ELSEVIER

Catalysis Today 57 (2000) 323–330

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Molecular structure and reactivity of the group V metal oxides

Israel E. Wachs [a,*], Laura E. Briand [b], Jih-Mirn Jehng [c], Loyd Burcham [a], Xingtao Gao [a]

[a] *Zettlemoyer Center for Surface Studies and Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA*
[b] *Centro de Investigacion y Desarrollo en Procesos Cataliticos, Universidad Nacional de La Plata, (1900) La Plata, Buenos Aires, Argentina*
[c] *Department of Chemical Engineering, National Chung-Hsing University, Taichung 402, Taiwan, ROC*

Abstract

The molecular structures and reactivity of the group V metal oxides (V_2O_5, Nb_2O_5 and Ta_2O_5) were compared. Their solid state structural chemistry, physical and electronic properties, number of active surface sites and their chemical reactivity properties were examined. For the bulk oxides, the solid state structural chemistry and the physical and electronic properties are well established. The number of active surface sites and the distribution of surface redox/acid sites were determined with methanol chemisorption and methanol oxidation, respectively. These studies revealed that the active surface sites present in pure V_2O_5 are primarily redox sites and the active surface sites in pure Nb_2O_5 are essentially acidic in nature. Furthermore, the surface redox sites present in pure V_2O_5 are orders of magnitude more active than the surface acid sites in pure Nb_2O_5. Consequently, the catalytic properties of bulk V_2O_5–Nb_2O_5 mixed oxides are dominated by the vanadia component. For the supported metal oxides, where the group V metal oxides are present as two-dimensional metal oxide overlayers, the structural and electronic properties are not well established in the literature. From a combination of molecular spectroscopic characterization methods (e.g., XANES, Raman, IR and UV–Vis DRS), it was possible to obtain this fundamental information. Methanol chemisorption studies demonstrated that a similar number of active surface sites are present in the supported vanadia and niobia catalyst systems. Similar to their bulk oxides, the surface vanadia species possess redox characteristics and the surface niobia species primarily possess acidic characteristics (Lewis acidity). The surface niobia species was a very sluggish redox site during oxidation reactions (e.g., methanol oxidation to formaldehyde and SO_2 oxidation to SO_3), but significantly promoted the surface vanadia redox sites for oxidation reactions that required dual surface redox and acid sites (e.g., butane oxidation to maleic anhydride and selective catalytic reduction of NO_x by NH_3 to produce N_2). These new fundamental insights are allowing for the molecular engineering of group V metal oxide catalysts (especially vanadia and niobia). In contrast, the molecular structure and reactivity properties of Ta_2O_5 catalysts are not yet established and will require significant research efforts. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Molecular structure; Methanol chemisorption; Methanol oxidation

1. Introduction

The group V metal oxide catalysts, both as bulk metal oxides and supported metal oxides, have received much attention in recent years. Two special issues of *Applied Catalysis* were recently devoted to the catalytic properties of vanadia [1,2]. Several issues of *Catalysis Today* have been devoted to the proceedings from symposia on Nb catalytic compounds [3–5]. In contrast to vanadia and niobia, our current understanding of tantala-based catalytic materials is rather limited [6]. No publications, however, have appeared that have compared the molecular structure and reactivity properties of the group V metal oxides. Thus, the objective of the present paper is to compare the molecular structure and reactivity

---

[*] Corresponding author. Tel.: +1-610-758-4274; fax: +1-610-758-6555.
E-mail address: iew0@lehigh.edu (I.E. Wachs).

PII: S0920-5861(99)00343-0

properties of the group V metal oxides (especially vanadia and niobia). The first portion of this paper focuses on the solid state structural chemistry, physical and electronic properties, and chemical reactivity (number of active surface sites and their redox/acidic catalytic properties) of the bulk group V metal oxides (three-dimensional phases). The second portion of this paper focuses on the solid state structural chemistry, physical and electronic properties, and chemical reactivity (number of active surface sites and their redox/acidic catalytic properties) of the supported group V metal oxides (two-dimensional phases).

2. Experimental

Experimental details of the catalyst synthesis, characterization, and the determination of the surface characteristics and catalytic properties can be found in other publications. The catalyst synthesis procedures are described in publications by Deo and Wachs (supported vanadia catalysts) [7,8], Jehng and Wachs and Jehng et al. (supported niobia catalysts and surface modified niobia catalysts) [9,10] and Guliants et al. (Nb promoted VPO catalysts) [11]. The spectroscopic characterization instrumentation employed were Raman [7], IR [12] and UV–Vis DRS [13]. The surface characteristics of the various catalysts were determined by the N_2 BET method [7] and CH_3OH chemisorption was performed in either a TGA apparatus [7,14] or in an IR spectrometer [12]. Additional details of the catalytic studies for methanol oxidation [7], SO_2 oxidation [15], propane oxidative dehydrogenation [16], butane oxidation to maleic anhydride [17] and the selective catalytic reduction of NO_x by NH_3 [18] can be found in the associated references. The hydrogen temperature programmed reduction system and procedure is described in Ref. [13].

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 is well documented in the literature [19–21]. The bulk V(+5) oxides consist of VO_4 units that may be present as isolated, dimerized or polymerized chains (orthovanadate, pyrovanadate or metavandate, respectively) and highly distorted VO_6 units that may be present as isolated units, clusters or sheets [20]. In contrast, the bulk Nb(+5) oxides rarely consists of NbO_4 units and prefer NbO_6 coordination [21]. The very large Nb(+5) cation has difficulty fitting into NbO_4 coordination and only a handful of such compounds are known. The NbO_6 units may be present as undistorted as well as distorted species and NbO_7 and NbO_8 units are also known. The bulk Ta(+5) oxides have a similar structural chemistry to the bulk Nb(+5) oxides and rarely consist of TaO_4 units [19]. Thus, the solid state structural chemistry of bulk V(+5) oxides tends to be very different than that of the Nb(+5) and Ta(+5) bulk oxides.

3.1.2. Physical and electronic properties

The melting temperature of the group V metal oxides increases with increasing atomic number (e.g., V_2O_5 (690°C), Nb_2O_5 (1512°C) and Ta_2O_5 (1872°C)). The melting points of these bulk, crystalline metal oxides have a very important effect on the surface mobility of these metal oxides since at the Tammann temperature, $T_{\mathrm{Tam}}=T_{\mathrm{mp}}/2$, the surface atoms begin to surface diffuse [22]. The Tammann temperatures for the group V metal oxides are 209°C for V_2O_5, 620°C for Nb_2O_5 and 800°C for Ta_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 readily spread out over other oxide surfaces. The group V metal oxides also possess different morphologies in the crystallized state: platelet for V_2O_5 and primarily isotropic for Nb_2O_5 and Ta_2O_5. The bandgap energies of these crystalline group V metal oxides were measured with UV–Vis diffuse reflectance spectroscopy (DRS) and 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. Thus, the semiconductor properties of the bulk, crystalline group V metal oxides decrease with increasing atomic number. In summary, the physical and electronic properties of bulk V_2O_5 tend to be very different from those of bulk Nb_2O_5 and Ta_2O_5.

3.1.3. *Chemical reactivity properties*

The chemical reactivity properties of bulk V_2O_5 and Nb_2O_5 are only reported below since the properties of bulk Nb_2O_5 and Ta_2O_5 are expected to be somewhat similar and only limited data are currently available about bulk Ta_2O_5.

Hydrogen temperature programmed reduction (TPR): The reduction properties of bulk V_2O_5 and Nb_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 ($V_2O_5 \rightarrow V_6O_{13}$), 705°C ($V_6O_{13} \rightarrow V_2O_4$) and 780°C ($V_2O_4 \rightarrow V_2O_3$). 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 Nb_2O_5 to bulk Nb_2O_4. These two comparative H_2-TPR experiments clearly demonstrate the ease with which bulk V_2O_5 reduces in comparison to bulk Nb_2O_5.

BET surface area and number of surface active sites: The BET surface areas of bulk V_2O_5 and Nb_2O_5 (T-phase) samples used in the present investigation were found to be 3.5 and 1.9 m^2/g, respectively. The number of surface active sites was determined by methanol chemisorption at 100°C with 2000 ppm of methanol in He. Under these conditions, physisorbed methanol is not present and only surface methoxy, $CH_3O_{(ads)}$, species are present [14]. The number of surface methoxy species for bulk V_2O_5 and Nb_2O_5 was found to be 0.67 and 2.98 μmol/m^2, respectively. The much lower number of specific surface active sites for bulk V_2O_5 compared to bulk Nb_2O_5 is a consequence of the different surface morphologies of these two metal oxides and their surface reactivity. The surface methoxy species preferentially form on the edges and do not react with the basal plane of crystalline V_2O_5 [23]. For crystalline Nb_2O_5, the isotropic morphology does not result in preferential formation of surface methoxy species on specific planes and adsorption occurs over the entire surface. Consequently, bulk Nb_2O_5 possesses about five times greater the number of specific surface active sites than bulk V_2O_5.

Methanol oxidation over pure metal oxides: The methanol oxidation reaction can simultaneously probe the surface redox, primarily the production of formaldehyde, and surface acidity, formation of dimethyl ether, of metal oxide catalysts [24]. Furthermore, the turnover frequencies ($TOF_{overall}$=number of methanol molecules consumed per active site per second; $TOF_{redox}=TOF_{overall}\times S$ (H_2CO selectivity); $TOF_{acid}=TOF_{overall}\times S$ (CH_3OCH_3 selectivity)) can be quantitatively determined from knowledge of the methanol conversion, H_2CO and CH_3OCH_3 production, and the number of surface active sites determined from methanol adsorption. For methanol oxidation at 300°C, the TOF_{redox} was determined to be 2.53 and 0.00 s^{-1} for bulk V_2O_5 and Nb_2O_5, respectively. The corresponding TOF_{acid} was determined to be 0.30 and 0.04 s^{-1} for V_2O_5 and Nb_2O_5, respectively. Thus, bulk V_2O_5 predominantly possesses surface redox characteristics (>90%) and bulk Nb_2O_5 exclusively possesses surface acidic characteristics (100%). Furthermore, the $TOF_{overall}$ is orders of magnitude greater for bulk V_2O_5 than bulk Nb_2O_5.

Oxidation reactions over mixed metal oxides: The methanol oxidation reaction was also used to probe the surface characteristics of a mixed 1% V_2O_5–Nb_2O_5 oxide formed by coprecipitation and calcination at 500°C (see Table 1). The $TOF_{overall}$ for this mixed oxide at 230°C was found to be 0.12 s^{-1}, which was calculated by assuming 100% dispersion of V(+5) on the surface (this assumption will be elaborated below), and a product selectivity of 62% H_2CO and 35% CH_3OCH_3 was obtained. For quantification of the

Table 1
Oxidative dehydrogenation reactions over bulk and supported V_2O_5–Nb_2O_5 mixed metal oxide catalysts

Reactions	$TOF_{overall}$ [a] (s^{-1})	
	V_2O_5–Nb_2O_5 bulk mixed oxide	V_2O_5/Nb_2O_5 supported
CH_3OH oxidation to H_2CO at 230°C	0.012	0.80
$CH_3CH_2CH_3$ ODH to CH_2CHCH_3 at 425°C	0.018	0.039

[a] TOF for the supported V_2O_5/Nb_2O_5 catalysts was determined by assuming 100% dispersion of the surface vanadia species (confirmed by Raman spectroscopy). TOF for the bulk mixed oxide catalysts was calculated by assuming 100% dispersion of V (+5) on the surface (see text for additional discussion).

TOF, a comparative experiment was performed with a supported 1% V_2O_5/Nb_2O_5 catalyst where the vanadia component was confirmed with Raman spectroscopy to be 100% dispersed on the surface. For the supported 1% V_2O_5/Nb_2O_5 catalyst, the $TOF_{overall}$ was found to be $0.80\,s^{-1}$ with a selectivity of 92% H_2CO and 8% CH_3OCH_3. Comparison of the $TOF_{overall}$ of the mixed and supported 1% V_2O_5–Nb_2O_5 catalysts reveals that only ∼10–15% of the vanadia is actually present on the surface of the mixed metal oxide catalyst. This conclusion is consistent with the much higher H_2CO selectivity for the supported catalyst relative to the mixed metal oxide catalyst (92 and 62%, respectively). The similar product selectivities for the bulk V_2O_5 and supported 1% V_2O_5/Nb_2O_5 catalysts during methanol oxidation further demonstrate that the surface vanadia sites are dominating the catalytic properties of these metal oxides. Thus, the surface vanadia sites are the active sites in bulk V_2O_5–Nb_2O_5 mixed metal oxide catalysts during oxidative dehydrogenation reactions.

The oxidative dehydrogenation of propane to propylene was also investigated over supported and mixed metal oxide catalysts containing 2% V_2O_5–Nb_2O_5 (see Table 1) [16]. It was found that the vanadia was approximately equally distributed between the surface and bulk in the mixed 2% V_2O_5–Nb_2O_5 coprecipitated catalyst since the supported 2% V_2O_5/Nb_2O_5 catalyst, containing 100% dispersion of surface vanadia, exhibited a TOF that was twice as high for this reaction. Furthermore, bulk Nb_2O_5 was essentially inactive for this oxidative dehydrogenation reaction. V–P–O catalysts are employed industrially to oxidize *n*-butane to maleic anhydride and the influence of *surface* Nb and V promotion to such a catalyst was recently examined (1.2% butane in air and 380°C) [11]. A $VOHPO_4\cdot 0.5\ H_2O$ precursor, prepared by the organic method, was impregnated with Nb-alkoxide, which corresponded to approximately 0.25 Nb surface coverage, and the catalyst was equilibrated in 1.2% butane in air at 400°C. The $TOF_{overall}$ for butane conversion and TOF_{man} for maleic anhydride production were measured. The $TOF_{overall}$ was found to increase from ∼5 to $8\times10^{-4}\,s^{-1}$ and the TOF_{man} was found to increase from ∼2 to $4\times10^{-4}\,s^{-1}$. These findings reveal that surface niobia sites promote the activation and oxidation of *n*-butane to maleic anhydride in bulk V–P–O mixed oxide catalysts. The exact origin of this promotion is not clear at present, but may be due to either the surface niobia Lewis acid sites or the enhancement of the surface V redox sites via a ligand effect [8]. Analogous studies with the addition of the equivalent of 0.25 V surface coverage essentially did not affect the performance of the bulk V–P–O catalyst since surface vanadia redox sites were already present on the mixed metal oxide catalyst surface.

3.2. Supported group V metal oxides

Supported metal oxide catalysts 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 [2,21,25–27]. In contrast, essentially no such corresponding publication is currently available about supported tantalum oxide catalysts. Consequently, only supported vanadia and niobia catalysts will be discussed below.

3.2.1. Solid state structural chemistry

The molecular structures of surface vanadia and niobia species have been extensively investigated with numerous spectroscopies in the past few years. Surface metal oxide species change their coordination upon adsorption of moisture at temperatures below 200°C, but retain their dehydrated structures at elevated temperatures (even in the presence of moisture and during catalytic reactions). Thus, only the dehydrated molecular structures of the supported vanadia and niobia species will be discussed in the present paper.

Solid state ^{51}V NMR [28], XANES [29] and UV–Vis DRS [30] characterization studies have shown that the surface vanadia species possess VO_4 coordination. Raman and IR studies reveal that both terminal V=O and bridging V–O–V bonds are present in these surface vanadia overlayers [7,31]. Combined Raman and IR studies, coupled with oxygen-18 isotopic exchange experiments, confirm that only one terminal V=O bond exists on each surface vanadia species (mono-oxo structure containing one terminal V=O bond and three bridging V–O–M bonds, where M can be either another V or the support cation) [32]. At low surface vanadia coverages, the surface vanadia species are primarily isolated; at high surface vanadia coverages, the surface vanadia species are substantially polymerized. Monolayer surface coverages correspond to 7–8 V atoms/nm^2 [25,30]. An exception is the V_2O_5/SiO_2 system, where only isolated surface vanadia species are present and maximum coverage corresponds to $\sim$3 V atoms/nm^2 [33]. The preparation method does not affect the molecular structures of the surface vanadia species, but can affect their dispersion (especially on the weakly interacting SiO_2 surface) [34]. Interestingly, the low Tammann temperature of vanadia results in the spontaneous dispersion of V_2O_5 on oxide supports [22,35,36].

XANES characterization studies have demonstrated that the surface niobia species possess NbO_4 coordination at low surface coverages and NbO_6 coordination at high surface coverages [37,38]. Raman and IR studies reveal that both terminal Nb=O and bridging Nb–O–Nb bonds are present in these surface niobia overlayers [39,40]. Combined Raman and IR studies have confirmed that only one terminal Nb=O bond exists on each surface niobia species (mono-oxo structure). At low surface niobia coverages, the surface niobia species are primarily isolated and present as NbO_4 species. At high surface niobia coverages, the surface niobia species are substantially polymerized and present as NbO_6 species. Monolayer surface coverages correspond to 5–6 Nb atoms/nm^2 [25]. The slightly lower surface niobia densities, relative to the surface vanadia species, are probably related to the additional oxygen atoms associated with the six-coordinated surface niobia species at high surface coverages. An exception is the Nb_2O_5/SiO_2 system, where only isolated surface niobia species are present and maximum coverage correspond to $\sim$2 Nb atoms/nm^2. The preparation method does not affect the molecular structures of the surface niobia species, but can affect their dispersion (especially on the weakly interacting SiO_2 surface) [26]. In contrast to V_2O_5, the much higher Tammann temperature of niobia does not result in spontaneous dispersion of Nb_2O_5 on oxide supports [4].

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 do become mobile and diffuse over the oxide supports at temperatures significantly in excess of their bulk Tammann temperatures. This is well documented for supported vanadia catalysts because of the very low Tammann temperature of bulk V_2O_5 [35,36,41]. The surface niobia species are more stable on oxide supports because of the much higher Tammann temperature of bulk Nb_2O_5 [41]. The bandgap energies of the supported vanadia catalysts are much higher than that of bulk V_2O_5 (3–4 eV vs. 2.3 eV, respectively), which reflect the highly dispersed state of the surface vanadia species on the oxide supports [30]. The bandgap energies of the supported vanadia catalysts decrease slightly with increasing surface vanadia coverage because of the increase in the extent of polymerization. The bandgap energy of the supported vanadia catalysts is also somewhat dependent on the specific oxide support ligand. Corresponding UV–Vis data for supported niobia and tantalum oxide catalysts are not currently available.

3.2.3. Chemical reactivity properties

Hydrogen temperature programmed reduction: The reduction characteristics of the surface vanadia and niobia species were determined by H_2-TPR. The following reduction temperatures were observed for monolayer coverages of the supported vanadia catalysts: 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). In all cases, the extent of reduction corresponded to reduction of V(+5) to V(+3) and only one reduction peak was observed. The influence of the oxide support upon the surface vanadia species is clearly evident since the reduction temperatures vary $\sim$100°C with the different oxide supports. The corresponding H_2 TPR experiments did not show any reduction of the supported niobia catalysts and only a trace amount of reduction was observed for Nb_2O_5/TiO_2 at 550°C. Thus, similar to bulk V_2O_5 and Nb_2O_5, the supported vanadia species are relatively easy to reduce and the surface niobia species are very resistant to reduction.

Number of surface active sites: The number of surface active sites present in the supported vanandia and niobia catalysts was determined by methanol chemisorption [12,14]. The number of surface methoxy species adsorbed per surface vanadia species at monolayer coverages was found to be 0.35 for V_2O_5/Al_2O_3, 0.49 for V_2O_5/TiO_2 and 0.30 for V_2O_5/ZrO_2. In all cases, the surface methoxy to surface vanadia ratio was significantly less than 1/1 and corresponded from about 1/3 to 1/2. The low values are most probably due to the presence of lateral interactions in the surface methoxy overlayer. Essentially similar numbers of surface methoxy species adsorbed per surface niobia species were obtained at monolayer coverages: 0.38 for Nb_2O_5/Al_2O_3, 0.43 for Nb_2O_5/TiO_2 and 0.41 for Nb_2O_5/ZrO_2. As for the supported vanadia catalysts, the surface methoxy to surface niobia ratio was significantly less than 1/1 and corresponded from about 1/3 to 1/2 due to lateral interactions in the surface methoxy overlayer. Thus, the number of surface active sites is comparable for supported vanadia and niobia catalysts.

Methanol oxidation over supported metal oxides: The reactivity properties of the supported vanadia and niobia catalysts were probed with the methanol oxidation reaction at 230°C. The supported vanadia catalysts yielded H_2CO as the primary reaction product, which reflects the redox nature of the surface vanadia species. The TOF_{redox} for the supported vanadia catalysts was found to vary over three orders of magnitude: $V_2O_5/ZrO_2>V_2O_5/TiO_2>V_2O_5/Nb_2O_5\gg V_2O_5/Al_2O_3\gg V_2O_5/SiO_2$ [7]. This reactivity pattern correlated with the decreasing electronegativity of the oxide support ligand and is attributed to the electron density on the bridging V–O-support bond [42]. The lower the electronegativity of the oxide support cation, the higher the electron density of the bridging V–O-support bond. The increased electron density increases the basicity of the bridging V–O-support bond, which enhances the hydrogen abstraction steps during the oxidative dehydrogenation of methanol to formaldehyde [12]. In contrast to the supported vanadia catalysts, the supported niobia catalysts did not yield any formaldehyde and reflects the absence of redox sites on these catalysts. The lack of redox nature for the supported niobia catalysts is consistent with their resistance towards reduction during the H_2 TPR experiments. The primary reaction product from the supported niobia catalysts was CH_3OCH_3 and the TOF_{acid} was about 1-2 orders of magnitude lower than the TOF_{redox} for the supported vanadia catalysts. Thus, as with the bulk V_2O_5 and Nb_2O_5 catalysts, the supported vanadia catalysts exhibit much higher $TOF_{overall}$ than the supported niobia catalysts.

Oxidation reactions over supported mixed metal oxides: The above reactivity studies demonstrated that surface vanadia species primarily behave as redox sites and that surface niobia species primarily behave as acidic sites. However, some oxidation reactions require the presence of surface redox and surface acid sites (e.g., butane oxidation over V–P–O catalysts) [43]. Thus, the influence of surface niobia acidic sites upon supported V_2O_5/TiO_2 catalysts was investigated for several different oxidation reactions and the results are presented in Table 2.

For methanol oxidation, the surface vanadia redox sites are very active for this oxidative dehydrogenation reaction and the surface niobia acid sites are totally inactive. Furthermore, the addition of the surface niobia species to the surface vanadia species on TiO_2 did not affect the TOF_{redox} for this reaction. Consequently, the methanol oxidative dehydrogenation reaction requires only one surface vanadia site and surface niobia species cannot promote this reaction [8]. For SO_2 oxidation, both the surface vanadia and surface niobia sites are active for this oxygen insertion reaction, but the surface vanadia species are about an order of magnitude more active than the surface niobia sites. The low TOF_{redox} of the surface niobia species on TiO_2

Table 2
Oxidation reactions over supported vanadia and niobia catalysts

Reaction	$TOF_{redox}{}^a$ (s^{-1})		
	1% V_2O_5/TiO_2	6% Nb_2O_5/TiO_2	6% Nb_2O_5/1% V_2O_5/TiO_2
CH_3OH oxidation to H_2CO at 230°C	2.0×10^{-1}	0	1.6×10^{-1}
SO_2 oxidation to SO_3 at 400°C	1.1×10^{-4}	3.5×10^{-5}	3.1×10^{-4}
Butane oxidation to maleic anhydride at 221°C	2.8×10^{-5}	–	17.8×10^{-5}
SCR of NO/NH_3 to N_2 at 200°C	2.9×10^{-4}	–	2.1×10^{-3}

[a] TOF for 1% V_2O_5/TiO_2 and 6% Nb_2O_5/TiO_2 was calculated for 100% dispersed surface vanadia and niobia (confirmed by Raman spectroscopy), respectively. TOF for 6% Nb_2O_5/1% V_2O_5/TiO_2 was calculated by normalizing to the 100% dispersed surface vanadia (confirmed by Raman spectroscopy) since the redox activity is dominated by the surface vanadia for this supported mixed metal oxide catalyst.

is consistent with its very limited reduction observed during the H_2-TPR experiments. The addition of the surface niobia species to the supported vanadia/titania catalyst yields a higher TOF_{redox}, but this is just the sum of the individual TOF_{redox} for the surface vanadia and niobia species. Thus, SO_2 oxidation requires only one surface site for oxygen insertion and the surface niobia species can only enhance this reaction to a very limited extent [15,44]. For butane oxidation to maleic anhydride, the surface vanadia redox sites are expected to be significantly more active than the surface niobia acidic sites, but quantitative data for the supported niobia catalysts are not available. Nevertheless, the addition of the surface niobia species to the surface vanadia species on TiO_2 results in a factor of ~6 enhancement in the TOF_{redox}. The promotion of surface vanadia by the surface niobia species reveals that this complex oxidation reaction, which proceeds by oxidative dehydrogenation and oxygen insertion steps, requires dual surface redox and surface acid sites [17,45]. For the NO_x/NH_3 selective catalytic reduction (SCR) to N_2, the surface vanadia species on TiO_2 are much more active and selective than the surface niobia species on TiO_2 [18,46]. The Nb_2O_5/TiO_2 catalyst is more than an order of magnitude less active than the 1% V_2O_5/TiO_2 catalyst and N_2 selectivities of ~80 and ~100% are obtained, respectively. The addition of the surface niobia species to the surface vanadia species on TiO_2 results in about an order of magnitude enhancement in the TOF_{redox} and a selectivity of 100%. The promotion of surface vanadia species by the surface niobia species reveals that this oxidation/reduction reaction proceeds via dual sites requiring both surface redox and surface acid sites and that the surface niobia sites are very efficient acidic surface sites [47]. Pyridine adsorption experiments have shown that the surface niobia sites on TiO_2 exclusively possess Lewis acidity [40]. In summary, the surface niobia acidic sites are not efficient redox sites, but promote oxidation reactions over efficient surface vanadia redox sites that require adjacent surface redox and surface acid sites.

4. Conclusions

The structure and reactivity properties of the bulk and supported group V metal oxides have been compared. Bulk V(+5) metal oxides possess both VO_4 and VO_6 sites, which are highly distorted. Bulk Nb(+5) metal oxides prefer NbO_6 sites, which are both regular and highly distorted. Pure V_2O_5 is predominantly a redox metal oxide, but also possesses a minor amount of reactive surface acid sites. In contrast to V_2O_5, pure Nb_2O_5 essentially only possesses reactive surface acid sites. In bulk V_2O_5–Nb_2O_5 mixed metal oxide catalysts, the surface vanadia sites are the active sites for oxidative dehydrogenation reactions because of their significantly greater TOF_{redox} relative to the surface niobia sites. In bulk V–P–O mixed metal oxide catalysts, the surface niobia acidic sites promote the activation and oxidation of butane to maleic anhydride. Supported vanadia catalysts possess surface V(+5) species, which are present as isolated and polymerized mono-oxo VO_4 sites. The surface vanadia species primarily possess redox properties, but also possess a minor amount of surface acidity. Supported niobia catalysts possess surface Nb(+5) species, which are present as isolated and polymerized mono-oxo NbO_4 and NbO_6 sites, respectively. The surface niobia species primarily possess Lewis acidity and are extremely sluggish towards redox processes. The preparation methods do not affect the molecular structures of the surface vanadia and niobia sites, but can affect their surface density at monolayer coverages on the early interacting SiO_2 support. The electronegativity of the oxide support ligand strongly affects the redox/acid properties of the surface vanadia and niobia species. The acidic surface niobia sites promote oxidation reactions over supported vanadia catalysts that require dual surface redox-acid sites. In summary, the molecular engineering of supported vanadia and niobia catalysts is now possible from the current fundamental understanding. Very little is currently known about the structure and reactivity properties of supported tantalum oxide catalysts and much more work will have to be done on such tantalum oxide catalysts in the future.

Acknowledgements

The financial support of the Office of Basic Energy Sciences at the Department of Energy is gratefully acknowledged (Grant DE-FG02-93ER14350).

References

[1] F. Trifiro, B. Grzybowska, Appl. Catal. A (Special Issue) 157 (1997).
[2] G.C. Bond, J.C. Vedrine, Catal. Today (Special Issue) 20 (1994).
[3] E.I. Ko, Catal. Today (Special Issue) 8 (1) (1990).
[4] K. Tanabe, Catal. Today (Special Issue) 16 (3/4) (1993).
[5] K. Tanabe, Catal. Today (Special Issue) 28 (1/2) (1996).
[6] T. Ushikubo, Catal. Today 58 (2000), this issue.
[7] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 323.
[8] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 335.
[9] J.-M. Jehng, I.E. Wachs, J. Mol. Catal. 67 (1991) 369.
[10] J.-M. Jehng, A.M. Turek, I.E. Wachs, Appl. Catal. A 83 (1992) 179.
[11] V.V. Guliants, J.B. Benziger, S. Sundaresan, I.E. Wachs, D. Hirt, Catal. Lett. 62 (1999) 87.
[12] L.J. Burcham, I.E. Wachs, Catal. Today 49 (1999) 467.
[13] X. Gao, S.R. Bare, J.L.G. Fierro, I.E. Wachs, J. Phys. Chem. B 103 (1999) 618.
[14] L. Briand, I.E. Wachs, in: 215th ACS National Meeting, Paper No. 39, Catal. Secretariat Div., Dallas, TX, 29 March–2 April 1998.
[15] J.P. Dunn, H.G. Stenger Jr., I.E. Wachs, J. Catal. 181 (1999) 233.
[16] T.C. Watling, G. Deo, K. Seshan, I.E. Wachs, J.A. Lercher, Catal. Today 28 (1996) 139.
[17] I.E. Wachs, J.-M. Jehng, G. Deo, B.M. Weckhuysen, V.V. Guliants, J.B. Benziger, S. Sundaresan, J. Catal. 170 (1997) 75.
[18] I.E. Wachs, G. Deo, B.M. Weckhuysen, A. Andreini, M.A. Vuurman, M. De Boer, M.D. Amiridis, J. Catal. 161 (1996) 211.
[19] A.F. Wells, Structural Inorganic Chemistry, Oxford University, London, 1984.
[20] G. Deo, I.E. Wachs, J. Haber, Crit. Rev. Surf. Chem. 4 (1994) 141.
[21] J.-M. Jehng, I.E. Wachs, Chem. Mater. 3 (1991) 100.
[22] C.-B. Wang, Y. Cai, I.E. Wachs, Langmuir 15 (1999) 1223.
[23] W.E. Farneth, F. Ohuchi, R.H. Staley, U. Chowdhry, A.E. Sleight, J. Phys. Chem. 89 (1985) 2493.
[24] J.M. Tatibouet, Appl. Catal. A 148 (1997) 213.
[25] I.E. Wachs, Catal. Today 27 (1996) 437.
[26] J.-M. Jehng, I.E. Wachs, Catal. Today 16 (1993) 417.
[27] I.E. Wachs, B.M. Weckhuysen, Appl. Catal. A 157 (1996) 67.
[28] H. Eckert, I.E. Wachs, J. Phys. Chem. 93 (1989) 6796.
[29] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 84 (1989) 2987.
[30] A. Khodakov, B. Olthef, A.T. Bell, E. Iglesia, J. Catal. 181 (1999) 205.
[31] G.T. Went, S.T. Oyama, A.T. Bell, J. Phys. Chem. 94 (1990) 4240.
[32] G. Ramis, C. Cristiani, P. Forzatti, G. Busca, J. Catal. 124 (1990) 574.
[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] H. Knozinger, E. Taugler, Catalysis 10 (1993) 1.
[36] J. Haber, T. Machej, E.M. Serwicka, I.E. Wachs, Catal. Lett. 32 (1995) 101.
[37] S. Yoshida, T. Tanaka, T. Hanada, T. Hiraiwa, H. Kanai, Catal. Lett. 12 (1992) 277.
[38] T. Tanaka, T. Yoshida, H. Yoshida, H. Aritani, T. Funabiki, S. Yoshida, J.-M. Jehng, I.E. Wachs, Catal. Today 28 (1996) 71.
[39] J.-M. Jehng, I.E. Wachs, J. Phys. Chem. 95 (1991) 7373.
[40] J. Datka, A.M. Turek, J.-M. Jehng, I.E. Wachs, J. Catal. 135 (1992) 186.
[41] I.E. Wachs, J.-M. Jehng, F.D. Hardcastle, Solid State Ionics 32 (33) (1989) 904.
[42] R.T. Sanderson, Polar Covalence, Academic Press, New York, 1983.
[43] F. Cavani, F. Trifiro, Catalysis 11 (1994) 146.
[44] J.P. Dunn, H.G. Stenger Jr., I.E. Wachs, Catal. Today 51 (1999) 301.
[45] V.V. Guliants, Catal. Today 51 (1999) 255.
[46] K.V. Vikulov, A. Andreini, E.K. Poels, A. Bliek, Catal. Lett. 25 (1994) 49.
[47] N.-Y. Topsoe, J.A. Dumesic, H. Topsoe, J. Catal. 151 (1995) 241.