

Quantification of Active Sites for the Determination of Methanol Oxidation Turn-over Frequencies Using Methanol Chemisorption and in Situ Infrared Techniques.

2. Bulk Metal Oxide Catalysts

Lloyd J. Burcham,[†] Laura E. Briand,[‡] and Israel E. Wachs*.[§]

Zettlemoyer Center for Surface Studies and Department of Chemical Engineering,
Lehigh University, Bethlehem, Pennsylvania 18015, and Centro de Investigacion y
Desarrollo en Procesos Cataliticos, Universidad Nacional de La Plata, Calle 47 No. 257,
(1900) La Plata, Argentina

Received January 4, 2001. In Final Form: May 8, 2001

Bulk metal oxide catalysts, especially bulk mixed-metal molybdates such as $\text{Fe}_2(\text{MoO}_4)_3$, often exhibit high methanol oxidation activity and selectivity. However, the difficulties involved in determining active surface site densities on these catalysts have, in the past, generally prevented side-by-side comparisons of their *intrinsic* activities, or turn-over frequencies (TOFs). In the present study, high temperature (110 °C) methanol chemisorption and in-situ infrared spectroscopy have been employed to directly and quantitatively determine the number of active metal oxide surface sites available for methanol oxidation. The IR spectra indicate that methanol chemisorption on these catalysts produces both associatively adsorbed, intact Lewis-bound surface methanol species ($\text{CH}_3\text{OH}_{\text{ads}}$, species I) on acidic sites, as well as dissociatively adsorbed surface methoxy species ($-\text{OCH}_3$, species II) on less acidic or basic sites. In fact, the Lewis acidity of bulk mixed-metal molybdates *relative to the methanol probe molecule* was found to decrease as follows: $\text{Fe}_2(\text{MoO}_4)_3$, NiMoO_4 (species I predominates) > MnMoO_4 , CoMoO_4 , ZnMoO_4 , $\text{Al}_2(\text{MoO}_4)_3$ > $\text{Ce}(\text{MoO}_4)_2$ > $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ > $\text{Zr}(\text{MoO}_4)_2$ (species II predominates). It also appears that Mo cations are the primary methanol chemisorption sites in many of the bulk mixed-metal molybdates, including commercially important $\text{Fe}_2(\text{MoO}_4)_3$. By quantifying the surface concentrations of the adsorbed methoxylated reaction intermediates from the IR spectra, it was then possible to normalize the catalytic methanol oxidation activities for the calculation of TOFs. The methanol oxidation TOFs of bulk molybdates were shown to be relatively similar to those of model supported catalysts with the same co-cation (e.g., MoO_3/NiO vs NiMoO_4)—possibly due to the formation of a “monolayer” of surface molybdenum oxide species on the surfaces of the bulk metal molybdates. In addition, the bulk mixed-metal molybdates were found to exhibit the same ligand effect as that discovered previously in supported metal oxide catalysts, in which the TOF generally decreases with increasing ligand cation electronegativity due to electronic variations in localized M–O–Ligand bonds.

Introduction

Bulk metal oxide catalysts are commercially important for the production of formaldehyde, especially $\text{Fe}_2(\text{MoO}_4)_3$ – MoO_3 mixtures and other bulk mixed-metal molybdates.^{1,2} However, the development of fundamental structure–reactivity relationships in these systems has been limited by the difficulty involved in determining the number of active metal oxide surface sites present during reaction. Such knowledge is critical for the calculation of methanol oxidation turn-over frequencies over bulk metal oxides (TOF = methanol molecules converted to formaldehyde per second per *active surface metal oxide site*). The TOFs themselves are important because they provide the best basis for comparison of intrinsic catalytic activities between different catalysts.^{2–4} Active surface site density

measurements for metal and supported metal catalysts are often made using the chemisorption of CO , H_2 , and O_2 probe molecules to quantify the active metal surface area,^{2–4} but the chemisorption of these traditional probe molecules on metal oxides is more difficult. Instead, the use of methanol as a chemisorption probe molecule provides a more feasible method for quantifying active surface site densities in metal oxide catalysts, since methanol is easily chemisorbed onto metal oxide surfaces. Moreover, the chemisorbed methoxylated surface species have been shown to be the reactive surface intermediates in methanol oxidation.^{5,6} Thus, methanol is also the ideal probe molecule for titration of the specific metal oxide surface sites involved in methanol oxidation.

In part 1 of the present two-paper series,⁷ an IR spectroscopy-based methodology was developed for quantitative methanol chemisorption using supported metal oxides as model systems. Supported metal oxide catalysts consist of an active metal oxide (MoO_3 , V_2O_5 , Cr_2O_3 , Nb_2O_5 , Re_2O_7 , WO_3 , etc.) molecularly dispersed as a spectroscopically distinguishable, two-dimensional surface metal oxide overlayer on a high surface area oxide support (Al_2O_3 ,

* Corresponding author. Phone: 610-758-4274. Fax: 610-758-6555. E-mail: ieuw0@lehigh.edu.

[†] Present address: Congoleum Corporation, P.O. Box 3127, Mercerville, NJ 08619.

[‡] Centro de Investigacion y Desarrollo en Procesos Cataliticos.
[§] Zettlemoyer Center for Surface Studies and Department of Chemical Engineering.

(1) Gerberich, H. R.; Seaman, G. C. Formaldehyde. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John Wiley and Sons: New York, 1994; Vol. 11, pp 929–951.

(2) Tatibouët, J. M. *Appl. Catal. A* **1997**, *148*, 213.

(3) Thomas, J. M.; Thomas, W. J. *Principles and Practice of Heterogeneous Catalysis*; VCH Publishers: New York, 1997.

(4) Ribeiro, F. H.; Schach von Wittenau, A. E.; Bartholomew, C. H.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* **1997**, *39*, 49.

(5) Holstein, W. L.; Machiels, C. J. *J. Catal.* **1996**, *162*, 118.

(6) Burcham, L. J.; Wachs, I. E. *Catal. Today* **1999**, *49*, 467.

(7) Burcham, L. J.; Briand, L. E.; Wachs, I. E. *Langmuir* **2001**, *17*, 6164.

SiO₂, TiO₂, ZrO₂, CeO₂, MgO, etc.). For such supported metal oxide catalysts, previous studies had taken the number of metal oxide metal atoms deposited on the oxide support surface to be the number of active surface sites.^{8,9} However, using methanol chemisorption and IR techniques it was found in part 1⁷ that a steric limitation of about 0.3 methoxylated surface species exists per active deposited metal oxide metal atom across all supported metal oxides. Methanol oxidation TOFs calculated using these new methanol chemisorption surface site densities were about 3 times higher than the TOFs previously estimated using the total number of deposited metal oxide metal atoms. Nevertheless, the fundamental support effect observed previously (TOFs for MoO₃ and V₂O₅ supported on oxides of Zr ~ Ce > Ti > Al ≫ Si) remained virtually unchanged as a general trend and correlated with the support cation electronegativity—most likely through the bridging M—O—Support bonds.⁷

For bulk metal oxides, it is generally more difficult to distinguish, spectroscopically or otherwise, the active surface metal oxide sites from the metal—oxygen bonds present within the framework lattice structure. Bulk metal oxide active site densities and methanol oxidation TOF's have been occasionally reported using crystal structure models¹⁰ or by gravimetric methanol chemisorption,^{11–13} but a generally accepted method has not yet been developed. Many authors^{14–23} propose oxygen chemisorption as a general method, in which the bulk (or supported) catalyst is reduced only at the surface and then reoxidized to determine the number of surface active metal oxide sites by the amount of oxygen consumed. However, this technique is very sensitive to over-reduction beyond the surface layer and is rather indirect.^{17,24–26} Another proposed method is the benzaldehyde-ammonia titration (BAT), in which benzaldehyde is selectively chemisorbed only on basic sites associated with inactive oxide supports (oxides of Al, Ti, Zr, etc.) and the benzonitrile produced by subsequent NH₃ flow is used to quantify the exposed inactive and active surface areas.^{27–29} However, this

indirect method also suffers from nonselective adsorption and assumptions regarding the spatial dimensions of the surface active sites in the active surface area.²⁶ In all of these cases, the probe molecules employed are quite different from the organic molecules typically involved in oxidation reactions.

The works of Farneth et al.^{11–13} on bulk MoO₃ and Sleight et al.³⁰ on Fe₂(MoO₄)₃ were perhaps the first to suggest that quantitative methanol chemisorption may be a viable method for determining the active site density in bulk metal oxides. Gas-phase methanol is well-known to chemically adsorb on oxide surfaces at low temperatures (<150 °C) to form stable methoxy (–OCH₃) surface species.^{31–33} At higher temperatures these methoxy surface species have been shown to be the reactive intermediates in methanol oxidation.^{5,32,33} By gravimetrically measuring the amount of methanol uptake at saturation during chemisorption on MoO₃ and Fe₂(MoO₄)₃ powders, these authors found that the isotropic ferric molybdate contained slightly higher saturation site densities than the layered structure of MoO₃. They concluded that all surface Mo cations are active for methanol adsorption in the molybdate, but only 12% of Mo surface cations adsorb methanol in MoO₃ and only on the non-(010) planes. These authors also found that the methanol adsorption stoichiometry to surface methoxy species and water must be incorporated into any quantitative chemisorption measurements that are obtained gravimetrically. In their case, the water produced by adsorption was quantified by trapping methods. However, these studies were further complicated by performing the initial methanol adsorption at room temperature, since both physically adsorbed methanol and chemisorbed surface methoxy species were produced under these conditions. A summary of additional IR, calorimetric, gravimetric, and volumetric methanol adsorption studies on metal oxides may be found in the introduction of part 1⁷ in the present two-paper series.⁷

The primary objective of the present study (part 2 of the present two-paper series) is to determine the number of active surface metal oxide sites in bulk metal oxide catalysts using the quantitative methanol chemisorption and infrared spectroscopy titration method developed previously on supported metal oxides in part 1.⁷ Infrared spectroscopy has been chosen as the detection method, in part, because the adsorbed surface methoxy species produce strong IR signals. More importantly, and unlike other “blind” gravimetric, calorimetric, or volumetric methods that require assumptions about adsorption stoichiometry or separate experimental measurements to account for water produced upon adsorption, the use of IR spectroscopy can quantify the surface methoxy species directly. Methanol has been chosen as the probe molecule because of its high reactivity toward oxides (unlike CO, H₂, and O₂) and its relevance to the methanol oxidation reaction. The second objective of this study is

(8) Wachs, I. E.; Deo, G.; Vuurman, M. A.; Hu, H.; Kim, D. S.; Jehng, J. M. *J. Mol. Catal.* **1993**, *82*, 443.

(9) Wachs, I. E. *Catal. Today* **1996**, *27*, 437.

(10) Hu, H.; Wachs, I. E. *J. Phys. Chem.* **1995**, *99*, 10911.

(11) Farneth, W. E.; McCarron, E. M.; Sleight, A. W.; Staley, R. H. *Langmuir* **1987**, *3*, 217.

(12) Farneth, W. E.; Staley, R. H.; Sleight, A. W. *J. Am. Chem. Soc.* **1986**, *108*, 2327.

(13) Farneth, W. E.; Ohuchi, F.; Staley, R. H.; Chowdhry, U.; Sleight, A. W. *J. Phys. Chem.* **1985**, *89*, 2493.

(14) Desikan, A. N.; Huang, L.; Oyama, S. T. *J. Phys. Chem.* **1991**, *95*, 10050.

(15) Chary, K. V. R.; Vijayakumar, V.; Rao, P. K. *Langmuir* **1990**, *6*, 1549.

(16) Reddy, B. M.; Chary, K. V. R.; Rama Rao, B.; Subrahmanyam, V. S.; Sunandana, C. S.; Nag, N. K. *Polyhedron* **1986**, *5*, 191.

(17) Majunke, F.; Baerns, M.; Baiker, A.; Koepfel, R. A. *Catal. Today* **1994**, *20*, 53.

(18) Rao, P. K.; Narasimha, K. *ACS Symp. Ser.* **1993**, *523*, 231.

(19) Chary, K. V. R. *J. Chem. Soc., Chem. Commun.* **1989**, 104.

(20) Reddy, B. M.; Manohar, B.; Reddy, E. P. *Langmuir* **1993**, *9*, 1781.

(21) Chary, K. V. R.; Rao, B. R.; Subrahmanyam, V. S. *Appl. Catal.* **1991**, *74*, 1.

(22) Arena, F.; Frusteri, F.; Parmaliana, A. *Appl. Catal. A* **1999**, *176*, 189.

(23) Nag, N.; Chary, K.; Subrahmanyam, V. *J. Chem. Soc., Chem. Commun.* **1986**, 1147.

(24) Faraldos, M.; Anderson, J. A.; Banares, M. A.; Fierro, J. L. G.; Weller, S. W. *J. Catal.* **1997**, *168*, 110.

(25) Tanabe, S.; Davis, H. E.; Wei, D.; Weber, R. S. In *Studies in Surface Science and Catalysis (Proceedings of the 11th International Congress on Catalysis)*; Hightower, J. W., Delgass, W. N., Iglesia, E., Bell, A. T., Eds.; Elsevier: Amsterdam, 1996; Vol. 101, p 337.

(26) Deo, G.; Wachs, I. E.; Haber, J. *Crit. Rev. Surf. Chem.* **1994**, *4*, 141.

(27) Niwa, M.; Sano, M.; Yamada, H.; Murakami, Y. *J. Catal.* **1995**, *151*, 285.

(28) Yamada, H.; Niwa, M.; Murakami, Y. *Appl. Catal. A* **1993**, *96*, 113.

(29) Niwa, M.; Yamada, H.; Murakami, Y. *J. Catal.* **1992**, *134*, 331.

(30) Cheng, W.-H.; Chowdhry, U.; Ferretti, A.; Firment, L. E.; Groff, R. P.; Machiels, C. J.; McCarron, E. M.; Ohuchi, F.; Staley, R. H.; Sleight, A. W. in *Heterogeneous Catalysis (Proceedings of the Second Symposium of the IUCCP of the Department of Chemistry, Texas A&M)*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1984; p 165.

(31) Lavalley, J. C. *Catal. Today* **1996**, *27*, 377.

(32) Busca, G. *Catal. Today* **1996**, *27*, 457.

(33) Busca, G.; Elmi, A. S.; Forzatti, P. *J. Phys. Chem.* **1987**, *91*, 5263.

to calculate methanol oxidation TOFs over a wide range of bulk metal oxide catalysts, including commercially important bulk molybdate catalysts. These TOF calculations will, for the first time, allow for direct comparisons of the *intrinsic* methanol oxidation activities in bulk and supported metal oxides (supported metal oxide TOFs having been obtained in part 1⁷), and will hopefully shed new insight into the previously masked structure–reactivity relationships of bulk metal oxides. It is of particular interest to ascertain whether the same ligand effect occurs in bulk molybdate catalysts as was observed upon varying the oxide support in supported metal oxides.

2. Experimental Section

2.1. Catalyst Preparation. Some of the pure bulk metal oxides were obtained from commercial sources (γ -Al₂O₃ with 180 m²/g from Harshaw, P-25 TiO₂ with 55 m²/g from Degussa, CeO₂ with 36 m²/g from Engelhard, SiO₂ with 320 m²/g from Cabot, ZrO₂ with 39 m²/g from Degussa, and Bi₂O₃ and ZnO from Aldrich). Other pure bulk metal oxides were prepared by thermal decomposition at 400 °C of hydrated precursors (WO₃ from H₂-WO₄, Eastman Chemicals; Nb₂O₅ from Nb₂O₅ · nH₂O, Niobium Products Co.) or of nitrate or alkoxide precursors for NiO, Fe₂O₃, MoO₃, and V₂O₅. Bulk mixed-metal molybdates were prepared from the same precursors using a coprecipitation technique that is described in detail elsewhere,³⁴ and supported metal oxides were prepared according to the methods described in part 1 of the present two-paper series.⁷ Phase purities were determined by XRD and Raman spectroscopy (see ref 35 for experimental details), and surface areas were determined with BET instrumentation (Quantasorb model OS-9).

2.2. In Situ Infrared Experiments and Methanol Oxidation Activity. The in-situ infrared experiments were performed with a BioRad FTS-40A FTIR spectrometer equipped with a DTGS detector. The IR was operated in transmission mode using a specially designed in-situ cell that has been previously described.⁶ Calibration of the surface methoxy IR signal was achieved by quantitatively dosing known amounts of methanol (Alfa Aesar, semiconductor grade) onto the catalysts at 110 °C under vacuum, using a system and procedure described in detail in part 1.⁷ The stepwise quantitative adsorption was carried out at 110 °C to ensure that the methanol only adsorbed as surface methoxy species (otherwise, the known μ moles of methanol introduced onto the sample would not correspond to the μ moles of surface methoxy species). At lower adsorption temperatures, the methanol adsorbs to form both surface methoxy species and physisorbed methanol, while at higher temperatures the surface methoxy species react to form formaldehyde and other products. Catalytic data were obtained using an isothermal fixed-bed reactor operated under differential conditions, following a similar procedure as described in ref 36 and in part 1.⁷ Methanol oxidation was performed at 380 °C for bulk molybdates and at 300 °C for pure bulk oxides.

3. Results

3.1. IR Spectra and Band Assignments. The experimental results and calculations are presented in Figures 1–6 and in Tables 1–3. The IR spectra of the surfaces prior to CH₃OH adsorption have been subtracted from the spectra of methanol-exposed surfaces in order to isolate the surface signals arising from methanol chemisorption. As indicated in Figures 1 and 2, the IR spectra in the C–H stretching region exhibit four intense, sharp bands at \sim 2960/2935 and \sim 2850/2835 cm⁻¹, as well as two weak and broad bands at \sim 2895 and \sim 2991 cm⁻¹, all due to the presence of methoxylated surface species. Additional bands appear in the lower frequency region at \sim 1460, \sim 1440, \sim 1370, \sim 1160, and \sim 1050 cm⁻¹ (see Table

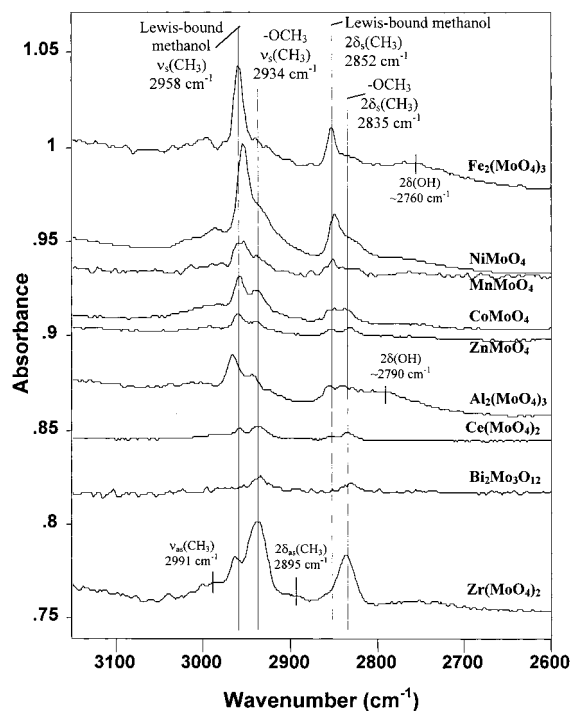


Figure 1. Difference spectra (normalized to 10 mg) of adsorbed methoxylated surface species on bulk molybdate catalysts in the C–H stretching region.

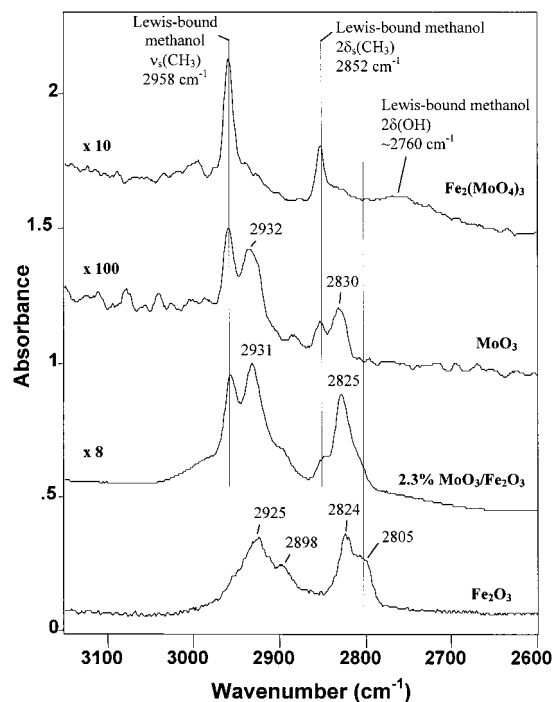


Figure 2. Difference spectra (normalized to 10 mg) of adsorbed methoxylated surface species on Mo–Fe oxide catalysts in the C–H stretching region.

1). It was shown in part 1 of the present two-paper series⁷ that these IR bands arise from two distinctly different methoxylated surface species: an intact, methanol-like species (species I) and a dissociated surface methoxy species (species II, –OCH₃). It was also shown in part 1⁷ and by other authors^{31,32,37–40} that species I is best described as a strongly Lewis-coordinated methanol

(34) Briand, L.; Gambaro, L.; Thomas, H. *J. Catal.* **1996**, *161*, 839.

(35) Burcham, L. J.; Wachs, I. E. *Spectrochim. Acta Part A* **1998**, *54*, 1355.

(36) Deo, G.; Wachs, I. E. *J. Catal.* **1994**, *146*, 323.

(37) Busca, G.; Rossi, P. F.; Lorenzelli, V.; Benaissa, M.; Travert, J.; Lavalley, J.-C. *J. Phys. Chem.* **1985**, *89*, 5433.

Table 1. IR Frequencies (cm⁻¹) of Adsorbed Methoxylated Surface Species on Bulk Metal Oxide Catalysts after Saturation with 10 Torr of Methanol and Subsequent Evacuation (I = Species I; II = Species II)

catalyst	$\nu_{\text{as}}(\text{CH}_3)^a$	$\nu_{\text{s}}(\text{CH}_3)$		$2\delta_{\text{as}}^b$	$2\delta_{\text{s}}(\text{CH}_3)$		δ_{as}	δ_{s}	$\delta(\text{OH})$	$r(\text{CH}_3)^b$	$\nu_{\text{s}}(\text{CO})$
		I	II		I	II					
Fe ₂ (MoO ₄) ₃	2996	2958			2852		1462	1445	1335	1168	1052 ^a 1090
CoMoO ₄	2989	2958	2938		2852	2836	1446	1439	1381	1157	1056 1105
NiMoO ₄	2985	2953	2934 ^a	2894	2849	2826 ^a	1462	1447	1367	1175	1115 ^b 1057 ^b
MnMoO ₄	2984	2955	2938 ^a	2905	2851	2825 ^a	1469	1442	1389		1059 ^b 1116 ^b
ZnMoO ₄	2991	2959	2939	2901	2853	2832	1469	1447	1381		1071 ^b 1112 ^b
Bi ₂ Mo ₃ O ₁₂	2976		2935	2891		2830	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
Al ₂ (MoO ₄) ₃	3005	2965	2943	2923	2854	2840	1461	1447	1399	<i>c</i>	<i>c</i>
Ce(MoO ₄) ₂	2983	2958	2937	2893	2854	2835	1449	1439	1375	1150	1052 1115 ^b
Zr(MoO ₄) ₂	2991	2962 ^b	2937	2895	2857 ^a	2836	1449 ^d	1449 ^d		1186	1063 1142
Al ₂ O ₃	2978	2955 ^a	2941	2899	2839 ^a	2820	1477	1455		1189	1098 1035 ^a
Bi ₂ O ₃	2989		2912	2855		2787	1459	1440			1041 1094 ^b
CeO ₂	2979	2948	2919	2889	2842	2811	1463	1450		1197	1111 1048 1021
Fe ₂ O ₃		2925	2898 ^a		2824	2805 ^a	1460	1439			1071 1024 ^a 1155 ^b
MoO ₃		2958	2932	2882	2852	2830	1440 ^d	1440 ^d	1364	1176	1062 1123 ^b
Nb ₂ O ₅	2995	2955 ^a	2928	2891		2829	1451	1437		1151 ^a	1109 1036 ^a
NiO	2947	2913	2875	2860	2805	2791 ^a	1422 ^d	1422 ^d			1095 1069
SiO ₂	2997	2960		2928	2860		1478	1463	<i>c</i>	<i>c</i>	<i>c</i>
TiO ₂	2978	2948	2924	2891	2843 ^a	2822	1457	1438	1367	1155	1121 1054
V ₂ O ₅			2922	2887		2827	1445	1429		1149	1059
WO ₃	2988	2955	2932	2910	2848	2834	1459	1443	1391	1157	1121
ZnO			2932	2906		2819	<i>c</i>	<i>c</i>	<i>c</i>	1184	1054
ZrO ₂	2947		2925	2903		2818	1465 ^d	1465 ^d		1161	1059

^a Shoulder. ^b Very weak. ^c Opaque region. ^d Broad and unresolved.

adduct on surface metal cations (Lewis acid sites), and not to weakly bound physisorbed methanol as has been previously suggested.^{41–44}

According to Busca et al.^{32,33} and Lavalley et al.,⁴⁵ the bands at 2930 and 2830 cm⁻¹ are assigned to dissociated species II and arise from Fermi resonance between the symmetric stretch (ν_{s}) and first overtone of the symmetric bend ($2\delta_{\text{s}}$) of CH₃ units in adsorbed OCH₃ species, respectively. The unusual intensity of these symmetric stretching bands is attributed to the Fermi resonance occurring between them.³³ The bands at 2950 and 2850 cm⁻¹ are assigned to the same modes occurring in the undissociated species I. The less-resolved and weaker shoulder around 2990 cm⁻¹ is assigned to the asymmetric stretch (ν_{as}) of the CH₃ units in these methoxylated surface species, and the broad and weak band at ~2900 cm⁻¹ is due to the overtone of the asymmetric -CH₃ bend ($2\delta_{\text{as}}$)

in these species. Low-frequency modes (see Table 1) are assigned to CH₃ bending vibrations at 1460 cm⁻¹ (δ_{as}) and 1440 cm⁻¹ (δ_{s}), and to C–O stretching modes at ~1050 cm⁻¹ (ν_{s}). Finally, the vibrational bands associated with the OH group of intact species I include a strong band at ~1370 cm⁻¹ due to an OH bending mode, $\delta(\text{O–H})$; the overtone of this band, $2\delta(\text{O–H})$, at ~2760 cm⁻¹; and O–H stretching modes, $\nu(\text{O–H})$, in the region 3100–3500 cm⁻¹.^{31,32,37–40}

As is apparent from Figures 1 and 2, greater or comparable IR band intensities of the intact, surface Lewis-bound species I relative to the dissociated surface methoxy species II is generally observed for the bulk mixed-metal molybdates. A similar trend was also observed for supported-MoO₃ catalysts at monolayer coverages.⁷ Nevertheless, the Zr(MoO₄)₂ (Figure 1), Bi₂Mo₃O₁₂ (Figure 1) and 2.3% MoO₃/Fe₂O₃ (Figure 2) catalysts exhibit greatest band intensities at 2930/2830 cm⁻¹ due to dissociated surface methoxy species II, which is similar to the behavior found previously for supported-V₂O₅ and supported-Nb₂O₅ catalysts at monolayer coverage.⁷ These differences in the relative ratios of surface species I to species II in bulk and supported mixed-metal oxides after methanol chemisorption were shown in part 1⁷ to be related to differences in the Lewis acidities of the metal oxide adsorption sites. Acidic sites generally favor the formation of intact, Lewis-bound surface methoxylated species I, while basic sites favor the formation of dissoci-

(38) (a) Borello, E.; Zecchina, A.; Morterra, C. *J. Phys. Chem.* **1967**, *71*, 2938. (b) Borello, E.; Zecchina, A.; Morterra, C.; Ghiotti, G. *J. Phys. Chem.* **1967**, *71*, 2945.

(39) Ramis, G.; Busca, G.; Lorenzelli, V. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 1591.

(40) Busca, G.; Lorenzelli, V. *J. Catal.* **1980**, *66*, 155.

(41) Groff, R. P. *J. Catal.* **1984**, *86*, 215.

(42) Beebe, T. P.; Crowell, J. E.; Yates, J. T. *J. Phys. Chem.* **1988**, *92*, 1296.

(43) Groff, R. P.; Manogue, W. H. *J. Catal.* **1984**, *87*, 461.

(44) Spitz, R. N.; Barton, J. E.; Barteau, M. A.; Staley, R. H.; Sleight, A. W. *J. Phys. Chem.* **1986**, *90*, 4067.

(45) Lavalley, J. C.; Sheppard, N. *Spectrochim. Acta.* **1972**, *28A*, 2091.

ated methoxy surface species II (see Discussion section for more details).

The pure bulk oxides also exhibit clear distinctions in the nature of the methoxylated surface species formed upon methanol chemisorption based on whether the catalyst is a primarily basic (ionic) or primarily acidic (covalent) oxide.⁴⁶ Table 1 indicates that the basic oxides (Bi₂O₃, Fe₂O₃, NiO, ZnO, and ZrO₂) do not adsorb methanol as intact, Lewis-bound surface species because no bands are detected at 2950/2850 cm⁻¹, nor at ~1370 cm⁻¹. Moreover, the basicity of these oxides not only favors methanol dissociation but also the formation of ionic surface methoxide species, (CH₃O)⁻, with relatively low-frequency C–H stretching modes (~2910/2800 cm⁻¹). The presence of multiple dissociated surface methoxy species is also indicated by multiple C–O stretching bands in the region 1050–1150 cm⁻¹ and by multiple C–H stretching bands in the region 2900–2940 and 2800–2825 cm⁻¹. Other authors^{32,47,48} have assigned these multiple dissociated surface methoxy species to terminal and bridged methoxy groups, bridged methoxies generally possessing the lower C–O stretching vibrations.

Conversely, the covalent and Lewis-acidic oxides (Al₂O₃, MoO₃, Nb₂O₅, SiO₂, WO₃, and V₂O₅) and the amphoteric oxides (TiO₂, CeO₂) produce dissociated surface methoxy species with higher C–H stretching frequencies (2930/2830 cm⁻¹), as well as intact Lewis-bound species with C–H stretches at 2950/2850 cm⁻¹. Busca et al.^{32,33} and Lavalley et al.⁴⁵ have also noted that the relative intensity of the CH₃ stretching modes to the CH₃ bending modes is generally much lower for covalent metal oxides and much higher for the basic, ionic metal oxides that form ionic methoxide species (bending modes barely detectable). Multiple C–O vibrations in some cases (e.g., MoO₃) again suggest multiple methoxylated surface species, but it is difficult to assign these low-frequency modes specifically to dissociated or intact species. Assignments of C–O vibrations to specific methoxylated surface species is also complicated by a CH₃ rocking mode around 1150 cm⁻¹ and, in supported metal oxides, by the metal–oxygen double bonds found around 980–1030 cm⁻¹.^{8,9} Therefore, assignments given in Table 1 for the C–O stretching region should be taken as tentative.

3.2. Quantification of Adsorbed Methoxylated Surface Species. Quantification of the number of active metal oxide sites by methanol chemisorption was performed using the procedure described in part 1⁷ of the present two-paper study,⁷ so only a brief description is given here. The IR band intensities associated with the methoxylated surface species (species I and II) were calibrated by determining the integrated molar extinction coefficient, or IMEC, using the volumetric dosing method described by Emeis.⁴⁹ Doses of ~5 Torr of methanol (0.86 μmol CH₃OH in the 3.19 mL dosing volume) were sequentially exposed to the sample, followed by spectrum acquisition after each dose. The IR band intensities of the C–H stretching modes due to adsorbed methoxylated surface species increase with the number of doses until the catalyst surface is saturated with adsorbed methoxylated surface species. Saturation is indicated by a gas-phase methanol band appearing at 2981 cm⁻¹ in the C–H

Table 2. Integrated Molar Extinction Coefficients with 95% Confidence Limits for the 2δ_s(CH₃) Bands in the 2800–2850 cm⁻¹ Region over Bulk Metal Oxide Catalysts

Bulk Metal Oxides	
catalyst	IMEC (cm/μmol)
Fe ₂ (MoO ₄) ₃	2.42 ± 39%
CoMoO ₄	1.58 ± 39%
NiMoO ₄	0.67 ± 10%
MnMoO ₄ ^a	3.89 ± 58%
ZnMoO ₄	0.92 ± 21%
Bi ₂ Mo ₃ O ₁₂ ^a	2.34 ± 99%
Al ₂ (MoO ₄) ₃	4.56 ± 9.8%
Ce(MoO ₄) ₂	0.44 ± 6.4%
Zr(MoO ₄) ₂	3.48 ± 51%
Al ₂ O ₃	1.38 ± 1.9%
Bi ₂ O ₃ ^b	~24
CeO ₂ ^a	28.8 ± 52%
Fe ₂ O ₃	1.78 ± 25%
MoO ₃ ^b	~0.9
Nb ₂ O ₅	0.99 ± 6.7%
NiO	1.69 ± 40%
SiO ₂	0.48 ± 13%
TiO ₂	1.53 ± 12%
V ₂ O ₅ ^a	1.21 ± 71%
WO ₃	0.67 ± 5.3%
ZnO ^b	~4.3
ZrO ₂	3.44 ± 12%

^a Denotes 68% confidence limits. ^b Confidence limits not reported (only two data points available).

stretching region and a much stronger band appearing at 1033 cm⁻¹ in the C–O vibrational region. Final saturation of the sample with 10 Torr methanol, followed by evacuation of the gas phase, yields the desired saturation of the catalyst surface by adsorbed methoxylated surface species.

The IMEC values were calculated by collectively integrating the IR bands at 2830–2850 cm⁻¹ in the spectra of the initial doses, where a linear relationship exists between the integrated IR band intensity and the number of methanol molecules adsorbed by the catalyst surface. More specifically, the linear relationship is Beer's law and the slope is the IMEC. The IR bands in the region 2830–2850 cm⁻¹ were collectively chosen as the best signal for quantification because they are well-defined and have relatively little overlap with other vibrational bands in the spectra. The IMECs determined by this method are presented in Table 2 for methoxylated surface species on bulk mixed-metal molybdates and on pure bulk metal oxides with 95% confidence limits (also see part 1⁷ for additional error estimations based on analysis of equilibrium methanol adsorption isotherm data). Note that the variation in IMEC values is most likely due to the combined effects of radiation scattering, particle size effects, compositional effects, and other phenomenon, but that the present interest in IMECs concerns their use as a signal calibration. Therefore, the IMECs reported in Table 2 are given primarily as illustration of the signal calibration methodology, although they could also be used as a starting point for future studies regarding IMEC variations in adsorbed methoxylated surface species.

Last, the amount of methanol chemisorbed on the catalysts after final saturation was calculated from the integrated absorbances of the saturated spectra by using the IMEC values obtained from the initial doses. From these calculations it was possible to determine the catalyst site densities (sites per m²) and methanol oxidation turnover frequencies (TOFs, the activities per site), both of which are presented in Table 3. Note that the process of compressing the catalyst powders into thin IR wafers was previously found to have essentially no effect on the microporosity or number of accessible sites.⁷ Also, com-

(46) Ai, M. *J. Catal.* **1978**, *54*, 426.

(47) (a) Badri, A.; Binet, C.; Lavalley, J.-C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1159. (b) Binet, C.; Daturi, M.; Lavalley, J.-C. *Catal. Today* **1999**, *50*, 207.

(48) (a) Ouyang, F.; Kondo, J. N.; Maruya, K.; Domen, K. *J. Phys. Chem. B* **1997**, *101*, 4867. (b) Ouyang, F.; Kondo, J. N.; Maruya, K.; Domen, K. *Catal. Lett.* **1998**, *50*, 179.

(49) Emeis, C. A. *J. Catal.* **1993**, *141*, 347.

Table 3. Site Densities (with 95% Confidence Limits) and Methanol Oxidation TOFs for Bulk Molybdate (380 °C) and Bulk Metal Oxide Catalysts (300 °C)^a

catalyst	$S_{\text{bet}} = \text{m}^2/\text{gram}$	$N_s = \mu\text{mol OCH}_3/\text{m}^2$	activity at 380 or 300 °C = $\mu\text{mol}/\text{m}^2 \text{ s}$	% selectivity to oxidation products	TOF at 380 or 300 °C = s^{-1}
Fe ₂ (MoO ₄) ₃	9.6	2.50 ± 19%	9.6	61	2.34
CoMoO ₄	5.5	3.66 ± 24%	4.4	88	1.06
NiMoO ₄	39.1	2.75 ± 4.2%	2.6	100	0.95
MnMoO ₄ ^b	1.9	3.59 ± 41%	20.6	99	5.68
ZnMoO ₄	2.1	7.08 ± 9.6%	18.2	87	2.24
Bi ₂ Mo ₃ O ₁₂ ^b	0.22	19.9 ± 76%	23.4	100	1.18
Al ₂ (MoO ₄) ₃	11.2	2.35 ± 4.6%	9.4	26	1.04
Ce(MoO ₄) ₂	4.0	6.65 ± 3.4%	46.5	87	6.09
Zr(MoO ₄) ₂	31.0	0.74 ± 22%	36.0	65	31.5
Al ₂ O ₃	180	3.79 ± 1.0%	3.79	0.00	0.00
Bi ₂ O ₃ ^c	0.22	~11.5	115	20	2.00
CeO ₂ ^b	2.4	1.96 ± 24%	0.58	100	0.30
Fe ₂ O ₃	21.4	7.83 ± 8.5%	16.6	64	1.36
MoO ₃ ^{c,d}	4.8	~0.85	0.52	88	0.54
Nb ₂ O ₅	96.8	2.85 ± 3.9%	0.14	0.00	0.00
NiO	43.2	4.22 ± 12%	34.1	83	6.70
SiO ₂	320	0.18 ± 7.1%	0.0002	77 (CO ₂)	0.00
TiO ₂	55	4.14 ± 6.1%	0.01	9.0 (CO _x)	0.00
V ₂ O ₅ ^b	3.5	5.82 ± 27%	9.72	90	1.50
WO ₃	14.7	3.14 ± 1.7%	0.63	0.00	0.00
ZnO ^c	8.9	~1.3	1.36	46	0.49
ZrO ₂	39	2.16 ± 3.1%	0.04	50	0.01

^a Note that TOF = [(activity)(selectivity)]/ N_s . ^b Denotes 68% confidence limits. ^c Confidence limits not reported (only two data points available). ^d For reference, the methanol oxidation TOF for MoO₃ at 380 °C is 4.45 s⁻¹.

parative methanol oxidation TOF observations of supported metal oxide catalysts have indicated that both types of methoxylated surface species, i.e., species I and species II, are likely involved in methanol oxidation over metal oxides (see part 1⁷). Consequently, the TOFs in Table 3 were calculated using the *total* site densities of methoxylated surface species as obtained by integrating all bands in the *region* 2800–2850 cm⁻¹.

4. Discussion

4.1. Methanol Chemisorption as a Mixed-Metal Oxide Surface Probe. The results above indicate that methanol chemisorption on bulk mixed-metal oxide catalysts produces both associatively adsorbed, intact Lewis-bound surface methanol species (CH₃OH_{ads}, species I), as well as dissociatively adsorbed surface methoxy species (–OCH₃, species II) and surface hydroxyls. In each adsorption pathway, the methoxyl group of methanol must first coordinate or bond with a Lewis acid cation surface site via the methanol oxygen lone pairs, thus requiring that methanol act as a base in this regard. However, the adsorbed methanol may also act as an acid toward an adjacent basic oxygen anion or basic surface hydroxyl by donation of the methanol alcoholic (and, in this case, acidic) proton to form the dissociated methoxy surface species II and either an adjacent surface hydroxyl or water. Alternatively, if the Lewis acid cation to which the methanol methoxyl group is bound is of sufficient strength and is not surrounded by highly basic oxygen anions or basic surface hydroxyls, then the methanol alcoholic proton will remain with the intact, Lewis-bound surface methoxylated species I. As is indicated in Figure 1 and Table 1, many metal oxide surfaces can accommodate both types of adsorbed methoxylated surface species simultaneously, although the relative amounts of each species vary from catalyst to catalyst.

This dual-pathway methanol chemisorption mechanism was similarly found to occur in supported metal oxide catalysts (see part 1⁷ of the present two-paper series⁷), and has been investigated on other metal oxides by Suda et al.,⁵⁰ Farneth et al.,^{11–13} Busca et al.,³³ and others.^{37,51,52} It was also shown in part 1⁷ that the intact, surface Lewis-

bound methanol species (species I) is generally stable to high temperatures (at least 100–200 °C) on Lewis-acidic surfaces even under vacuum. The adsorption temperature of 110 °C employed in part 1⁷ and in the present study, which is well above the boiling point of methanol at and below 1 atm, ensures that methoxylated surface species I is, in fact, a strongly Lewis-bound surface moiety and is *not* due to weakly physisorbed and perhaps multilayered methanol present at room temperature.

Differences in the C–H stretching band frequencies of these adsorbed methoxylated surface species were observed between basic oxides and acidic oxides and permit identification of the specific metal cation involved in methanol chemisorption on mixed metal oxides. In general, the most diagnostic bands for the determination of surface compositions in metal oxides are as follows: (a) the lowest C–H stretching band at ~2800 cm⁻¹, assigned to dissociated and ionic surface methoxide species on basic oxides; (b) the pair of bands having intermediate frequencies at ~2930/2830 cm⁻¹, assigned to dissociated but covalent surface methoxy groups (species II) on less basic oxides; and (c) the highest frequency pair of bands at ~2960/2850 cm⁻¹, assigned to Lewis-bound surface methanol (species I) on acidic oxides. For example, Figure 2 shows that Fe₂(MoO₄)₃ adsorbs methanol preferentially on molybdenum sites, since the C–H stretching bands of the methoxylated surface species on ferric molybdate are distinctly different from those of ionic methoxide on pure Fe₂O₃ but identical to those of intact species I on MoO₃ and 2.3% MoO₃/Fe₂O₃. Similar comparisons suggest Mo cations as the adsorption sites in other mixed metal molybdates, as well (see Table 1), where the covalent and relatively acidic (MoO₄)²⁻ molybdate units selectively adsorb methoxylated surface species that have higher frequency C–H stretches relative to those of the methoxide surface species adsorbed on the corresponding pure oxides of the basic cations (Fe, Co, Ni, etc.).

By comparison, in the supported metal oxides described

- (50) Suda, Y.; Morimoto, T.; Nagao, M. *Langmuir* **1987**, *3*, 99.
 (51) Kittaka, S.; Umezumi, T.; Ogawa, H.; Maegawa, H.; Takenaka, T. *Langmuir* **1998**, *14*, 832.
 (52) Rossi, P. F.; Busca, G. *Colloids Surf.* **1985**, *16*, 95.

in part 1⁷ most of the deposited metal oxides are rather acidic and most support oxides are basic: a fact that permits full dispersion of the acidic metal oxide onto the basic support via an acid–base titration of the support hydroxyls.^{8,9} Even the more acidic support oxides like alumina and silica usually possess sufficiently *different* Lewis acid strength relative to the deposited metal oxide that dispersion of the deposited metal oxide may occur via hydroxyl condensation. Therefore, in cases where the surface coverage of the deposited metal oxide is below monolayer, it is usually possible to distinguish between methoxylated surface species adsorbed on the different metal cation sites in supported metal oxides. For example, the methanol-exposed 10% V₂O₅/SiO₂ catalyst (see part 1) permits discrimination between methanol chemisorption on V and Si sites because silica adsorbs methanol associatively (Lewis-bound, species I) and surface vanadia sites adsorb methanol dissociatively (species II). Conversely, for MoO₃ dispersed on SiO₂, the adsorbed methoxy frequencies on Mo and Si sites are coincident and do not permit conclusive assignment of the methoxylated surface species to specific metal cations. It is probable that both sites are adsorbing methanol because silica surface area is definitely exposed on this submonolayer catalyst.

Thus, methanol chemisorption at 110 °C may be used as a probe of both surface composition and surface Lewis acidity for metal oxides. It is important to note that traditional measures of Lewis acidity at metal oxide surfaces using strong bases such as NH₃ or pyridine do not always predict the acid–base interaction that actually occurs between *methanol* and a metal oxide surface. For example, supported niobia, vanadia, and molybdena catalysts at monolayer coverages have been measured to be rather acidic using pyridine adsorption.⁵³ However, the results of part 1⁷ indicate that supported niobia and vanadia monolayer catalysts adsorb methanol almost exclusively in dissociated form ($-OCH_{3ads}$, species II) due to the deprotonation of intact, adsorbed methanol by nearby basic oxygen anions or basic hydroxyls. Supported MoO₃ at monolayer coverage produces both methoxylated surface species I and species II, indicating an amphoteric metal oxide surface relative to methanol.

Likewise, for the bulk mixed-metal molybdates presented in Figure 1, the Lewis acidity of the molybdate surfaces *relative to the methanol probe molecule* appears to decrease as follows: Fe₂(MoO₄)₃, NiMoO₄ (species I predominates) > MnMoO₄, CoMoO₄, ZnMoO₄, Al₂(MoO₄)₃ > Ce(MoO₄)₂ > Bi₂Mo₃O₁₂ > Zr(MoO₄)₂ (species II predominates). In general, these bulk mixed-metal molybdates, in similarity to the supported molybdena catalysts studied in part 1,⁷ have a strong tendency to adsorb methanol as Lewis-bound adducts rather than as the dissociated surface methoxy species favored by more basic oxide surfaces. Moreover, the Lewis basicity of the Fe, Ni, Bi, Zn, and Zr cocations *relative to the methanol probe molecule* was confirmed by the presence of ionic methoxides on the corresponding pure oxides (lowest C–H stretching bands at ~ 2800 – 2820 cm⁻¹, see Table 1). As previously noted, the absence of these methoxide signals in the spectra of the mixed-metal molybdates suggests that the basic cocations are relatively inaccessible for methanol chemisorption and that Mo cations are the primary adsorption centers for methanol.

4.2. Methanol Chemisorption for Quantification of Active Metal Oxide Surface Sites.

The high tem-

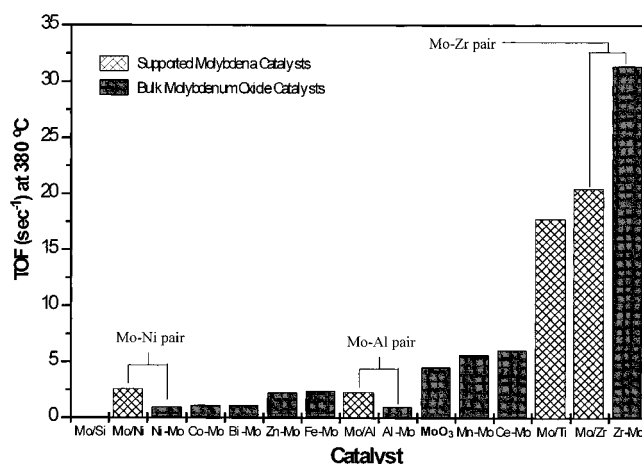


Figure 3. Direct, side-by-side comparisons of the methanol oxidation TOFs in bulk and supported molybdena catalysts using TOFs based on the methanol chemisorption site densities.

perature (110 °C) methanol chemisorption and in-situ IR technique used in the present study overcomes the uncertainties associated with the more complicated site density measurement procedures discussed in the Introduction by directly measuring the number of active surface intermediates in bulk metal oxides. Interestingly, Lewis-bound water (IR band at ~ 1610 cm⁻¹) was found to be easily displaced by the adsorbed methoxylated surface species in part 1, independently of whether the surface water was initially present adventitiously or was formed by condensation of surface hydroxyls following dissociative methanol chemisorption.⁷ Quantitatively, such an evolution of water from the oxide surface may allow for the assumption of complete water loss in high temperature (110 °C) gravimetric methanol adsorption studies. However, at lower adsorption temperatures the possibility of forming nondesorbing, surface-bound water from dissociative methanol chemisorption requires that the methoxylated surface species be quantified directly by, for example, IR spectroscopy (CeO₂,⁴⁷ ZnO, MgO,⁴⁴ MoO₃,⁴¹ SiO₂,³⁸ and ZrO₂⁴⁸), or that the water desorbed upon adsorption be independently measured if gravimetric methods are used.^{11–13,50} The technique used in the present study not only determines the number of adsorbed methoxylated surface intermediates *directly* by IR spectroscopy, but it also minimizes the amount of physisorbed methanol and physisorbed water by performing the methanol chemisorption at elevated temperature and under vacuum.

The active site densities and methanol oxidation TOFs presented in Table 3 for bulk mixed-metal molybdates and for pure bulk metal oxides provide unique new insights into the intrinsic catalysis of bulk metal oxides. For instance, the intrinsic activities (TOFs) of commercially relevant bulk molybdates are compared graphically in Figure 3 with each other and with the TOFs of the corresponding supported molybdena catalysts (data for the supported molybdena catalysts are taken from part 1 of the present two-paper series⁷). For the first time, it is possible to see that the intrinsic TOFs of model supported metal oxide catalysts are relatively similar to those of bulk mixed molybdates with the same co-cation (e.g., MoO₃/NiO vs NiMoO₄). There certainly are not orders of magnitude differences between such catalyst pairs, although large differences are observed between pairs (e.g., Mo–Al vs Mo–Zr) and among the bulk molybdates.

Furthermore, such a fundamental observation raises the possibility that the same ligand effect that is respon-

(53) (a) Turek, A. M.; Wachs, I. E.; DeCanio, E. *J. Phys. Chem.* **1992**, *96*, 5000. (b) Datka, J.; Turek, A. M.; Jehng, J.-M.; Wachs, I. E. *J. Catal.* **1992**, *135*, 186.

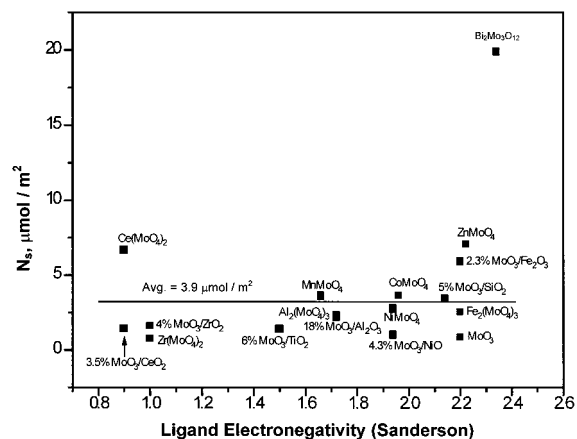


Figure 4. Methanol chemisorption site density vs ligand cation electronegativity in bulk and supported molybdena catalysts.

sible for the orders of magnitude variation of TOF in supported metal oxide catalysts (see part 17) may also apply to bulk mixed molybdates. More specifically, and by analogy to supported metal oxides, the electronegativity of the ligand (or support) cation likely controls the TOF in both bulk and supported molybdena catalysts, where more electropositive ligand cations correspond to greater TOFs. The specific molecular structures and coordinations of the molybdenum and cocation sites appear to be secondary to this localized electronic ligand effect imparted by the co-cation toward the surface active Mo cation.

Some tests of this hypothesis are given in Figures 4–6, the establishment of important noncorrelations being the subject of the first two of these figures. For instance, Figure 4 shows that the methanol chemisorption surface site densities, which average $\sim 3.9 \mu\text{mol}$ of methoxylated surface intermediates per m^2 , are independent of the ligand cation electronegativity in both supported and bulk molybdena catalysts. Only a mild increase in surface site density is observed for the bulk molybdates relative to the supported molybdena catalysts. Note that N_s for $\text{MoO}_3/\text{SiO}_2$ includes inactive spectator methoxy surface sites on exposed silica cations, and N_s for $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ may not be very accurate due to its extremely low surface area of $0.22 \text{ m}^2/\text{g}$. The variation in N_s for these samples, which is about $\pm 3.2 \mu\text{mol}/\text{m}^2$, also means that the average value of N_s ($3.9 \mu\text{mol}/\text{m}^2$) should only be taken as a rough average of methanol chemisorption site densities on oxides. Such an average figure has merit in indicating the relative scale of N_s , which is much lower than the surface sites densities reported for metals. However, calculations based on the average N_s value for methanol adsorbed on oxides should only be made in conjunction with its deviation, where minimum and maximum values of N_s (see Table 3) are used to “bound” the calculation. Additionally, while the error in N_s is most likely greater for samples with low surface area (e.g., $\text{Bi}_2\text{Mo}_3\text{O}_{12}$), the TOFs are *not* influenced directly by surface area measurements because the activity and N_s values are both normalized to the same surface area value, which is canceled upon calculation of TOF. At any rate, Figure 4 indicates that the specific ligand cation is not significantly related to site density.

Figure 5 reveals that the methanol oxidation TOF in bulk and supported molybdena catalysts is also not related to surface site density. This is expected based on the accepted mechanism for the unimolecular, single site decomposition of the adsorbed surface methoxy intermediates to formaldehyde,^{2,5,54} and reactions requiring more than one metal oxide site would have generated higher TOFs for catalysts with higher N_s values. Such a finding

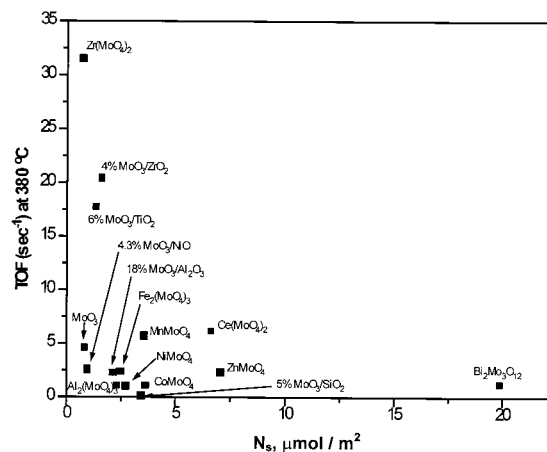


Figure 5. Methanol oxidation TOF vs methanol chemisorption site density in bulk and supported molybdena catalysts.

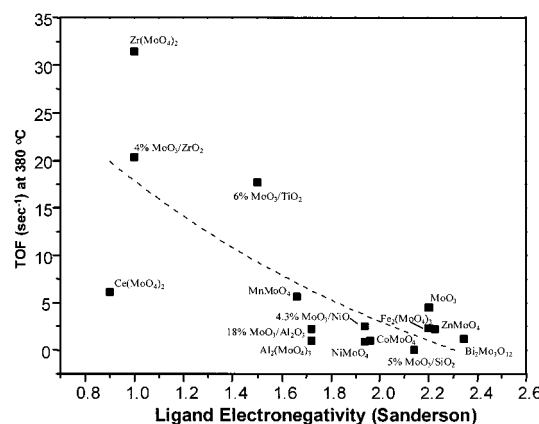


Figure 6. The ligand effect in bulk and supported molybdena catalysts.

further suggests that methanol chemisorption is a more reliable method for counting active sites than the BAT method, which has been applied to supported molybdena catalysts by Niwa et al.^{27–29,55} Using the BAT technique, these authors found that the TOF values indicated the need for two metal oxide sites (linear increase in TOF with MoO_3 loading)—in contradiction with the above-mentioned and fairly well-verified single site mechanism.^{2,5,54}

The clearest evidence that an electronic ligand effect controls the methanol oxidation TOF is given in Figure 6, where it can be seen that the TOF generally decreases with increasing ligand cation electronegativity. Note that the fitted exponential curve is added mainly to indicate the trend and does not imply a strictly exponential relationship, especially considering the concentration of data points in the region of higher ligand electronegativity. In particular, the correlation is rather scattered for ligand cation electronegativities below a value of about 1.6, and there is very little trend between TOF and ligand cation electronegativity above this value. Overall, however, Figure 6 still shows that low ligand cation electronegativities generally correspond to higher methanol oxidation TOFs. Moreover, this ligand effect is exhibited by both supported and bulk molybdate catalysts, the TOFs in the former having been extrapolated to $380 \text{ }^\circ\text{C}$ from their values at $250 \text{ }^\circ\text{C}$ (Arrhenius extrapolation based on data

(54) Wachs, I. E. In *Catalysis*; Spivey, J. J., Ed.; The Royal Society of Chemistry: Cambridge, 1997; Vol. 13m pp 37–54.

(55) Matsuoka, Y.; Niwa, M.; Murakami, Y. *J. Phys. Chem.* **1990**, *94*, 1477.

given in part 1⁷) in order to allow for direct comparison with the lower surface area bulk molybdates.

The origin of the ligand effect has been investigated in supported metal oxides by Wachs et al.^{6,8–10,36,54,56,57} and Bell et al.,⁵⁸ and a detailed discussion is given in part 1 of the present two-paper series.⁷ Well-characterized in-situ molecular structural studies have shown that structural variations in the number of M=O double bonds, the number of M–O–M polymerized bonds, and the coordination of the active metal oxide metal atom have far less impact on the TOF than does the choice of support oxide.^{6,8–10,36,54,56,57} In addition, it appears that the bridging M–O–Support bond (M = Mo, V, etc.) is the dominant reactive center in methoxy hydrogen abstraction during the formation of formaldehyde, based on recent quantum chemical calculations.^{59,60} Thus, the fundamental origin of the ligand effect in supported metal oxides appears to be related to the electronegativity of the support cation and its effect upon the redox behavior of the M–O–Support bond. Note that Sanderson electronegativity is preferred for its better handling of transition metal cations, and tabulated values are available.⁶¹

For the bulk metal molybdates, no such detailed surface models exist for describing the molecular structures of the active surface sites. In fact, studies of supported metal oxide catalysts have often been motivated by their applicability as “model” catalysts for these less tractable bulk oxides, and structure–reactivity relationships derived from the more easily characterized supported systems were expected to be extended by analogy to bulk oxides.^{2,8} Unfortunately, relatively little progress has been made in connecting the studies on model supported metal oxide catalysts to their bulk analogues. In the present study, the methanol chemisorption surface site density and corresponding methanol oxidation TOFs have been successfully and directly compared for the bulk and supported molybdate catalytic systems. The similarity in TOF between supported and bulk molybdate pairs (e.g., MoO₃/Al₂O₃ vs Al₂(MoO₄)₃, etc.) and the correlation of the TOF to ligand cation electronegativity in both supported and bulk systems strongly suggests that the ligand effect originates from the same source in each system. In fact, there is substantial evidence (XRD⁶² and reaction-induced metal oxide spreading experiments observed with in-situ Raman spectroscopy⁶³) suggesting that a “monolayer” of surface molybdenum oxide species exists on the surfaces of the bulk metal molybdates due to the lower surface energy of Mo=O bonds relative to surface hydroxyls.⁶³ Therefore, by analogy to the structure–reactivity relationships derived for supported metal oxide catalysts, it may be concluded that electronic variations in localized M–O–Ligand bonds are mainly responsible for differences in TOF in bulk metal oxides such as molybdates.

The methanol chemisorption and infrared technique used in the present study also has critical implications for the kinetic modeling of the methanol oxidation reaction,

in addition to its importance in developing the above-discussed fundamental insights regarding bulk metal oxide Lewis-acidity correlations and bulk metal oxide methanol oxidation TOF correlations. Specifically, recent in-situ methanol oxidation studies over oxide catalysts⁶⁴ showed that the fractional surface coverage of methoxylated surface intermediates relative to saturation coverage is between 0.3 and 0.68 under steady-state reaction conditions when chemisorption site densities are used to define the saturation coverage. Previous authors often assumed that the reaction proceeds in the low surface coverage regime (fractional coverage less than 0.2) when constructing kinetic models.⁵ Therefore, the use of methanol chemisorption site densities becomes very important for kinetic modeling, where it can no longer be assumed that methanol oxidation over oxides proceeds exclusively within the low surface coverage regime.

Last, note that it was shown in part 1⁷ that methanol oxidation TOFs are not especially dependent upon the ratio of species I to species II. This conclusion was based upon the fact that very different TOFs were found for supported metal oxide catalysts possessing similar distributions of methoxylated surface species I and species II,⁷ and that easy interconversion between various types of methoxylated surface species has been documented in other metal oxides.⁴⁸ Therefore, use of the *total* number of methoxylated surface species (species I plus species II) for calculating the active surface site densities and TOFs in metal oxides is a reasonable quantification procedure and has been utilized throughout the present investigation. This procedure is certainly preferred over the much less reliable deconvolution and curve-fitting techniques required for separate quantifications of species I and species II (see examples in part 1⁷). Nevertheless, it is worth qualitatively noting that the different ratios of methoxylated surface species may be related to formaldehyde selectivity. For example, low selectivity is generally obtained at high conversions in vanadia-based catalysts due to the readsorption of formaldehyde product on vanadia sites and their further oxidation to carbon oxides, whereas molybdena-based catalysts generally maintain their selectivity at high conversions.^{1,2} Therefore, it is possible that the presence of intact, strongly Lewis-coordinated methanol species (species I) prevents or blocks the readsorption of formaldehyde product in molybdena catalysts at high conversions.

5. Conclusions

Bulk metal oxide and bulk mixed-metal molybdate catalysts, many of which exhibit high methanol oxidation activity and selectivity, have been studied in the present investigation by high temperature (110 °C) methanol chemisorption and in-situ infrared spectroscopy. This technique was found to serve as both a probe of the surface chemistry of bulk metal oxide catalysts and as a powerful method for determining the surface density of active metal oxide sites available for methanol oxidation. Unlike more complicated site density measurement procedures such as oxygen chemisorption or the BAT method, this technique determines the number of adsorbed methoxylated surface intermediates *directly* by IR spectroscopy. Additionally, the amount of physisorbed methanol and physisorbed water is minimized by performing the methanol chemisorption at elevated temperature and under vacuum.

(64) (a) Burcham, L. J. *Ph.D. Dissertation*; Lehigh University: Bethlehem, PA, 2000; Chapter 5. (b) Burcham, L. J.; Badlani, M.; Wachs, I. E. *J. Catal.* **2000**. Submitted for publication.

(56) Wachs, I. E.; Weckhuysen, B. M. *Appl. Catal. A* **1997**, *157*, 67.

(57) Wachs, I. E.; Deo, G.; Juskelis, M. V.; Weckhuysen, B. M. In *Dynamics of Surfaces and Reaction Kinetics in Heterogeneous Catalysis*; Froment, G. F., Waugh, K. C., Eds.; Elsevier: Amsterdam, 1997; pp 305–314.

(58) Khodakov, A.; Olthof, B.; Bell, A. T.; Iglesia, E. *J. Catal.* **1999**, *181*, 205.

(59) Weber, R. S. *J. Phys. Chem.* **1994**, *98*, 2999.

(60) Tran, K.; Hanning-Lee, M. A.; Biswas, A.; Stiegman, A. E.; Scott, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 2618.

(61) (a) Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112. (b) Sanderson, R. T. *Inorg. Chem.* **1986**, *25*, 3518.

(62) Fagherazzi, G.; Pernicone, N. *J. Catal.* **1970**, *16*, 321.

(63) Wang, C.-B.; Cai, Y.; Wachs, I. E. *Langmuir* **1999**, *15*, 1223.

As a probe of surface chemistry, the IR spectra indicate that methanol chemisorption on bulk mixed-metal oxide catalysts produces both associatively adsorbed, intact Lewis-bound surface methanol species ($\text{CH}_3\text{OH}_{\text{ads}}$, species I) on acidic sites, as well as dissociatively adsorbed surface methoxy species ($-\text{OCH}_3$, species II) on less acidic or basic sites. Differences in the C–H stretching band frequencies of these adsorbed methoxylated species were observed between basic oxides (Bi_2O_3 , CeO_2 , Fe_2O_3 , NiO , ZnO , and ZrO_2) and acidic oxides (Al_2O_3 , MoO_3 , Nb_2O_5 , SiO_2 , TiO_2 , WO_3 , and V_2O_5) and permit identification of the specific metal cation involved in methanol adsorption on mixed oxides. In fact, it appears that Mo cations are the adsorption sites in many of the bulk mixed-metal molybdates, including the commercially important $\text{Fe}_2(\text{MoO}_4)_3$. These Mo sites also appear to have a strong tendency to adsorb methanol as Lewis-bound species I, in similarity with the supported molybdena catalysts studied in part 1.⁷ More generally, the Lewis acidity of bulk mixed-metal molybdates *relative to the methanol probe molecule* was found to decrease as follows: $\text{Fe}_2(\text{MoO}_4)_3$, NiMoO_4 (species I predominates) > MnMoO_4 , CoMoO_4 , ZnMoO_4 , $\text{Al}_2(\text{MoO}_4)_3$ > $\text{Ce}(\text{MoO}_4)_2$ > $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ > $\text{Zr}(\text{MoO}_4)_2$ (species II predominates).

By spectroscopically quantifying the amount of these adsorbed methoxylated surface intermediates (species I and species II, collectively) present on the bulk metal oxides after saturation of the surfaces with methanol, it was possible to determine the number of active metal oxide surface sites available for methanol oxidation. Then, using methanol oxidation TOFs determined from these methanol chemisorption site densities it became possible to compare the intrinsic catalytic activities of different bulk metal oxides with themselves and, perhaps for the first time, with supported metal oxides (using data from part 1⁷). In particular, the intrinsic TOFs of bulk molybdates were

shown to be relatively similar to those of model supported catalysts with the same cocation (e.g., MoO_3/NiO vs NiMoO_4), possibly due to the formation of a “monolayer” of surface molybdenum oxide species on the surfaces of the bulk metal molybdates. Moreover, the same electronic ligand effect appears to control the methanol oxidation TOF in both bulk as well as supported metal oxide catalysts, since TOF generally decreases with increasing ligand cation electronegativity in both groups. Therefore, by analogy to the structure–reactivity relationships derived for supported metal oxide catalysts it may be concluded that electronic variations in localized M–O–Ligand bonds are mainly responsible for differences in TOF in bulk metal oxides such as molybdates.

Variations in the ratios of methoxylated surface species I to species II further suggest that the presence of intact, strongly Lewis-coordinated methanol species (species I) may prevent or block the readsorption of formaldehyde product in molybdena catalysts at high conversions to account for the favorable selectivity behavior of these systems. Last, the methanol chemisorption surface site densities themselves may influence future kinetic modeling of the methanol oxidation reaction, since recent studies⁶⁴ indicate that a much larger fractional surface coverage of adsorbed methoxylated surface reaction intermediates are present during methanol oxidation than is generally assumed.⁵ As a result, the methanol chemisorption/infrared technique presented in this study may have additional applications beyond its present use for calculating methanol oxidation TOFs.

Acknowledgment. The authors gratefully acknowledge the United States Department of Energy, Basic Energy Sciences (Grant DEFG02-93ER14350), for financial support of this work.

LA010010T