

Molecular structure and reactivity of the Group V metal oxides

Israel E. Wachs^{a,*}, Yongsheng Chen^a, Jih-Mirn Jehng^b,
Laura E. Briand^c, Tsunehiro Tanaka^d

^a Zettlemoyer Center for Surface Studies and Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA

^b Department of Chemical Engineering, National Chung-Hsing University, Taichung 402, Taiwan, ROC

^c Centro de Investigacion y Desarrollo en Procesos Cataliticos, CONICET, Univ. Nacional de La Plata, Calle 47 No. 257,
(1900) La Plata, Buenos Aires, Argentina

^d Department of Molecular Engineering, School of Engineering, Kyoto University, Kyoto 606-01, Japan

Abstract

The physical, electronic and reactivity properties of bulk and supported Group V metal oxides (V, Nb, Ta and Db) were compared at the molecular level. Dubnium is a very short-lived element, ~60 s, whose properties have not been extensively studied, but can be predicted from knowledge of the other members of the Group V metal oxides. Bulk V₂O₅ possesses platelet morphology with the active surface sites only located at the edges: primarily surface redox sites and some surface acidic sites. Bulk Nb₂O₅ and Ta₂O₅, as well as to be expected for bulk Db₂O₅, possess isotropic morphologies and the active surface sites relatively homogeneously dispersed over their surfaces: only surface acidic sites. However, the bifunctional bulk V₂O₅ was found to exhibit a much higher specific acidic catalytic activity than the acidic bulk Nb₂O₅ and Ta₂O₅, the latter being almost identical in their specific acidic catalytic activity. The bulk properties of the Group V metal oxides were essentially transferred to the analogous supported Group V metal oxides, where the active Group V metal oxides were present as a two-dimensional monolayer on various oxide supports (e.g., Al₂O₃, TiO₂, ZrO₂ as well as Nb₂O₅ and Ta₂O₅). For supported vanadia catalysts, the active surface sites were essentially redox sites, with the exception of supported V₂O₅/Al₂O₃ that also contained strong acidic sites. For supported niobia and tantalum catalysts, as well as to be expected for supported dubnium catalysts, the active surface sites were exclusively acidic sites. However, the TOF_{redox} for the supported vanadia catalysts and the TOF_{acidic} for the supported niobia and tantalum catalysts varied over several orders of magnitude as a function of the specific oxide support with the electronegativity of the oxide support cation. However, the TOF_{redox} varied inversely to that of the TOF_{acidic} variation because of the opposite requirements of these active surface sites. Surface redox sites are enhanced by reduction and surface acidic sites are enhanced by stabilization (lack of reduction). The current fundamental understanding of the Group V metal oxides allows for the molecular engineering of their metal oxide applied catalytic materials.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium oxide; Niobium oxide; Tantalum oxide; Dubnium oxide; Bulk; Supported; Molecular structure; Surface redox sites; Surface acidic sites (Bronsted and Lewis); Surface basic sites; Temperature programmed reduction (H₂-TPR); Methanol oxidation; Propane oxidative dehydrogenation (ODH)

1. Introduction

The Group V metal oxides (bulk mixed metal oxides and supported metal oxides) have received much attention in recent years. Two special issues of *Catalysis Today* and one special issue of *Applied Catalysis*

* Corresponding author. Tel.: +1-610-758-4274;

fax: +1-610-758-6555.

E-mail address: iew0@lehigh.edu (I.E. Wachs).

have recently been devoted to the catalytic properties of vanadium oxide [1–3]. Several issues of *Catalysis Today* have been devoted to symposia on niobium oxide catalytic compounds [4–7] with the latter symposium also extended to vanadium oxide and tantalum oxide compounds. In contrast to vanadia and niobia, our current understanding of tantalum-based catalytic materials is rather limited with only one publication on tantalum appearing in the proceedings of the previous symposium [8]. Furthermore, the most recent member of the Group V elements, the heaviest and short-lived dubnium (isotopes with half-lives of 1.5–34 s because they are synthesized by nuclear reactions), has not received any attention at the last symposium because its extremely short lifetime precludes any realistic studies of this newest member of the Group V metal oxides. In a previous review paper of the molecular structure and properties of the Group V metal oxides, the emphasis was on vanadia and niobia because of the extensive structural and reactivity information available about these metal oxides and the lack of data about tantalum and dubnium at that time [9]. Thus, the present review paper of the Group V metal oxides will be extended to also include the molecular structure and reactivity properties of the tantalum and dubnium members of the Group V metal oxides.

2. Experimental

The experimental details of the catalyst synthesis procedures of supported vanadia [9,10] and supported niobia [11,12] can be found in the associated references. The supported tantalum was synthesized by incipient wetness impregnation with ethanol solutions of tantalum ethoxide (HC Starck, 99.99%) under flowing nitrogen in a glove box. The impregnated catalysts were initially dried overnight at room temperature in the glove box, further dried at 120 °C for 2 h, and then calcined in flowing air at 500 °C for 5 h. Bulk V_2O_5 was synthesized by calcining ammonium metavanadate, NH_4VO_3 (Alfa Aesar), at 450 °C for 3 h, bulk Nb_2O_5 was synthesized by calcining niobic acid, $Nb_2O_5 \cdot nH_2O$ (Niobium Products Company), at 800 °C for 2 h, and bulk Ta_2O_5 was obtained from HC Starck without any additional treatments. All oxides were pretreated in flowing O_2/He at 400 °C for 1 h prior to the physical and chemical probe characteri-

zation experiments in order to remove the presence of adsorbed moisture from the metal oxide surfaces. The supported Group V metal oxides were physically characterized by Raman [13], IR [14], UV-Vis DRS [15], XANES/EXAFS [16], solid-state ^{51}V NMR [17] and chemically probed by the N_2 BET physical adsorption method and various chemisorption probe molecules (pyridine [14], CO_2 [14], SO_2 [18] and CH_3OH [19]), hydrogen temperature programmed reduction (H_2 -TPR) [20] and CH_3OH oxidation [10,19] as well as propane oxidative dehydrogenation (ODH) reactions [21]. The experimental details can be found in the experimental sections of the above references [9–21].

3. Results and discussion

3.1. Bulk Group V metal oxides

3.1.1. Solid-state structural chemistry

The solid-state structural chemistry of the Group V metal oxides in the crystalline state, with the exception of dubnium, is well-documented in the literature [22,23]. In contrast, no information about the solid-state chemistry of dubnium oxide is known because of the very short lifetime of this transient element (maximum of ~60 s). It should be noted that the various Group V metal oxides were calcined between 450 and 800 °C to assure that their corresponding oxyhydrates, $M_2O_5 \cdot nH_2O$, were decomposed and only the pure metal oxide M_2O_5 phases were present in the samples employed in this study (confirmed with Raman spectroscopy). The Group V oxyhydrate stability trend is tantalum \gg niobia $>$ vanadia and dubnium oxyhydrate would be expected to be the most stable. Bulk V(+5) oxides consist of both VO_4 units, isolated and polymerized, as well as highly distorted VO_5/VO_6 units, isolated or polymerized. In contrast, bulk Nb(+5) and Ta(+5) oxides rarely consist of NbO_4 or TaO_4 units and prefer NbO_5/NbO_6 and TaO_5/TaO_6 coordination. The very large Nb(+5) and Ta(+5) cations have difficulty fitting into NbO_4/TaO_4 coordination and only a handful of such compounds are known. The NbO_5/NbO_6 and TaO_5/TaO_6 units may be present as undistorted as well as distorted species and NbO_7/TaO_7 and NbO_8/TaO_8 units are also known. Dubnium oxide would be expected to follow the trend in the Group V metal oxides and primarily

consist of $\text{DbO}_5/\text{DbO}_6$ as well as some DbO_7 and DbO_8 units. Thus, the solid-state structural chemistry of bulk V(+5) oxides tends to be very different than that of the other Group V metal oxides (Nb, Ta and Db).

3.1.2. Physical and electronic properties

The melting temperature of the Group V metal oxides increases with increasing atomic number: V_2O_5 (690 °C), Nb_2O_5 (1512 °C), Ta_2O_5 (1873 °C) and is estimated for Db_2O_5 to be greater than 2000 °C. The melting points of bulk, crystalline metal oxides have a very important effect on the surface mobility of metal oxides since at the Tammann temperature, $T_{\text{Tam}} = T_{\text{mp}}/2$, the surface atoms begin to diffuse [24]. The Tammann temperatures for the Group V metal oxides are 209 °C for V_2O_5 , 620 °C for Nb_2O_5 , 800 °C for Ta_2O_5 and estimated to be ~900 °C for Db_2O_5 . Consequently, under typical catalytic reaction conditions (200–600 °C), V_2O_5 is significantly above its Tammann temperature and the surface V(+5) species become very mobile and spread out over other oxide surfaces. The Group V metal oxides also crystallize in different morphologies since V_2O_5 forms platelets and isotropic crystals are found for Nb_2O_5 and Ta_2O_5 . By analogy Db_2O_5 would also be expected to crystallize in an isotropic morphology. The Sanderson electronegativity values of the fully oxidized Group V metal oxides are V(2.51) and Nb(1.42) [25]. Unfortunately, the electronegativity value for Ta(+5) is not available, as well as Db(+5), but can be reasonably estimated by comparison with the electronegativity values of the corresponding Group VI fully oxidized metal oxides: Cr(3.37), Mo(2.2) and W(1.67) [25]. The comparison suggests that the electronegativity of Ta(+5) is ~0.9 and Db(+5) should be ~0.7. Thus, the electronegativity of the Group V metal oxides decreases as the atomic number increases, which is similar to that for the adjacent Group VI and Group IV fully oxidized metal oxides. The band gap energies of the bulk Group V metal oxides were found to be 2.3 eV for V_2O_5 , 3.4 eV for Nb_2O_5 and 4.0 eV for Ta_2O_5 from UV-Vis DRS measurements. The band gap energy of Db_2O_5 is estimated to be about 4.5 eV from the above trend. Thus, the semiconductor properties, ease of reduction and creation of oxygen vacancies, of the bulk crystalline Group V metal oxides decrease with increasing atomic number. In summary, the physical and elec-

tronic properties of bulk V_2O_5 tend to be very different from those of the other bulk Group V metal oxides.

3.1.3. Chemical reactivity properties

Hydrogen Temperature Programmed Reduction (H_2 -TPR). The reduction properties of bulk V_2O_5 , Nb_2O_5 and Ta_2O_5 were compared with H_2 -TPR. Bulk V_2O_5 reduction initiated at ~600 °C and reduction occurred in three stages at ~675 °C ($\text{V}_2\text{O}_5 \rightarrow \text{V}_6\text{O}_{13}$), ~705 °C ($\text{V}_6\text{O}_{13} \rightarrow \text{V}_2\text{O}_4$) and ~780 °C ($\text{V}_2\text{O}_4 \rightarrow \text{V}_2\text{O}_3$). Bulk Nb_2O_5 reduction initiated at ~800 °C and only very mild reduction occurred since temperatures of ~1300 °C are needed to reduce bulk $\text{Nb}_2\text{O}_5 \rightarrow \text{Nb}_2\text{O}_4$. Bulk Ta_2O_5 exhibited some extremely minor reduction between 400 and 500 °C as well as 800–900 °C, but very high temperatures in excess of 1000 °C are required to reduce bulk $\text{Ta}_2\text{O}_5 \rightarrow \text{Ta}_2\text{O}_4$. Although no corresponding H_2 -TPR information about bulk Db_2O_5 is available, it is also expected to be resistant to reduction similarly to bulk Nb_2O_5 and Ta_2O_5 . These comparative H_2 -TPR experiments clearly demonstrate the ease with which V_2O_5 reduces in comparison with the other Group V bulk metal oxides.

Surface density of number of active surface sites. The BET surface areas of the bulk V_2O_5 , Nb_2O_5 (T-phase) and Ta_2O_5 (L-phase) used in the present investigation were found to be 3.5, 1.9 and 4.0 m²/g, respectively. The number of active surface sites was determined by methanol chemisorption at 100 °C, this adsorption temperature was chosen since it assured that physically adsorbed methanol would not be present and that only surface methoxy intermediates and chemisorbed methanol bound to Lewis acid sites were present on the metal oxide surfaces [19]. The surface density of the number of active surface sites was found to be 0.4, 1.8 and 2.9 per nm² for bulk V_2O_5 , Nb_2O_5 and Ta_2O_5 , respectively. The much lower surface density of active surface sites for bulk V_2O_5 compared to bulk Nb_2O_5 and Ta_2O_5 is a consequence of the different morphologies of these Group V metal oxides and their surface reactivity. Methanol preferentially chemisorbs on the edges of bulk V_2O_5 platelets and not on the basal planes [26,27]. For crystalline Nb_2O_5 and Ta_2O_5 , the isotropic morphology does not result in preferential chemisorption on specific planes and adsorption occurs over the entire surface. Consequently, bulk Nb_2O_5 and Ta_2O_5 possess

~ 4 and ~ 7 the number of active surface sites per square meter, respectively, than bulk V_2O_5 . It is interesting that even between the two isotropic metal oxides, bulk Ta_2O_5 possesses about a 50% higher surface density of active surface sites than bulk Nb_2O_5 . Bulk Db_2O_5 is expected to follow this pattern and should be isotropic with an even higher surface density of active surface sites than bulk Ta_2O_5 .

Methanol oxidation. In addition to determining the surface density of the number of surface sites, the methanol oxidation products also reflect the nature of the active surface sites: H_2CO as well as some CH_3OOCH and $H_2C(OCH_3)_2$ from surface redox sites, CH_3OCH_3 from surface acidic sites and CO_2 from surface basic sites. Furthermore, the turnover frequencies ($TOF_{\text{overall}} = \text{number of methanol molecules converted per active surface site per second}$ and TOF_{redox} , TOF_{acidic} or TOF_{basic} represent the number of H_2CO as well as some CH_3OOCH and $H_2C(OCH_3)_2$, CH_3OCH_3 or CO_2 molecules formed per active surface site per second, respectively) can be quantitatively determined from knowledge of the methanol conversion, product selectivity and the surface density of the number of active surface sites (see above section). For methanol oxidation at 230°C , bulk V_2O_5 exhibits a TOF_{redox} of $3.8 \times 10^{-1} \text{ s}^{-1}$, a TOF_{acidic} of $4.0 \times 10^{-2} \text{ s}^{-1}$ and a TOF_{basic} of 0.00 s^{-1} ; bulk Nb_2O_5 exhibits a TOF_{redox} of 0.00 s^{-1} , a TOF_{acidic} of $7.0 \times 10^{-3} \text{ s}^{-1}$ and a TOF_{basic} of 0.00 s^{-1} ; and bulk Ta_2O_5 exhibits a TOF_{redox} of 0.00 s^{-1} , a TOF_{acidic} of $6.0 \times 10^{-3} \text{ s}^{-1}$ and a TOF_{basic} of 0.00 s^{-1} . The methanol oxidation TOF_{overall} order over the different bulk metal oxides follows the trend $V_2O_5 > Nb_2O_5 \sim Ta_2O_5$. Bulk Db_2O_5 would be expected to behave similarly to bulk Nb_2O_5 and Ta_2O_5 with only reaction products reflecting the exclusive presence of surface acidic sites. Thus, bulk V_2O_5 predominantly possesses surface redox characteristics ($\sim 90\%$) and the remaining bulk Group V metal oxides exclusively possess surface acidic characteristics (100%). Furthermore, the bulk V_2O_5 surface is significantly more reactive than the other Group V bulk metal oxide surfaces in the formation of reaction products originating from surface redox sites as well as surface acidic sites.

Propane Oxidative Dehydrogenation over bulk mixed metal oxides. Mixed metal oxides of $V_2O_5-Nb_2O_5$ and $V_2O_5-Ta_2O_5$ were prepared by impregnation of the Nb- and Ta-oxyhydrate supports with

a V-isopropoxide/isopropanol solution under a nitrogen environment and calcining at elevated temperatures to form the bulk mixed metal oxides. The BET surface areas of the 2% $V_2O_5-Nb_2O_5$ and 3% $V_2O_5-Ta_2O_5$ mixed oxides were found to be 6.8 and $0.86 \text{ m}^2/\text{g}$, respectively. The lower surface area of the 3% $V_2O_5-Ta_2O_5$ mixed metal oxide than the 2% $V_2O_5-Nb_2O_5$ mixed metal oxide is a consequence of the higher V_2O_5 concentration and calcination temperature employed in the synthesis of the former. The mixed metal oxides and the bulk Nb_2O_5 and Ta_2O_5 metal oxides were chemically probed with the propane oxidative dehydrogenation (ODH) reaction to propylene at 425°C . Bulk Nb_2O_5 and Ta_2O_5 were essentially inactive for this reaction due to the absence of active surface redox sites and Db_2O_5 would be expected to behave similarly. In contrast, the $V_2O_5-Nb_2O_5$ and $V_2O_5-Ta_2O_5$ mixed metal oxides were active for this reaction because of the presence of active surface redox sites originating from the vanadia sites on their surfaces (similar results would be expected for $V_2O_5-Db_2O_5$ mixed metal oxides if such materials could be synthesized). The fraction of vanadia on the surfaces of the $V_2O_5-Nb_2O_5$ and $V_2O_5-Ta_2O_5$ mixed metal oxides could also be quantitatively determined by comparing the overall propane ODH activity of these catalysts with their corresponding model supported vanadia analogues where the vanadia is 100% dispersed on the Nb_2O_5 and Ta_2O_5 supports (see Section 3.2) because bulk Nb_2O_5 and Ta_2O_5 are essentially inactive for this reaction. From such side-by-side comparative propane ODH studies it was found that for 2% $V_2O_5-Nb_2O_5$ and 3% $V_2O_5-Ta_2O_5$ mixed metal oxides the fraction of vanadia on these surfaces was $\sim 50\%$ and 3%, respectively. The remaining vanadia was dissolved as a solid solution in the bulk lattice of the mixed metal oxides and was *not active* for the propane ODH reaction. Thus, the surface vanadia redox sites are the active surface redox sites in $V_2O_5-Nb_2O_5$ and $V_2O_5-Ta_2O_5$ mixed metal oxide catalysts during oxidative dehydrogenation reactions.

3.2. Supported Group V metal oxides

Supported metal oxides consist of two-dimensional surface metal oxide overlayers on oxide supports (e.g., Al_2O_3 , TiO_2 , SiO_2 , etc.). Supported vanadia and

niobia catalysts have received much attention and several reviews can be found in the literature [3–6,9,28–30]. In contrast, no such corresponding publications are currently available about supported tantalum oxide catalysts and, of course, none exist for supported dubnium oxide catalysts. The review below will compare the properties of all the supported Group V metal oxides and predict those of supported dubnia since such materials cannot be synthesized in the laboratory due to the very short lifetime of this element.

3.2.1. Solid-state structural chemistry

Surface metal oxide species on oxide supports change their coordination upon adsorption of moisture at temperatures below $\sim 200^\circ\text{C}$, but retain their dehydrated structures at elevated temperatures (even in the presence of moisture and during numerous catalytic oxidation reactions). Thus, only the dehydrated molecular structures of the supported Group V metal oxide species are discussed below.

Solid-state ^{51}V NMR [17], XANES/EXAFS [16] and UV-Vis DRS [15] characterization studies have demonstrated that the surface vanadia species possess VO_4 coordination. In addition, Raman and IR studies have revealed that the surface VO_4 species only contain one terminal $\text{V}=\text{O}$ bond and three bridging $\text{V}-\text{O}-\text{M}$ bonds (where M can be either another V or the support cation) [15,31,32]. At low surface vanadia coverages, the surface vanadia species is primarily isolated; at high surface vanadia coverages, the surface vanadia species is both isolated and polymerized. Monolayer surface coverages correspond to 7–8 V atoms/ nm^2 [10]. An exception is the supported $\text{V}_2\text{O}_5/\text{SiO}_2$ system, where only isolated surface vanadia species is present and maximum attainable surface coverage corresponds to less than 3 V atoms/ nm^2 [33]. The preparation method of supported vanadia catalysts does not affect the molecular structures of the surface vanadia species, but can affect the dispersion (especially on the weakly interacting SiO_2 surface) [28,33,34]. Interestingly, the low Tammann temperature of the bulk V_2O_5 results in the spontaneous dispersion of V_2O_5 on the oxide supports, with the exception of the weak interacting SiO_2 support [24,34].

XANES/EXAFS [35,36] and UV-Vis DRS [37] characterization studies have demonstrated that the surface niobia species possess NbO_4 coordination at

low surface coverage and highly distorted $\text{NbO}_5/\text{NbO}_6$ coordination at high surface coverage. Furthermore, Raman and IR studies have revealed that the surface niobia species possess only one terminal $\text{Nb}=\text{O}$ bond and 3–5 bridging $\text{Nb}-\text{O}-\text{M}$ bonds (where M can be either another Nb or the support cation) [38]. The surface NbO_4 species is isolated, primarily present at low surface coverage, and the surface $\text{NbO}_5/\text{NbO}_6$ species is polymerized (bridging $\text{Nb}-\text{O}-\text{Nb}$ bonds), at intermediate and high surface coverage. An exception is the supported $\text{Nb}_2\text{O}_5/\text{SiO}_2$ system where only isolated surface NbO_4 species is present [36–38]. Monolayer surface coverage correspond to 5–6 Nb atoms/ nm^2 with the exception of supported $\text{Nb}_2\text{O}_5/\text{SiO}_2$ where the maximum achievable surface density is less than 2 Nb atoms/ nm^2 due to the low reactivity of this silica support surface [38]. The slightly lower monolayer surface niobia density, relative to the surface vanadia species, is most probably related to the additional oxygen atoms associated with the surface $\text{NbO}_5/\text{NbO}_6$ structures at higher surface coverage. The preparation method does not affect the molecular structures of the surface niobia and tantalum species, but can affect their dispersion (especially on the weakly interacting SiO_2 surface) [29]. In contrast to bulk V_2O_5 , the much higher Tammann temperature of bulk Nb_2O_5 does not result in spontaneous dispersion of Nb_2O_5 on oxide supports [24].

XANES and UV-Vis DRS characterization studies have demonstrated that the surface tantalum species possess TaO_4 coordination at low surface coverage and highly distorted $\text{TaO}_5/\text{TaO}_6$ coordination at intermediate and high surface coverage [39–41]. Furthermore, Raman studies, with the aid of ^{16}O – ^{18}O exchange experiments, further revealed that the surface tantalum species possess only one terminal $\text{Ta}=\text{O}$ bond and 3–5 bridging $\text{Ta}-\text{O}-\text{M}$ bonds (where M can be either another Ta or the support cation) [42]. The isolated surface TaO_4 species is present at low surface coverage and especially on the SiO_2 support [40,41]. The polymerized species is present at intermediate and high surface coverage, with the exception of SiO_2 [40]. Monolayer surface coverage corresponds to 5–6 Ta atoms/ nm^2 with the exception of $\text{Ta}_2\text{O}_5/\text{SiO}_2$ where the maximum achievable surface density is ~ 1 Ta atom/ nm^2 [40]. Thus, the molecular structures and surface densities of the surface tantalum species on oxide supports are very similar

to those found for surface niobia species on oxide supports. Although no experimental data are available for supported niobia catalysts, they would also be expected to exhibit the same surface molecular structures and monolayer surface densities experimentally determined above for the surface niobia and tantalum species.

3.2.2. Physical and electronic properties

Unlike the bulk metal oxides, the surface metal oxide species present in supported metal oxide catalysts do not undergo a melting point transition from solid to liquid. However, the surface metal oxide species can become mobile and surface diffuse over the oxide supports at temperatures in excess of their bulk Tammann temperatures. This phenomenon is well-documented for supported vanadia catalysts because of the very low Tammann temperature of bulk V_2O_5 [24]. The low Tammann temperature of bulk V_2O_5 also leads to the volatilization of bulk V_2O_5 during many reactions. A very important practical advantage of supported vanadia catalysts is that the surface vanadia species are stabilized by the oxide support from volatilizing under reaction conditions. The surface niobia and tantalum species are much more stable on oxide supports and no reports on their surface mobility have been found in the literature because of their very high Tammann temperatures that are 620 and 800 °C, respectively. The supported niobia catalysts are expected to be even less mobile on the oxide supports since Nb_2O_5 should possess an even higher Tammann temperature.

The band gap energies of the supported Group V metal oxides are usually significantly higher than their corresponding bulk metal oxides because the band gap energy decreases with the number of metal oxide nearest neighbors [37,43,44]. Consequently, at low surface coverage the band gap energy is the highest because of the presence of isolated MO_4 species and decreases with increasing surface coverage as the concentration of polymerized surface VO_4 , NbO_5/NbO_6 or TaO_5/TaO_6 species increases on the oxide supports, with the exception of the SiO_2 support where surface MO_4 species are almost exclusively present below the maximum surface coverage [37,40,41,44]. Supported niobia catalysts would be expected to give similar trends since their molecular structures with surface coverage are expected to be the

same as that found for the surface niobia and tantalum species.

3.2.3. Chemical reactivity properties

3.2.3.1. Surface redox sites. The reduction characteristics of the surface vanadia species were determined by H_2 -TPR. Supported vanadia catalysts containing monolayer coverage resulted in the following reduction peak temperatures: V_2O_5/ZrO_2 (430 °C), V_2O_5/TiO_2 (470 °C), V_2O_5/Al_2O_3 (496 °C) and V_2O_5/SiO_2 (514 °C). The extent of reduction was quantitatively monitored by a calibrated thermal conductivity detector (AMI-100 system, Zeton Altamira Instruments) and all the supported vanadia catalysts were reduced from $V(+5) \rightarrow V(+3)$ with only one reduction peak being observed for each catalyst during the H_2 -TPR experiment. The reduced surface vanadia (+3) species were readily reoxidized to surface vanadia (+5) species during temperature programmed oxidation (TPO), which confirms the redox nature of the supported surface vanadia species. The influence of the oxide support on the H_2 -TPR peak of the supported vanadia catalysts is rather pronounced since the reduction peak temperatures of the surface vanadia species varied ~ 100 °C with V_2O_5/ZrO_2 being the most reactive and V_2O_5/SiO_2 being the least reactive. The low reactivity of the supported V_2O_5/SiO_2 catalyst is not exclusively related to the presence of isolated surface vanadia species on this catalyst system because the relatively unreactive polymerized surface vanadia species on the supported V_2O_5/Al_2O_3 catalyst is also a relatively unreactive catalyst system. Thus, the supported vanadia species are always surface redox sites.

The corresponding H_2 -TPR experiments of the supported niobia catalysts containing monolayer coverage did not exhibit any reduction of the surface niobia species and only a trace amount of reduction was observed for Nb_2O_5/TiO_2 at ~ 550 °C. An analogous experiment with a supported Ta_2O_5/Al_2O_3 catalyst also did not show any reduction of the surface tantalum species. Similarly, supported niobia would also not be expected to undergo reduction during the H_2 -TPR experiment. Thus, with the exception of supported vanadia species, the other supported Group V metal oxides are very resistant to reduction and are not surface redox sites.

3.2.3.2. Surface acidic sites. The surface acidity of the supported Group V metal oxides on alumina possessing almost monolayer coverage was quantitatively chemically probed by IR during pyridine adsorption, which readily discriminates between surface Bronsted (chemisorbed protonated pyridine) and surface Lewis acid sites (chemisorbed pyridine) [14,45]. The alumina support exhibits only the presence of surface Lewis acid sites, $0.66/\text{nm}^2$. However, the supported vanadia/alumina and the supported niobia/alumina catalysts both exhibited the presence of surface Bronsted and Lewis acid sites, with the number of surface Lewis acid sites reduced by these surface metal oxide overlayers. The supported vanadia catalyst was found to possess $0.44/\text{nm}^2$ of surface Bronsted acid sites and $0.23/\text{nm}^2$ of surface Lewis acid sites. The corresponding supported niobia catalyst was found to possess $0.18/\text{nm}^2$ of surface Bronsted acid sites and $0.51/\text{nm}^2$ of surface Lewis acid sites. Monolayer coverage of surface tantalum on alumina was not investigated, but at low surface coverage only surface Lewis acid sites were detected and at ~ 0.75 monolayer coverage surface Bronsted acid sites were also detected [41]. Similar results were also obtained for almost monolayer coverage of other metal oxides on the alumina support (chromia, molybdena, tungsta, rhenia) [14,46]. Therefore, the surface acidity on alumina would be expected to mimic the surface acidity characteristics of supported niobia and tantalum on alumina. For the surface Lewis acid sites present on supported niobia catalysts the strength of these surface acidic sites was found to depend on the specific oxide support [45]: $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{ZrO}_2$. The same trend was found for the strength of the surface Lewis acid sites of supported tantalum catalysts [41]: $\text{Al}_2\text{O}_3 > \text{ZrO}_2$. Quantitative examination of the surface Bronsted and Lewis acid sites for the alumina supported vanadia and niobia catalysts reveals several interesting observations: (1) the surface density of all surface acid sites is constant at $\sim 0.67/\text{nm}^2$, (2) only a minor fraction of the surface metal oxide species contain surface acidity (~ 0.09 for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and ~ 0.12 for $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$), (3) the fraction of surface metal oxide species that possess surface Bronsted acid sites is ~ 0.06 for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and ~ 0.03 for $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ and (4) the fraction of the surface metal oxide species that possess surface Lewis acid sites is ~ 0.03 for $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ and ~ 0.09 for $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$. Thus, only a very minor fraction

of the supported Group V metal oxide species possesses surface Bronsted acidity and the surface vanadia species possesses about twice the amount of surface Bronsted acidity as the surface niobia species.

The disparity in the surface Bronsted acidity of the surface vanadia and niobia species on TiO_2 and ZrO_2 supports is further enhanced, where the surface vanadia species possesses both surface Bronsted and Lewis acid sites and the surface niobia species only contains surface Lewis acid sites [45,47,48]. Surface tantalum on ZrO_2 also follows the behaviour of surface niobia species on ZrO_2 [41]. For the isolated surface vanadia, niobia and tantalum species on SiO_2 there are no surface Bronsted acid sites, which suggest that surface Bronsted acid sites can only form in the presence of polymerized surface sites on other oxide supports (alumina, titania, zirconia) [47,48]. This tentative conclusion is further supported by the observation that surface Bronsted acid sites are only observed at high surface metal oxide coverage where the concentration of polymerized surface vanadia, niobia and tantalum species is greatest [14,46–48]. Consequently, surface vanadia species are always expected to possess a greater number of surface Bronsted acid sites than the surface niobia species and may partly account for the higher $\text{TOF}_{\text{acidic}}$ found for bulk V_2O_5 , which contains surface Bronsted acid sites [49], than bulk Nb_2O_5 and Ta_2O_5 , which do not contain surface Bronsted acid sites after calcination at 500°C [8,45]. Although no pyridine adsorption studies can be performed with supported niobia catalysts their surface acidity characteristics are expected to be analogous to the supported niobia and tantalum catalysts because of the same surface molecular structures and surface metal oxide densities. Thus, the surface vanadia species have a higher surface density of Bronsted acid sites than the other supported Group V surface metal oxide species, but Bronsted acidity is only retained for the fully oxidized surface metal oxide species. Recent *in situ* Raman studies during many different oxidation reactions have revealed that the surface vanadia species is essentially fully oxidized under reaction conditions [50].

3.2.3.3. Surface basic sites. No surface basic sites were found for monolayer coverage of the surface vanadia and niobia species on alumina, as determined by CO_2 chemisorption, since the basic surface Al–OH sites were essentially completely titrated by the surface

Group V metal oxide overlayers [14]. Surface basic sites would also not be expected to be present for alumina supported tantalum and niobia species at monolayer surface coverage. Similarly, the surface support-OH basic sites are also titrated on other oxide supports by the surface metal oxide overlayers at monolayer surface coverage. This was also confirmed by SO₂ chemisorption experiments for supported vanadia catalysts on different oxide supports [18]. The absence of active surface basic sites for the supported Group V metal oxides is also reflected in the methanol oxidation chemical probe reaction products (see Section 3.2.3.5).

3.2.3.4. Surface density of the total number of active surface sites. The number of active surface sites present in supported metal oxide catalysts were determined by methanol chemisorption (see Section 3.1.3). It was generally found that for all supported metal oxides investigated (vanadia, niobia, chromia, molybdena, tungsta) that the molar ratio of chemisorbed methanol to surface metal oxide is $\sim 1/3$, which indicates that there must be significant lateral repulsions among the methanol adsorbates [19,51]. Although supported tantalum catalysts were not examined in the prior study, there is no reason to expect the ratio of chemisorbed methanol to surface tantalum, and for that matter also supported niobia catalysts, would be much different than $\sim 1/3$. Thus, the surface density of the total number of active surface sites should be comparable, within a factor of $\sim 50\%$, for all the supported Group V metal oxides (as shown in Table 1). Furthermore, comparison of the surface densities of

the total number of active surface sites of the bulk and supported Group V metal oxides presented in Table 1 reveals that (1) the supported vanadia catalysts contain a factor of ~ 20 times greater active surface sites per square nanometer than the anisotropic bulk V₂O₅ that contains the active surface sites only at the edges of the platelets, (2) the supported niobia catalysts contain ~ 2 – 3 times the surface density of number of active surface sites as isotropic bulk Nb₂O₅ and (3) the supported tantalum catalysts contain ~ 2 times the surface density of number of active surface sites than isotropic bulk Ta₂O₅. Supported niobia catalysts would be expected to follow this trend and possess a slightly higher surface density of active surface sites than bulk Nb₂O₅. Thus, the only Group V metal oxide where the surface density of the total number of active surface sites is significantly enhanced by forming a two-dimensional surface metal oxide overlayer on an oxide support is vanadium oxide because of the isotropic morphology and specific edge reactivity of bulk V₂O₅, which is not present in the surface vanadia monolayer catalysts.

3.2.3.5. Methanol oxidation. The TOF_{redox} and Selectivity_{redox} for the different supported vanadia catalysts and bulk V₂O₅ are presented in Table 2 for methanol oxidation at 230 °C. The methanol conversion was maintained below 10% to minimize the formation of secondary products, which might distort the production of primary reaction products from surface redox, acidic and basic sites. Bulk V₂O₅ yields 90% selectivity to redox products and 10% selectivity to acidic products, without the formation of any products

Table 1

Surface density of number of active surface sites on bulk and supported Group V metal oxides

Oxide support	V (atoms/nm ²)	Nb (atoms/nm ²)	Ta (atoms/nm ²)
Al ₂ O ₃	7.3	4.8	4.5
ZrO ₂	6.8	5.8	6.3
TiO ₂	7.9	5.8	6.6
Nb ₂ O ₅	8.5	–	–
Ta ₂ O ₅	8.8	–	–
Bulk V ₂ O ₅	0.4 ^a	–	–
Bulk Nb ₂ O ₅	–	1.8 ^a	–
Bulk Ta ₂ O ₅	–	–	2.9 ^a

^a The number of active surface sites for the bulk metal oxides was determined by methanol chemisorption.

Table 2

Methanol oxidation over supported vanadia, monolayer surface coverage, and bulk V₂O₅ catalysts at 230 °C

Catalyst	TOF _{redox} (s ⁻¹)	Selectivity _{redox} (%)
Bulk V ₂ O ₅	1.1 × 10 ⁰ ^a	90
V ₂ O ₅ /CeO ₂	1.0 × 10 ⁰	100
V ₂ O ₅ /ZrO ₂	1.7 × 10 ⁻¹	99
V ₂ O ₅ /TiO ₂	1.1 × 10 ⁻¹	100
V ₂ O ₅ /Nb ₂ O ₅	8.5 × 10 ⁻²	98
V ₂ O ₅ /Ta ₂ O ₅	7.6 × 10 ⁻²	100
V ₂ O ₅ /Al ₂ O ₃	6.8 × 10 ⁻³	50
V ₂ O ₅ /SiO ₂	2.0 × 10 ⁻³	97

^a Number of active surface sites determined by CH₃OH chemisorption (see Table 1). All supported vanadia catalysts were normalized to the number of surface vanadia species.

originating from surface basic sites. The supported vanadia catalysts, with the exception of V_2O_5/Al_2O_3 , are more selective than bulk V_2O_5 for the formation of redox products, which may be related to the reduced reactivity of the active surface acidic sites present for most of the supported vanadia catalysts. However, the very high acidic product selectivity and low redox product selectivity of V_2O_5/Al_2O_3 is related to the unusually large number of surface acidic sites, especially Bronsted acidic sites, of this catalytic system (see Section 3.2.3.2). The surface acid sites of the supported vanadia catalysts, with the exception of V_2O_5/Al_2O_3 , must not be very active because of the almost exclusive formation of redox products for these catalysts during methanol oxidation. No reaction products that would be expected to originate from surface basic sites, CO_2 and CO , were formed on any of the vanadia catalysts, which is consistent with the absence of surface basic sites (see Section 3.2.3.3). Even below monolayer surface coverage for the supported vanadia catalysts, where surface basic sites are present on the exposed oxide support, no CO_2 and CO were formed, reflecting the low reactivity of surface basic sites for methanol oxidation. Thus, the surface redox sites are generally much more active than the surface acidic sites for supported vanadia catalysts and the surface basic sites, when present, are the least active surface sites for methanol oxidation.

It is interesting to note that the surface vanadia sites on the different oxide supports are not more active than the active surface vanadia sites found at the edge of bulk V_2O_5 . The active surface vanadia sites on ZrO_2 and TiO_2 are about an order of magnitude less active than the active surface vanadia sites on bulk V_2O_5 . The surface vanadia sites on Nb_2O_5 and Ta_2O_5 are almost comparable in activity to the surface vanadia sites on ZrO_2 and TiO_2 and the surface vanadia sites on Al_2O_3 and SiO_2 are more than an order of magnitude less active than the active surface sites on Nb_2O_5 and Ta_2O_5 . For propane ODH, the same trend in TOF values was found for supported vanadia catalysts, over two orders of magnitude variation, with the exception that the supported V_2O_5/Ta_2O_5 catalyst was found to be slightly more active than the supported V_2O_5/Nb_2O_5 catalyst [52]. The three orders of magnitude trend in methanol oxidation specific activity generally correlates with the electronegativity of the support cations. As the support cation electroneg-

ativity decreases ($Si(2.14) > Al(1.71) > Ti(1.5) \sim Nb(1.42) > Ta(0.9) \sim Zr(0.9) > Ce(0.6)$ [25,53]), slightly more electronic charge is left on the bridging V–O–support bond that imparts a more basic character to the bridging oxygen, and this reactive redox oxygen has been shown to be the active surface site for many different oxidation reactions [52]. Supported V_2O_5/Db_2O_5 would be expected to be more active than V_2O_5/ZrO_2 because of the anticipated slightly lower electronegativity of Db(+5) than Zr(+4) (see Section 3.1.2). This same reduction reactivity trend was also observed during the H_2 -TPR experiments, $Zr > Ti \gg Al > Si$ (see Section 3.2.3.1). Thus, the oxide support ligand has a pronounced effect on the reactivity of the surface vanadia species, which can be tuned by many orders of magnitude for different oxidation reactions [53].

The TOF_{acidic} values during methanol oxidation for the different supported niobia catalysts and bulk Nb_2O_5 are presented in Table 3. Only reaction products originating from surface acidic sites were obtained during methanol oxidation (100% CH_3OCH_3), which is consistent with the absence of surface redox and basic sites on these niobia materials (see Sections 3.2.3.1 and 3.2.3.3). In contrast to the supported vanadia catalysts, all the supported niobia catalysts exhibited significant enhancements in their TOF values relative to bulk Nb_2O_5 and the surface niobia species on alumina is the most active acidic sites, which is presumably associated with the presence of surface Bronsted acid sites that are only found for this catalyst system as well as the strongest surface Lewis acidic sites found for this system [45] (see Section 3.2.3.2). Furthermore, the TOF_{acidic} appears to increase with the electronegativity of the oxide support

Table 3
Methanol oxidation over supported niobia, monolayer surface coverage, and bulk Nb_2O_5 catalysts at 230 °C

Catalyst	TOF_{acidic} (s^{-1})	Selectivity _{acidic} (%)
Nb_2O_5/Al_2O_3	2.0×10^{-1}	100
Nb_2O_5/ZrO_2	5.0×10^{-2}	100
Nb_2O_5/TiO_2	4.0×10^{-2}	100
Nb_2O_5/Ta_2O_5	3.1×10^{-2}	100
Bulk Nb_2O_5	2.1×10^{-2} ^a	100

^a Number of active surface sites determined by CH_3OH chemisorption (see Table 1). All supported niobia catalysts were normalized to the number of surface niobia species.

Table 4

Methanol oxidation over supported tantalum, monolayer surface coverage, and bulk Ta₂O₅ catalysts at 300 °C

Catalyst	TOF _{acidic} (s ⁻¹)	Selectivity _{acidic} (%)
Ta ₂ O ₅ /Al ₂ O ₃	2.5 × 10 ⁻¹	100
Bulk Ta ₂ O ₅	9.0 × 10 ⁻² ^a	100
Ta ₂ O ₅ /ZrO ₂	8.0 × 10 ⁻³	100
Ta ₂ O ₅ /TiO ₂	3.0 × 10 ⁻³	100

^a Number of active surface sites determined by CH₃OH chemisorption (see Table 1). All supported tantalum catalysts were normalized to the number of surface tantalum species.

cation, which is the inverse trend found above for the TOF_{redox} of supported vanadia catalysts.

The TOF_{acidic} and Selectivity_{acidic} values for the different supported tantalum catalysts and bulk Ta₂O₅ are presented in Table 4. Only reaction products originating from surface acidic sites were obtained during methanol oxidation (100% CH₃OCH₃), which is consistent with the absence of surface redox and basic sites on these tantalum materials (see Sections 3.2.3.1 and 3.2.3.3). Unlike the supported niobia catalyst systems, only supported Ta₂O₅/Al₂O₃ exhibited a higher TOF_{acidic} than bulk Ta₂O₅. Among the supported tantalum catalysts, the Ta₂O₅/Al₂O₃ catalyst exhibited the highest TOF_{acidic}, which, analogous to Nb₂O₅/Al₂O₃, should be the only catalyst system with surface Brønsted acid sites and the strongest surface Lewis acid sites. However, the supported niobia catalysts possess a higher TOF_{acidic} than the supported tantalum catalysts since significantly higher reaction temperatures are required to obtain the same TOF_{acidic} value for supported Ta₂O₅/Al₂O₃ than Nb₂O₅/Al₂O₃, 300 and 230 °C, respectively. Similarly to the supported niobia catalyst systems, the TOF_{acidic} for the supported tantalum catalysts appears to qualitatively increase with the electronegativity of the oxide support cation, which is the inverse trend found for surface redox sites of the supported vanadia catalysts.

The catalytic properties for the supported dubnia catalysts are expected to follow the pattern for supported niobia and tantalum catalysts presented in Tables 3 and 4, with only the presence of active surface acidic sites yielding CH₃OCH₃ during methanol oxidation. Furthermore, the TOF_{acidic} of the surface dubnia sites should be much less active than the supported tantalum catalysts and higher reaction tempera-

Table 5

Predicted methanol oxidation over supported dubnia, monolayer surface coverage, and bulk Db₂O₅ catalysts at 400 °C

Catalyst	TOF _{acidic} (s ⁻¹)	Selectivity _{acidic} (%)
Bulk Db ₂ O ₅	~9 × 10 ⁻¹ ^a	100
Db ₂ O ₅ /Al ₂ O ₃	~2 × 10 ⁻¹ ^b	100
Db ₂ O ₅ /ZrO ₂	~8 × 10 ⁻³ ^b	100
Db ₂ O ₅ /TiO ₂	~3 × 10 ⁻³ ^b	100

^a Assumed same value as found for bulk Ta₂O₅.

^b Assumed similar values for supported tantalum catalysts at 300 °C.

tures would be required to obtain comparable values, which are estimated below in Table 5. In contrast, bulk Db₂O₅ would be expected to exhibit a comparable TOF_{acidic} value to bulk Nb₂O₅ and Ta₂O₅ since the latter two exhibit almost identical values. Thus, bulk Db₂O₅ would be estimated to possess a TOF_{acidic} that is comparable or greater than the supported dubnia catalysts (especially supported Db₂O₅/Al₂O₃).

4. Conclusions

The fundamental molecular structures, nature of active surface sites and their molecular structure–reactivity/selectivity relationships of the Group V metal oxides have seen a significant advance in recent years, as reflected by the contributions to this special issue of *Catalysis Today*. Bulk V₂O₅ possesses platelet morphology and the active surface sites are only present at the edges of the platelets. Bulk Nb₂O₅ and Ta₂O₅, and also expected for bulk Db₂O₅, possess an isotropic morphology and the active surface sites are relatively homogeneously distributed on these oxide surfaces. Bulk V₂O₅ exhibits the presence of surface redox and acidic sites, with the latter being a minor component. Bulk Nb₂O₅ and Ta₂O₅, and also expected for bulk Db₂O₅, only exhibit the presence of surface acidic sites. Interestingly, the surface acidic sites on the bifunctional bulk V₂O₅ were more active than the surface acidic sites on bulk Nb₂O₅ and Ta₂O₅. For the bulk Group V mixed metal oxides, V₂O₅–Nb₂O₅ and V₂O₅–Ta₂O₅, the active surface sites for methanol oxidation and propane ODH were found to be the surface vanadia redox sites (this was further confirmed by an extensive study of bulk

mixed metal vanadates reported in this special issue of *Catalysis Today* by Briand et al.).

The supported Group V metal oxides were only found to possess redox sites for the supported vanadia catalysts, with the exception of the supported V_2O_5/Al_2O_3 catalyst, but surface acidic sites were also present on these bifunctional catalytic materials. The supported niobia and tantalum catalysts, and also expected for supported zirconia, only possess surface acidic sites. Both surface Brønsted and Lewis acidic sites were determined on the supported metal oxides. Supported vanadia catalysts always contained both surface Brønsted and Lewis acidic sites at monolayer surface coverage, with the exception of supported V_2O_5/SiO_2 that only possessed surface Lewis acidic sites. Alumina supported niobia and tantalum catalysts contained both surface Brønsted and Lewis acidic sites, but all other supported niobia and tantalum catalytic materials only contained surface Lewis acidic sites. The surface acidic sites for supported zirconia catalysts would be expected to parallel the characteristics found for the supported niobia and tantalum catalysts. No surface basic sites were found to be present for monolayer surface coverage of the supported Group V metal oxides. The specific redox activity of the supported vanadia catalysts was found to be a strong function of the specific oxide support ligand, $Ce > Zr > Ta > Nb \sim Ti > Al > Si$, which varied by three orders of magnitude and increased with the decreasing electronegativity of the specific oxide support cation. The specific acidic activity of the supported niobia and tantalum catalysts, as also expected for the supported zirconia catalysts, were found to vary by 1 to 2 orders of magnitude for the different oxide supports, $Al > Zr \sim Ti \sim Ta$, and increased with the increasing electronegativity of the specific oxide support cation, inversely to the reactivity pattern of the supported vanadia redox sites.

The current fundamental molecular level understanding of bulk and supported Group V metal oxides allows for the rational molecular engineering of applied Group V metal oxide catalysts. Additional fundamental studies on tantalum-based catalysts are still required since their physical, electronic and chemical properties have not been fully explored at this time (e.g., bulk mixed metal tantalates, silicate-based tantalum molecular sieves and their supported analogues).

Acknowledgements

The authors would like to acknowledge the generous support of Niobium Products and HC Starck for the niobium oxide and tantalum oxide studies, respectively, as well as NSF (CTS-9901643) and DOE-Basic Energy Sciences (grant DEFG02-93ER14350) for supporting the vanadium oxide investigations. The authors are also extremely grateful to David Brown and Heather Haught of Zeton Altamira (Pittsburgh, PA, USA) for efficiently performing the H_2 -TPR studies on the tantalum oxide catalysts at the time of the writing of this manuscript.

References

- [1] G.C. Bond, J.C. Vedrine, *Catal. Today* 20 (1) (1994) (special issue).
- [2] J.C. Vedrine, *Catal. Today* 56 (4) (2000) (special issue).
- [3] F. Trifiro, B. Grzybowska, *Appl. Catal. A* 157 (1997) (special issue).
- [4] E.I. Ko, *Catal. Today* 8 (1) (1990) (special issue).
- [5] K. Tanabe, *Catal. Today* 16 (3–4) (1993) (special issue).
- [6] K. Tanabe, *Catal. Today* 28 (1–2) (1996) (special issue).
- [7] M. Schmal, V. Teixeira da Silva, F.B. Noronha, *Catal. Today* 57 (3–4) (2000).
- [8] T. Ushikubo, *Catal. Today* 57 (3–4) (2000) 331.
- [9] I.E. Wachs, L.E. Briand, J.-M. Jehng, L. Burcham, X. Gao, *Catal. Today* 57 (2000) 323.
- [10] G. Deo, I.E. Wachs, *J. Catal.* 146 (1994) 323; G. Deo, I.E. Wachs, *J. Catal.* 146 (1994) 335.
- [11] J.-M. Jehng, I.E. Wachs, *J. Mol. Catal.* 67 (1991) 369.
- [12] J.-M. Jehng, A.M. Turek, I.E. Wachs, *Appl. Catal. A* 83 (1992) 179.
- [13] M.A. Vuurman, I.E. Wachs, *J. Phys. Chem.* 96 (1992) 5008.
- [14] A.M. Turek, I.E. Wachs, *J. Phys. Chem.* 96 (1992) 5000.
- [15] L.J. Burcham, G. Deo, X. Gao, I.E. Wachs, *Topics Catal.* 11–12 (2000) 85.
- [16] M. Ruitenbeek, A.J. van Dillen, F.M.F. de Groot, I.E. Wachs, J.W. Geus, D.C. Koningsberger, *Topics Catal.* 10 (2000) 241.
- [17] H. Eckert, I.E. Wachs, *Mater. Res. Soc. Symp. Proc.* 111 (1988) 455; H. Eckert, I.E. Wachs, *J. Phys. Chem.* 93 (1989) 6796.
- [18] J.P. Dunn, J.-M. Jehng, D.S. Kim, L.E. Briand, H.G. Stenger, I.E. Wachs, *J. Phys. Chem. B* 102 (1998) 6212.
- [19] L.E. Briand, W.E. Farneth, I.E. Wachs, *Catal. Today* 62 (2000) 219.
- [20] X. Gao, S.R. Bare, J.L.G. Fierro, I.E. Wachs, *J. Phys. Chem. B* 103 (1999) 618.
- [21] X. Gao, J.-M. Jehng, I.E. Wachs, *J. Catal.* 209 (2002) 43.
- [22] A.F. Wells, *Structural Inorganic Chemistry*, Oxford University, London, 1984.
- [23] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworths/Heinemann, Oxford, Chapter 22, 1997.

- [24] C.-B. Wang, Y. Cai, I.E. Wachs, *Langmuir* 15 (1999) 1223.
- [25] R.T. Sanderson, *J. Chem. Edu.* 65 (1988) 112.
- [26] M. Badlani, I.E. Wachs, *Catal. Lett.* 75 (2001) 137.
- [27] L.E. Briand, I.E. Wachs, *Catal. Today*, this issue.
- [28] I.E. Wachs, B.M. Weckhuysen, *Appl. Catal. A* 157 (1997) 67.
- [29] J.-M. Jehng, I.E. Wachs, *Catal. Today* 16 (1993) 417.
- [30] I.E. Wachs, J.-M. Jehng, G. Deo, H. Hu, N. Arora, *Catal. Today* 28 (1996) 199.
- [31] G. Ramis, C. Cristiani, P. Forzatti, G. Busca, *J. Catal.* 124 (1990) 574.
- [32] B.M. Weckhuysen, J.-M. Jehng, I.E. Wachs, *J. Phys. Chem. B* 104 (2000) 7382.
- [33] X. Gao, S.R. Bare, B.M. Weckhuysen, I.E. Wachs, *J. Phys. Chem. B* 102 (1998) 10842.
- [34] T. Machej, J. Haber, A.M. Turek, I.E. Wachs, *Appl. Catal.* 70 (1991) 115.
- [35] S. Yoshida, T. Tanaka, T. Hanada, T. Hiraiwa, H. Kanai, *Catal. Lett.* 12 (1992) 277.
- [36] T. Tanaka, T. Yoshida, H. Yoshida, H. Aritani, T. Funabiki, S. Yoshida, J.-M. Jehng, I.E. Wachs, *Catal. Today* 28 (1996) 71.
- [37] X. Gao, I.E. Wachs, M.S. Wong, J.Y. Ying, *J. Catal.* 203 (2001) 18.
- [38] L.J. Burcham, J. Datka, I.E. Wachs, *J. Phys. Chem. B* 103 (1999) 6015.
- [39] T. Tanaka, H. Nojima, T. Yamamoto, S. Takenaka, T. Funabiki, S. Yoshida, *Phys. Chem. Chem. Phys.* 1 (1999) 5235.
- [40] Y. Chen, T. Tanaka, J.L.G. Fierro, I.E. Wachs, presented at the Fourth International Symposium on Group V Compounds, April 9–12, *J. Phys. Chem. B*, submitted for publication.
- [41] M. Baltes, A. Kytokivi, B.M. Weckhuysen, R.A. Schoonheydt, P. van der Voort, E.F. Vasante, *J. Phys. Chem. B* 105 (2001) 6211.
- [42] B.M. Weckhuysen, I.E. Wachs, Unpublished results.
- [43] R.S. Weber, *J. Catal.* 151 (1995) 470.
- [44] X. Gao, I.E. Wachs, *J. Phys. Chem. B* 104 (2000) 1261.
- [45] J. Datka, J.-M. Jehng, A.M. Turek, I.E. Wachs, *J. Catal.* 135 (1992) 186.
- [46] K. Segawa, W.K. Hall, *J. Catal.* 76 (1982) 133.
- [47] H. Miyata, K. Fuji, T. Ono, *J. Chem. Soc., Faraday Trans.* 84 (1) (1988) 3121.
- [48] M.D. Amirdis, R.V. Duvel, I.E. Wachs, *Appl. Catal. B* 20 (1999) 111.
- [49] V.M. Mastikhin, A.V. Nosov, V.V. Terskikh, K.I. Zamaraev, I.E. Wachs, *J. Phys. Chem.* 98 (1994) 13621.
- [50] M.A. Banares, I.E. Wachs, *J. Raman Spectrosc.* 33 (2002) 359.
- [51] L.J. Burcham, L.E. Briand, I.E. Wachs, *Langmuir* 17 (2001) 6164.
- [52] J.-M. Jehng, I.E. Wachs, *J. Catal.*, submitted for publication.
- [53] I.E. Wachs, *Catal.—A Specialist Period. Rep.* 13 (1998) 37.