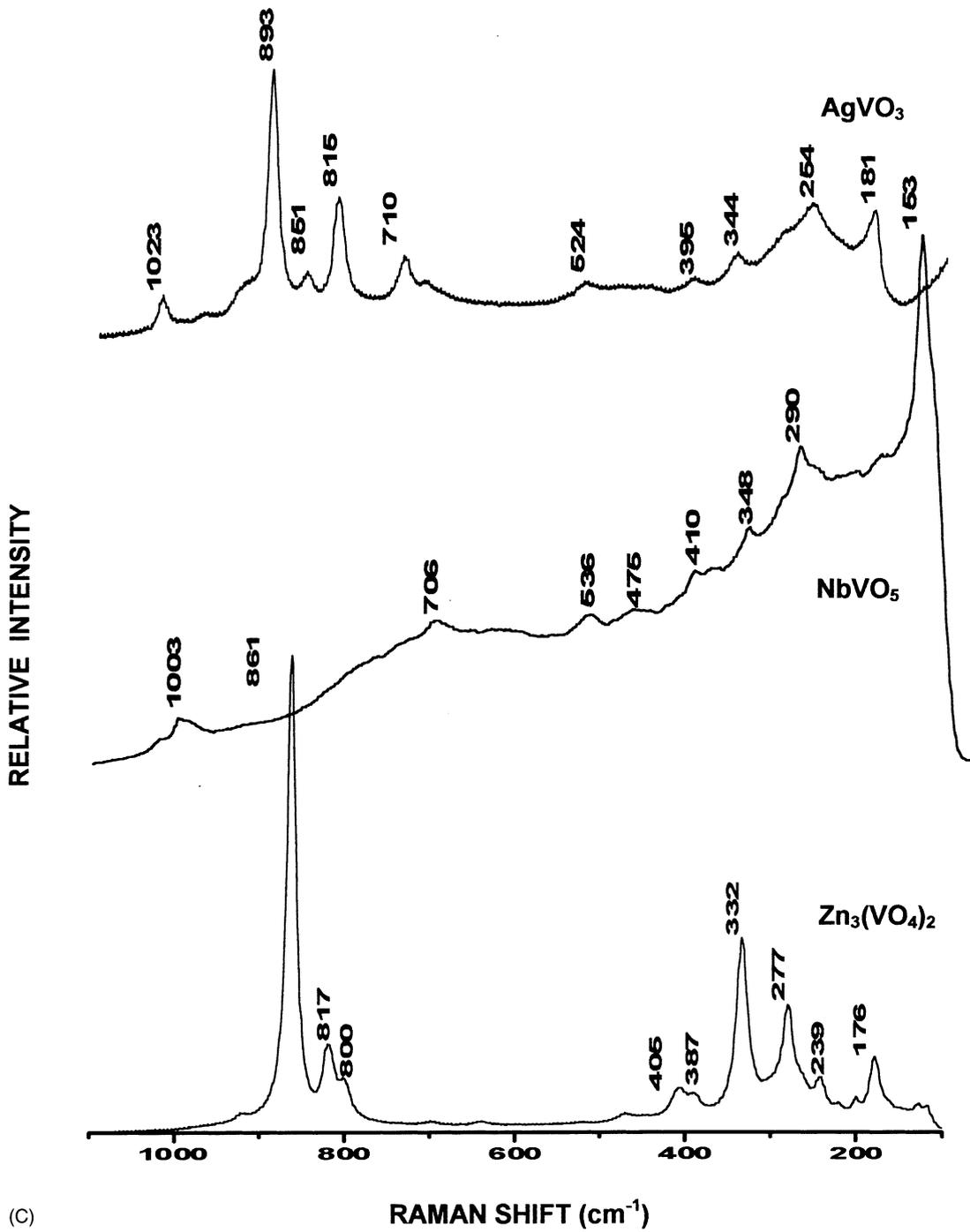


Fig. 1. Raman spectra of bulk metal vanadates.



(B)

Fig. 1. (Continued).



(C)

Fig. 1. (Continued).

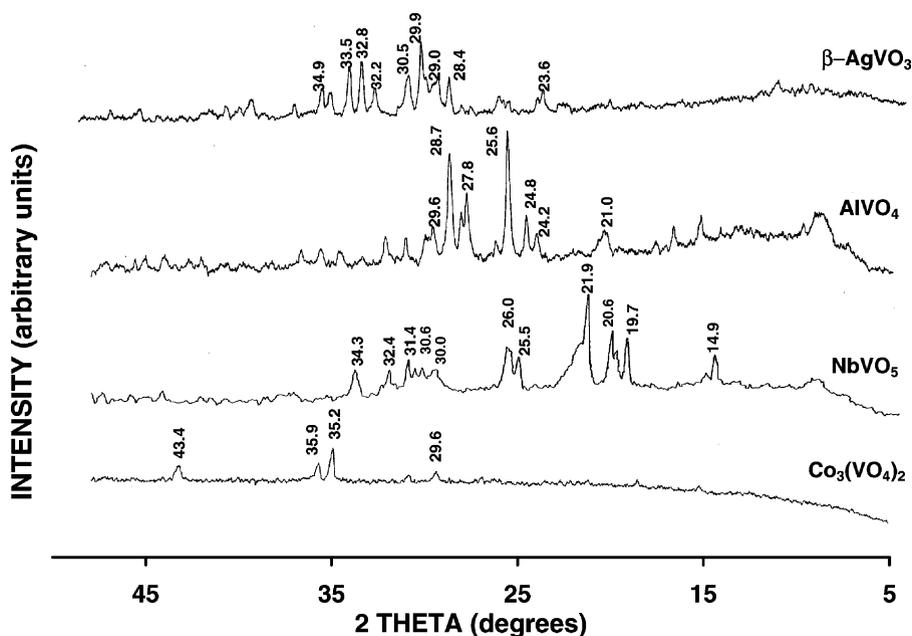


Fig. 2. XRD spectra of NbVO_5 , $\text{Co}_3(\text{VO}_4)_2$, AlVO_4 and $\beta\text{-AgVO}_3$.

no Raman spectra are available in the literature for these vanadates.¹ The XRD analysis showed that silver meta-vanadate also contains the $\text{Ag}_2\text{V}_4\text{O}_{11}$ phase ($2\theta = 23.6^\circ$, 29.0° , 30.5° , 32.2°) and NbVO_5 contains $\text{Nb}_{18}\text{V}_4\text{O}_{55}$ (shoulder at $2\theta \sim 22^\circ$) (see Fig. 2). No signals belonging to crystalline V_2O_5 (Raman bands at 994, 702, 527, 404, 284 and 146 cm^{-1} and XRD signals at $2\theta = 14.9^\circ$, 18.0° , 21.3° , 23.5° , 28.1°) or other metal oxide microcrystalline phases were detected which ensures the purity of the catalysts [5].

3.2. XPS surface analysis before and after methanol oxidation

Fig. 3 shows the surface atomic vanadium/metal ratio of bulk metal vanadates before and after the reaction with methanol. The figure compares the surface atomic ratio obtained through XPS analysis and the theoretical (bulk) ratio. Nickel, copper, zinc, silver, niobium and iron vanadate catalysts possess a higher

surface atomic vanadium/metal ratio than the value expected according to the bulk phase stoichiometry. This observation indicates a surface enrichment of vanadium species on bulk metal vanadates that cannot be attributed to the presence of an excess of bulk V_2O_5 according to the bulk phase analyses of the catalysts. The XPS analyses of magnesium, cobalt, manganese, aluminum and chromium vanadates show the opposite result. The surface atomic vanadium/metal ratio are lower than the theoretical ratio suggesting a surface enrichment of the metal cation (Mg, Co, Mn, Al, Cr).

The differences in the nature of the surface active sites of bulk metal vanadates would also lead to a different product distribution in the methanol reaction. The next section compares the selectivity of bulk metal vanadate catalysts, V_2O_5 and bulk metal oxides in order to obtain more information on the true surface composition of bulk metal vanadates.

3.3. Nature of the surface active sites of bulk metal vanadates from CH_3OH oxidation selectivity at low conversions

Comparison of the product distribution for methanol oxidation over bulk metal vanadates and

¹ X-ray diffraction spectra coincide with the following JCPDS-International Centre for Diffraction Data Files, 1997–1999: 46-0046 for NbVO_5 , 37-352 for $\text{Co}_3(\text{VO}_4)_2$, 39-276 for AlVO_4 and 29-1154, 20-1385 for $\beta\text{-AgVO}_3$ and $\text{Ag}_2\text{V}_4\text{O}_{11}$, respectively.

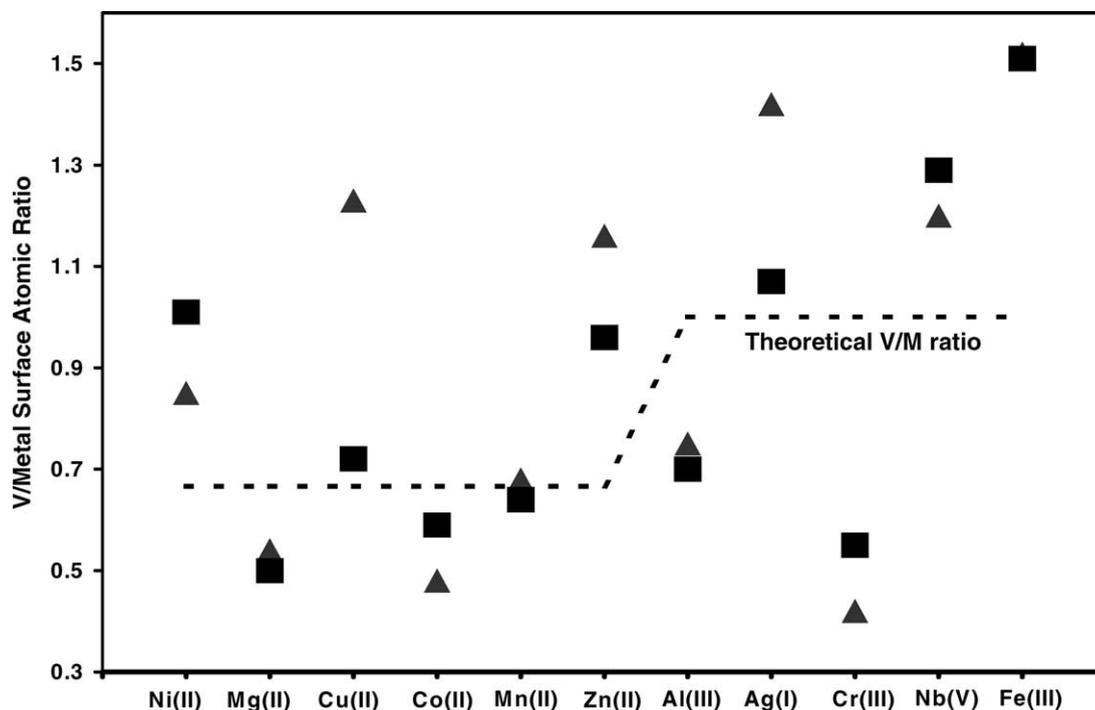


Fig. 3. Surface vanadium/metal atomic ratio of bulk metal vanadates: (■) before and (▲) after reaction with methanol.

the corresponding pure metal oxide provides more fundamental information about the nature of the surface active sites. Methanol is a probe molecule to determine the nature of surface active sites since the product distribution of methanol reaction is sensitive to the redox and/or acid–base properties of the surface active species. Redox sites catalyze the selective oxidation of methanol to formaldehyde, acid sites yield dimethyl ether and basic species produce CO_2 [15].

Tables 1 and 2 show the selectivity of bulk metal vanadates and pure metal oxides at low methanol conversions, respectively. Bulk metal vanadates possess a high selectivity to formaldehyde with some selectivity to dimethoxy methane (nickel vanadate), dimethyl ether (niobium, chromium and aluminum vanadates), methyl formate (magnesium, chromium and copper vanadates) and CO_2 (niobium and silver vanadates).

TOFs and selectivity results of methanol oxidation over pure metal oxide catalysts were determined in previous studies [5,6]. The data were obtained at different temperatures (typically 300°C) in order to maintain low methanol conversions. The surface

redox/acid sites of bulk V_2O_5 lead to a high selectivity to formaldehyde, along with dimethoxy methane and dimethyl ether. The redox/basic character of the surface active sites of MgO , NiO , MnO , Cr_2O_3 , CoO

Table 1
Specific surface area and selectivity of bulk metal vanadates toward methanol oxidation at low conversions

Catalyst	S_{BET} (m^2/g)	Selectivity (%) ^a				
		FA	DMM	DME	MF	CO_2
$\text{Mg}_3(\text{VO}_4)_2$	24.2	95.5	–	–	4.5	–
NbVO_5	15.6	87.9	–	3.2	–	8.5
CrVO_4	14.8	98.7	–	0.7	0.6	–
$\text{Mn}_3(\text{VO}_4)_2$	3.1	100.0	–	–	–	–
AlVO_4	8.4	98.0	–	2.0	–	–
AgVO_3	0.8	92.5	–	–	–	7.4
$\text{Ni}_3(\text{VO}_4)_2$	15.3	97.3	2.7	–	–	–
$\text{Co}_3(\text{VO}_4)_2$	8.9	100.0	–	–	–	–
$\text{Cu}_3(\text{VO}_4)_2$	3.3	95.0	–	–	5.0	–
FeVO_4	4.8	100.0	–	–	–	–
$\text{Zn}_3(\text{VO}_4)_2$	5.2	100.0	–	–	–	–

^a FA: formaldehyde; DMM: dimethoxy methane; DME: dimethyl ether; MF: methyl formate.

Table 2
TOF and selectivity of pure metal oxide catalysts toward methanol oxidation at low conversions

Catalyst (reaction temperature, °C)	TOF ^a (s ⁻¹)	Selectivity ^b (%)			
		FA	CO ₂	DME	Others ^c
MgO (300)	0.02	60.0	40.0	–	–
Nb ₂ O ₅ (300)	0.0	–	–	100.0	–
Cr ₂ O ₃ (290)	7.1	35.7	59.6	–	4.7
MnO (300)	31.0	79.5	20.5	–	–
Al ₂ O ₃ (300)	0.0	–	–	100.0	–
Ag ₂ O (300)	359.0	100.0	–	–	–
NiO (300)	6.4	82.6	17.4	–	–
CoO (270)	24.7	61.2	34.2	–	4.7
CuO (330)	15.9	100.0	–	–	–
Fe ₂ O ₃ (300)	3.3	57.9	–	36.4	5.7
ZnO (380)	18.2	32.7	31.5	–	35.7
V ₂ O ₅ (300)	9.8	79.0	–	10.5	10.4

^a Based on selective oxidation products (formaldehyde, methyl formate and dimethoxy methane).

^b TOF and selectivity data from Refs. [5,6].

^c Other products are methyl formate and dimethoxy methane.

and ZnO yield formaldehyde and CO₂. The surface acidic sites of Al₂O₃, Nb₂O₅ and Fe₂O₃ catalyze methanol dehydration to dimethyl ether. Formaldehyde is the only product of the methanol oxidation reaction over CuO and Ag₂O.

The XPS analyses discussed in the previous section suggested a surface enrichment of the metal cation on Mg₃(VO₄)₂, Co₃(VO₄)₂, Mn₃(VO₄)₂, AlVO₄ and CrVO₄. The presence of surface magnesium, cobalt, manganese and chromium sites would catalyze the total oxidation of methanol to CO₂ and an aluminum site would yield dimethyl ether according to the results obtained on the methanol oxidation over pure metal oxides. However, no CO₂ was observed on Mg₃(VO₄)₂, Co₃(VO₄)₂, Mn₃(VO₄)₂ and CrVO₄, and only 2% selectivity towards dimethyl ether is produced by AlVO₄ (see Table 1). The observation that bulk metal vanadates possess a high selectivity towards formaldehyde strongly suggests that the surface of bulk metal vanadates is composed of vanadium oxide sites with redox properties that cover the metal oxide sites and, thus, inhibit methanol total oxidation.

It is well known that V₂O₅ is unstable under the methanol oxidation environment due to the formation of a V-alkoxy complex at temperatures as low as 150 °C. The complex removes V₂O₅ from the catalytic bed and produces a deposit at the exit, the cooler

side, of the reactor. The current observation that the bulk metal vanadates being investigated for methanol oxidation were stable for 24 h at high methanol conversion further supports the Raman analyses that the bulk metal vanadates do not possess bulk microcrystalline V₂O₅ on their surfaces. Moreover, the selectivity results further suggest that surface vanadium oxide species are anchored to metal oxide atoms (MgO, NiO, MnO, Cr₂O₃, CoO, ZnO, Al₂O₃, Nb₂O₅ and Fe₂O₃) in a similar way to vanadium oxide supported catalysts.

3.4. Specific activity, TOF, for methanol selective oxidation over bulk metal vanadates, bulk metal molybdates and supported vanadium oxide catalysts

The number of surface active sites, reaction rates and turnover frequencies of the bulk metal vanadates during methanol oxidation are presented in Table 3. No correlation was observed between the density of active surface sites of the bulk metal vanadates and their reaction rates during methanol oxidation. The specific activity (TOF) of the bulk metal vanadates was calculated as the reaction rate towards redox products (formaldehyde, dimethoxy methane and methyl formate) per surface active site per second. The TOF values of the bulk metal vanadates are similar indicating that there is no significant influence of

Table 3
Number of surface active sites, reaction rate and turnover frequencies of bulk metal vanadates at low methanol conversion

Bulk metal vanadates	N _s (μmol/m ²)	Reaction rate ^a at 300 °C (μmol/m ² s)	TOF ^b (s ⁻¹)
Mg ₃ (VO ₄) ₂	0.6	0.8	1.4
NbVO ₅	1.6	5.1	3.1
CrVO ₄	0.7	10.2	14.4
Mn ₃ (VO ₄) ₂	3.9	1.4	0.4
AlVO ₄	2.7	6.0	2.2
AgVO ₃	21.1	35.7	1.6
Ni ₃ (VO ₄) ₂	0.4	1.8	4.3
Co ₃ (VO ₄) ₂	2.4	5.1	2.1
Cu ₃ (VO ₄) ₂	1.0	6.1	6.2
FeVO ₄	2.0	7.9	4.0
Zn ₃ (VO ₄) ₂	4.3	1.0	0.2

^a Activity based on overall methanol conversion at 300 °C.

^b Based on methanol partial oxidation products (formaldehyde, dimethoxy methane and methyl formate); reaction temperature: 300 °C.

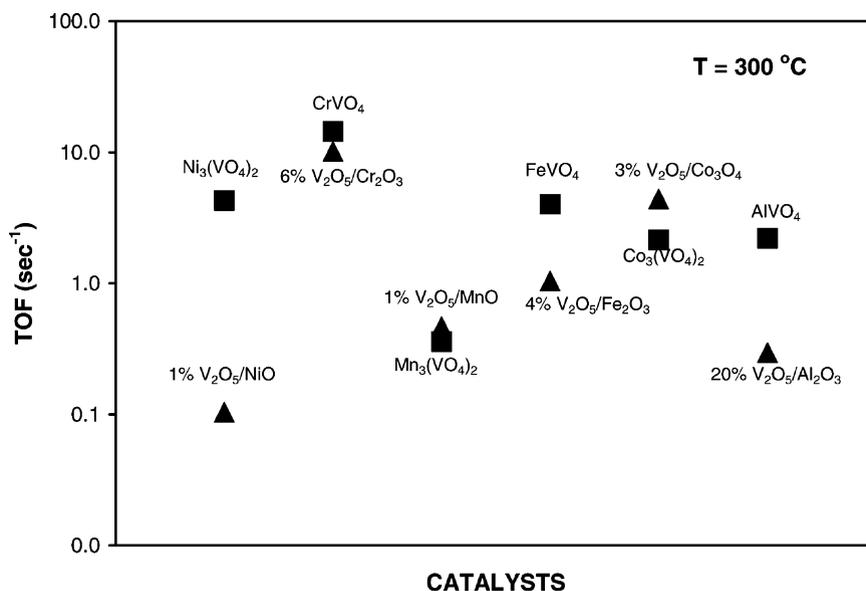


Fig. 4. Comparison of specific activity (TOF) of: (■) bulk metal vanadates and (▲) monolayer vanadium oxide supported catalysts.

the specific nature of the metal oxide cation (Mg, Ni, Mn, Cr, Co, Zn, Al, Nb, Fe, Cu, Ag) on the catalytic behavior. Moreover, there are significant differences between the TOF values of bulk metal vanadates and pure metal oxides which gives more evidences that the metal cations are not exposed on the surface of bulk metal vanadates (see Tables 2 and 3).

Knowledge of the TOF allows a direct comparison of the catalytic activity of different catalytic systems as a function of the nature of the surface active sites. Figs. 4 and 5 compare the TOF values of bulk metal vanadates with the corresponding supported vanadium oxide monolayer and bulk metal molybdate catalysts, respectively.

The TOF values of Ni₃(VO₄)₂, 1% V₂O₅/NiO; CrVO₄, 5% V₂O₅/Cr₂O₃; Mn₃(VO₄)₂, 1% V₂O₅/MnO; FeVO₄, 4% V₂O₅/Fe₂O₃; Co₃(VO₄)₂, 3% V₂O₅/Co₃O₄; AlVO₄ and 20% V₂O₅/Al₂O₃ reveal that bulk metal vanadates and supported vanadium oxide monolayer catalysts are somewhat similar. This behavior is in agreement with the methanol oxidation selectivity results presented above that both catalytic systems are composed of surface vanadium oxide species.

Previous studies demonstrated bulk metal molybdates are active at 380 °C for methanol selective

oxidation [5]. The TOF values of those catalysts were extrapolated to 300 °C in order to compare their values with the corresponding bulk metal vanadate catalysts. The extrapolation was performed considering that the activation energy for methanol reaction over molybdenum oxide catalysts is typically 20 kcal/mol [16]. Fig. 5 shows that, in general, bulk metal vanadates possess one order of magnitude higher TOF values ($\sim 2\text{--}14\text{ s}^{-1}$) than their corresponding bulk metal molybdates ($\sim 0.1\text{ s}^{-1}$) for methanol selective oxidation. The TOF values of pure V₂O₅ (9.8 s^{-1}) and MoO₃ (0.6 s^{-1}) crystals are also presented to demonstrate that the difference in the activity of bulk metal molybdates and vanadates is based on the nature of the surface species (in this case, VO_x vs. MoO_x). The results clearly show that surface vanadium oxide sites are more active than surface molybdenum oxide sites regardless of the bulk structure, bulk coordination or density of surface active sites.

The catalytic selectivity of the bulk metal vanadates observed at low methanol conversion is similar to that found for high methanol conversions. The selectivity of CrVO₄, NbVO₅, Ni₃(VO₄)₂, AlVO₄, FeVO₄ and AgVO₃ at 80–100% methanol conversion is shown in Table 4. These data were obtained at an average of 24 h under steady-state methanol oxidation reaction

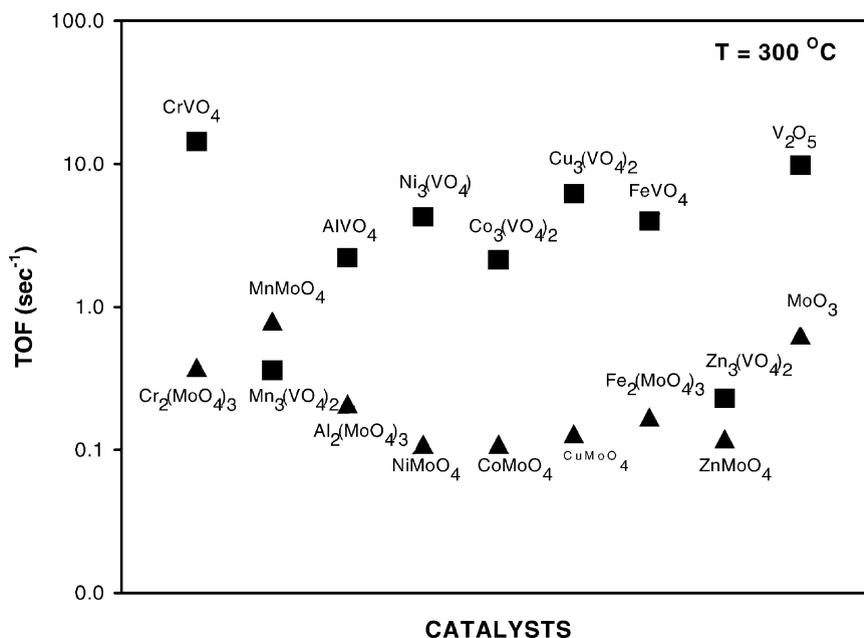


Fig. 5. Comparison of specific activity (TOF) of: (■) bulk metal vanadates and (▲) bulk metal molybdate catalysts.

conditions and demonstrate the high selectivity of bulk metal vanadates towards formaldehyde and the stability of these catalytic materials in the methanol oxidation environment.

The activity of the MoO₃/Fe₂(MoO₄)₃ catalyst used in the industrial production of methanol oxidation to formaldehyde is also shown in Table 4. The industrial catalyst losses molybdenum oxide during the reaction due to the formation of a molybdenum–methoxy complex that is volatile under reaction conditions. Therefore, the industrial catalyst is composed of a

MoO₃/Fe₂(MoO₄)₃ mixture with an excess of molybdenum trioxide to replenish the active Fe₂(MoO₄)₃ phase during the methanol oxidation reaction. In the absence of the excess MoO₃ phase, the Fe₂(MoO₄)₃ surface becomes depleted of surface MoOx sites and the exposed Fe oxide sites yield significant amounts of dimethyl ether rather than formaldehyde [17,18].

The current results reveal that bulk metal vanadate catalysts possess a similar activity and selectivity towards methanol selective oxidation as the industrial MoO₃/Fe₂(MoO₄)₃ catalyst without the addition of

Table 4

Catalytic activity of bulk metal vanadates and industrial MoO₃/Fe₂(MoO₄)₃ catalysts at high methanol conversion

Catalyst	CH ₃ OH conversion (%) at 300 °C	Selectivity (%)					CO ₂
		FA	DMM	DME	MF	CO	
CrVO ₄	96.0	90.4	–	0.7	–	8.9	–
NbVO ₅	100.0	90.0	–	2.0	–	8.0	–
Ni ₃ (VO ₄) ₂	96.2	94.0	–	1.0	–	5.0	–
AiVO ₄	90.5	94.5	–	2.0	1.0	2.5	–
Co ₃ (VO ₄) ₂	81.0	96.6	–	–	1.4	2.0	–
FeVO ₄	94.2	95.4	–	0.8	0.8	3.0	–
AgVO ₃	92.9	89.3	–	–	0.6	1.5	8.6
MoO ₃ /Fe ₂ (MoO ₄) ₃	91.4	94.8	–	3.1	–	2.1 ^a	–

^a Selectivity towards CO_x.

another metal oxide phase such as V_2O_5 . This observation is particularly important since both V_2O_5 and MoO_3 are volatile under the methanol oxidation reaction conditions, which results in catalyst deactivation and pressure built-up in the fixed-bed reactor. It is ultimately the pressure build-up due to the deposition of MoO_3 needles in the lower part of the fixed-bed reactor that determines the life of the commercial catalyst.

4. Conclusions

The comparison of the products distribution of methanol oxidation over bulk metal vanadate and pure metal oxide catalysts revealed that the surface of bulk metal vanadates is composed of vanadium oxide species approaching a surface two-dimensional layer. This surface monolayer is highly selective towards formaldehyde at low and high methanol conversions. Moreover, the stability of bulk metal vanadates under methanol oxidation suggests that the surface vanadium oxide species are anchored to the metal cation similarly to monolayer vanadium supported catalysts.

This study shows for the first time in the literature that methanol is a selective chemical probe for the quantification and determination of the nature of the surface active sites of bulk metal vanadates. The determination of the density of surface active sites through methanol chemisorption enables the calculation of the catalytic activity per active site (TOF). The specific activity allows the comparison of the catalytic activity of different materials based on the properties of their surface active sites.

Bulk metal vanadate catalysts possess similar TOF as V_2O_5 and monolayer vanadium supported catalysts and different to pure metal oxide catalysts. This observation gives further evidences that the surface of bulk metal vanadates is composed primarily by vanadium oxide species. These surface vanadium oxide species VO_x are more active than molybdenum oxide species MoO_x according to the lower TOFs of

MoO_3 and bulk metal molybdates than vanadium oxide based catalysts.

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References

- [1] L.E. Briand, W.E. Farneth, I.E. Wachs, *Catal. Today* 62 (2000) 219.
- [2] L.E. Briand, I.E. Wachs, *Stud. Sci. Catal.* 130 (2000) 305.
- [3] L.G. Burcham, L.E. Briand, I.E. Wachs, *Langmuir* 17 (2001) 6164.
- [4] L.G. Burcham, L.E. Briand, I.E. Wachs, *Langmuir* 17 (2001) 6175.
- [5] L.E. Briand, A.M. Hirt, I.E. Wachs, *J. Catal.* 202 (2001) 268.
- [6] M. Badlani, I.E. Wachs, *Catal. Lett.* 75 (2001) 137.
- [7] L.E. Briand, I.E. Wachs, US (Patent Pending) Provisional Application No. 60/341284.
- [8] S.R.G. Carrazán, C. Peres, J.P. Bernard, M. Rowet, P. Ruiz, B. Delmon, *J. Catal.* 158 (1996) 452.
- [9] V. Soenen, J.M. Herrmannand, J.C. Volta, *J. Catal.* 159 (1996) 410.
- [10] C.T. Au, W.D. Zhang, L.H. Wan, *Catal. Lett.* 37 (1996) 241.
- [11] O.S. Owen, H.H. Kung, *J. Mol. Catal.* 79 (1993) 265.
- [12] G. Saracco, V. Serra, C. Badini, V. Specchia, *Ind. Eng. Chem. Res.* 36 (1997) 2051.
- [13] C. Badini, G. Saracco, V. Serra, *Appl. Catal. B* 11 (1997) 307.
- [14] L.E. Briand, L.A. Gambaro, H.J. Thomas, *J. Catal.* 161 (1996) 839.
- [15] J.-M. Tatibouët, *Appl. Catal.* 148 (1997) 213.
- [16] C. Louis, J.-M. Tatibouët, M. Che, *J. Catal.* 109 (1988) 354.
- [17] L.E. Briand, I.E. Wachs, US Patent No. 6,037,290 (March 14, 2000).
- [18] A. Gibbson, I.E. Wachs, L.E. Briand, Proceedings of the AIChE Annual Meeting, Reno-NV, November 4–9, Paper 360 h, 2001.