Ethane and *n*-Butane Oxidation over Supported Vanadium Oxide Catalysts: An *in Situ* UV–Visible Diffuse Reflectance Spectroscopic Investigation

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The coordination/oxidation states of surface vanadium oxide species on several oxide supports (Al$_2$O$_3$, ZrO$_2$, SiO$_2$) during ethane and *n*-butane oxidation were examined by *in situ* UV–vis diffuse reflectance spectroscopy (DRS). Only a small amount of the surface V(V) cations are reduced to V(IV)/V(III) cations under present steady-state reaction conditions. The extents of reduction of the surface V(V) species are a strong function of the specific oxide support, V$_2$O$_5$/ZrO$_2$ > V$_2$O$_5$/Al$_2$O$_3$ > V$_2$O$_5$/SiO$_2$, and also correlate with their reactivities (turnover frequencies) for ethane and *n*-butane oxidation reactions. For ZrO$_2$-supported samples, the polymerized surface vanadia species were found to be more easily reduced than the isolated surface vanadia species in reducing environments (i.e., ethane or *n*-butane in He), but no significant differences in the extents of reduction were observed under present steady-state reaction conditions (i.e., ethane/O$_2$/He or *n*-butane/O$_2$/He). This observation is also consistent with the ethane oxidation catalytic study, which revealed that the polymerization degree, the domain size, of the surface vanadia species does not appear to significantly affect the reactivity of the supported vanadia catalysts for ethane oxidation.

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Key Words: V$_2$O$_5$/SiO$_2$, V$_2$O$_5$/ZrO$_2$ and V$_2$O$_5$/Al$_2$O$_3$ supported oxide catalysts; ethane and *n*-butane oxidation reactions; oxidation state; edge energy; temperature-programmed reduction; UV–visible diffuse reflectance spectroscopy.

INTRODUCTION

Supported vanadium oxide catalysts have attracted much attention in recent years as promising model catalysts for the oxidation and oxidative dehydrogenation of C$_2$–C$_4$ alkanes (1–6). Various factors such as reducibility, acidity–basicity, support effect, coordination geometry, and aggregation state (polymerization degree or VO$_x$ domain size) of the surface vanadium oxide species have been associated with the catalytic activity and selectivity of the supported vanadia catalysts (1–6). It is generally accepted that during oxidation reactions, the active surface V sites undergo a redox cycle. The degree of reduction of the catalyst under steady-state reaction conditions is thus associated with the equilibrium of reduction and reoxidation of the active sites. The degree of reduction of the catalysts, which has been associated with the increase in the binding strength of surface lattice oxygen, was proposed to be the major factor determining the reaction rates of butane oxidation and the selectivities to partial oxidation products (3). For well-dispersed vanadium oxide species on oxide supports, two types of surface vanadium oxide species are generally identified: isolated and polymeric vanadium oxide species. The ratio of polymerized to isolated surface vanadia species depends on the vanadia loading, the support surface area, and the specific nature of the support (1–5, 7). The catalytic behavior of the isolated and polymerized surface vanadia species for alkane oxidation is under discussion in the literature. For example, the turnover frequency for ethane oxidative dehydrogenation remains essentially constant for V$_2$O$_5$/Al$_2$O$_3$ catalysts at different vanadia loadings (6b). However, the low-vanadia-loading sample (V$_2$O$_5$/Al$_2$O$_3$) was reported to be more selective and less active than the high-vanadia-loading sample with more polymerized vanadium oxide species for butane oxidative dehydrogenation (3). For propane oxidative dehydrogenation over V$_2$O$_5$/Al$_2$O$_3$ catalysts, the selectivity remains constant (same selectivity-versus-conversion curve); the activity (if converted to TOF number from the literature results) is only slightly higher at a higher vanadia loading (less than 2 times) (9). Different results have also been reported that the polymerized surface vanadia species on supports are more selective and active than the isolated surface vanadia species for propane oxidative dehydrogenation (5). The reducibility of the surface vanadium oxide species also varies with the oxide support and the vanadia loading that is associated with the ratio of polymerized to isolated surface vanadium oxide species. However, the extent of reduction of the surface vanadium oxide species under steady-state reaction conditions has not yet been examined. The *in situ* measurement of the structure and oxidation states of the active surface vanadium oxide species is of key importance to a fundamental understanding of the relationship between

the catalytic performance and the redox ability and molecular structure of active surface species.

UV–vis diffuse reflectance spectroscopy (DRS) has been widely used to investigate the structures and oxidation states of various vanadium-containing solid oxides/compounds that possess the ligand-to-metal charge transfer (LMCT) transitions of V(V) in the region 20,000–48,000 cm^{-1} and d–d transitions of V(IV) and V(III) in the region 10,000–30,000 cm^{-1} (8). For supported vanadia catalysts, the catalysts have been studied before and/or after various treatments. For example, after propane oxidation, Eon et $al.$ (9) detected bands in the region 16,000–10,000 cm^{-1} due to d–d transitions of reduced vanadium oxide species on γ-Al$_2$O$_3$. In $situ$ DRS studies after reduction and reoxidation of vanadium oxide species in MCM-41 have been performed by Grubert et $al.$ (10). Hydrogen reduction results in broadbands in the region 10,000–25,000 cm^{-1} due to the reduced vanadium oxide species. Reoxidation causes the disappearance of the broadbands due to V(IV)/V(III), which demonstrated that in $situ$ UV–vis DRS can be used to monitor reduction and reoxidation cycles. Recent advances in in $situ$ UV–vis DRS studies of supported Cr oxide catalysts have been reported by Weckhuysen and Schoonheydt (11a). In $situ$ UV–vis DRS has been used to quantify reduced Cr oxide species (Cr$^{3+/2+}$) during isobutane dehydrogenation and the results demonstrate that the catalytic activity is directly proportional to the amount of reduced surface Cr oxide species. The reduction kinetics of supported Cr oxide species with CO have been studied by in $situ$ UV–vis DRS by monitoring the amount of Cr^{6+} as a function of reduction time. However, no in $situ$ DRS studies of supported vanadia catalysts have been performed to investigate the structure and oxidation state changes of surface vanadium cations under steady-state reaction conditions.

The present work focuses on the extent of reduction and structure/oxidation state changes of surface vanadium oxide species on different oxide supports during ethane and n-butane oxidation. The reducibility of the catalysts will be determined by the commonly employed H$_2$ temperature-programmed reduction experiment. The results obtained enable us to establish the relationship between the extent of reduction of the surface V sites, ratio of V(V) to V(VI)/V(III), during alkane oxidation reactions and the reactivity of the catalyst. These new in $situ$ DRS results are very informative for elucidating the nature of active surface sites under steady-state conditions and for providing fundamental insights into the reaction mechanisms.

EXPERIMENTAL

Catalyst preparation. The supports used for this study were SiO$_2$ (Cabosil EH-5, S_{BET} = 332 m^2/g), Al$_2$O$_3$ (Engelhard, S_{BET} = 222 m^2/g), and ZrO$_2$ (Degussa, S_{BET} = 34 m^2/g). The supported vanadia catalysts were prepared by incipient-wetness impregnation of isopropanol solutions of vanadium isopropoxide [VO(O-Pr^i)$_3$, Alfa-Aesar, 97% purity] on oxide supports. The catalysts were prepared inside a glove box with continuously flowing N$_2$. After impregnation, the samples were kept inside the glove box overnight. The samples were subsequently dried in flowing N$_2$ at 120°C for 1 h and at 300°C for 1 h, and were finally calcined in flowing air at 300°C for 1 h and at 450°C for 2 h.

UV–vis–NIR diffuse reflectance spectroscopy. The DRS experiments were conducted with a Varian Cary 5E UV–vis–NIR spectrophotometer. The vanadia loadings on all samples in the present work are 5% V$_2$O$_5$ or less since higher-vanadia-loading samples possess high noise-to-signal ratios and the Kubelka–Munk function equation is usually only valid at low metal cation concentrations for a quantitative determination of the absorbate, such as V and Cr cations (11). Two types of reflectance cells were employed, an in $situ$ Harrick cell and a quartz flow cell, which have been described in detail elsewhere (11a). In $situ$ diffuse reflectance spectra were taken in the range 200–800 nm using the Harrick DRS cell with the Praying Mantis diffuse reflectance attachment (DRA) to perform measurements under reaction conditions at high temperatures. The samples were calcined in the oven at 450°C for 2 h before immediate transfer to the in $situ$ cell. Then, the samples for the in $situ$ measurements were pretreated in O$_2$/He at 450°C for 1 h before any further treatment. Butane oxidation (C$_4$H$_{10}$/O$_2$/He = 1.2/8/90.8) and reduction (1.3% C$_4$H$_{10}$ in He) were performed at 230°C with a total flow rate of 50 mL/min, and ethane oxidation (C$_2$H$_6$/O$_2$/He = 2.4/8/81.6) and reduction (4.12% C$_2$H$_6$ in He) were performed at 450°C with a total flow rate of 90 mL/min. The dehydrated oxide supports recorded at 230°C (for n-butane oxidation/reduction) or 450°C (for ethane oxidation/reduction) were used as baselines for the corresponding supported vanadia catalysts. However, the quartz cell combined with the integration sphere DRA was used for the H$_2$-reduced samples as references. Reference diffuse reflectance spectra were recorded in the region 200–2200 nm at room temperature. A halon white (PTFE) reflectance standard was used as the baseline. The spectra of the dehydrated supported vanadia samples were obtained after the samples were calcined at 500°C in flowing O$_2$/He for 1 h. The spectra of the reduced samples were taken after the dehydrated supported vanadia samples were reduced at the desired temperature for 1 h in 10% H$_2$/Ar with a flow rate of 30 mL/min.

Diffuse reflectance spectra were processed with Bio-Rad Win-IR software, consisting of calculation of the Kubelka–Munk function [$F(R_\infty)$] from the absorbance. The edge energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of a plot of [$F(R_\infty) \times h\nu$]^2 against $h\nu$, where $h\nu$ is the incident photon energy (12).

H₂ Temperature-programmed reduction (TPR). TPR was carried out with an AMI-100 system (Zeton Altamira Instruments). The catalyst sample (∼60 mg) was loaded in a U-type quartz tube and pretreated at 500°C in flowing dry air for 1 h. After cooling in an Ar flow down to 150°C, the Ar gas was switched to a 10% H_2/Ar gas mixture. The temperature was then ramped from 150 to 700°C at a heating rate of 10°C/min in 10% H_2/Ar with a flow rate of 30 mL/min. An on-line TCD detector was used to record H_2 consumption, and CuO was used to verify the calibration of the instrument (the experimental error is within 10%).

Ethane oxidation. Ethane oxidation was carried out in an isothermal fixed-bed differential reactor. The catalyst (∼20 mg) was tested at various temperatures at atmospheric pressure. The reactant gas mixture of C_2H_6/O_2/He, molar ratio 1/2/8, was used at a total flow rate of 30 mL/min. The reactor effluent was analyzed with an on-line Hewlett–Packard Gas Chromatograph 5890 Series-II equipped with a TCD detector. A Chromosorb 107 column and a Molecular Sieve 5A packed column were used with a column isolation analysis system. The activity values, turnover frequency (TOF = number of ethane molecules converted per V atom per second), were obtained at the same reaction temperature of 550°C. The ethylene selectivity of the supported vanadia catalysts was obtained at an ethane conversion of 8% by varying the reaction temperature for each sample.

RESULTS AND DISCUSSION

H_2-TPR experiments of the supported vanadia catalysts showed that only one reduction peak was observed for each sample and the results are listed in Table 1. For the 1 and 4% V_2O_5/ZrO_2 and 5% V_2O_5/Al_2O_3 samples, the reduction peak maxima (T_{max}) are below 500°C. For the 1 and 5% V_2O_5/SiO_2 and 1% V_2O_5/Al_2O_3 samples, the reduction peak maxima are between 500 and 550°C. H_2 consumption values, represented as H/V atomic ratios, are also listed in Table 1 and are close to 2 for these samples, which indicates that the surface V(V) species are reduced predominantly to

TABLE 1

TPR Results and DRS Results of the Reduced Supported Vanadium Oxide Catalysts

Catalyst	T_{max} (°C)	H/V (atomic ratio)	T^a (°C)	Band max (cm⁻¹) (H₂-reduced)
1% V_2O_5/SiO_2	514	1.87	550	19,500; 17,400; ∼9000
5% V_2O_5/SiO_2	526	1.88	550	20,000–18,000; ∼9000
1% V_2O_5/Al_2O_3	550	1.94	550	22,700; 16,000; ∼9000
5% V_2O_5/Al_2O_3	496	1.75	500	23,100; 15,400; ∼9000
1% V_2O_5/ZrO_2	381	1.75	500	20,300; 16,000; ∼9000
4% V_2O_5/ZrO_2	407	1.76	500	∼18,800; ∼9000

[a]Temperature used for the DRS experiments to fully reduce V(V) species to V(IV)/V(III) species in the flow cell.
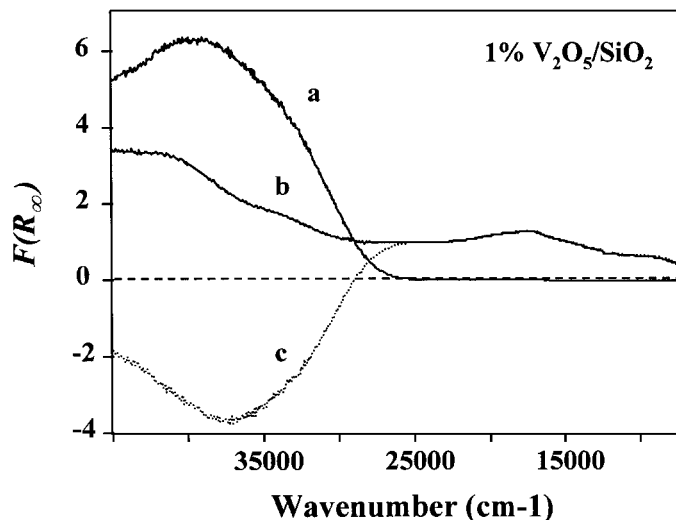

FIG. 1. UV–vis–NIR diffuse reflectance spectra of 1% V_2O_5/SiO_2 (a) in oxidized state and (b) after H_2 reduction at 550°C for 1 h. (c) Difference spectrum, (b)−(a).

surface V(III) species by hydrogen reduction. X-Ray photoelectron spectroscopy (XPS) experiments have shown (13, 14) that hydrogen reduction under the present reducing conditions usually reduces all V(V) cations to V(IV) or V(III) cations. Thus, the surface V(V) species of these catalysts are expected to be reduced mainly to V(III) after H_2 reduction at 500 or 550°C for 1 h and these reduction temperatures were employed for the reference DRS experiments.

The LMCT bands of V(V) are located mainly above 25,000 cm⁻¹, while V(IV) cations possess *d–d* electronic transitions in the region 10,000–30,000 cm⁻¹ and V(III) cations possess *d–d* electronic transitions in the region 8000–30,000 cm⁻¹ (8). UV–vis–NIR diffuse reflectance spectra for the 1% V_2O_5/SiO_2 sample in the oxidized and reduced states are shown in Fig. 1. The dehydrated, oxidized 1% V_2O_5/SiO_2 sample exhibits a LMCT transition above 25,000 cm⁻¹ with edge energy of 3.6 eV due to the surface isolated VO_4 species (15). After H_2 reduction, the intensity of the LMCT band centered at ∼38,000 cm⁻¹ significantly decreases due to the reduction of V(V) species, while broadbands due to V(III) and/or V(IV) *d–d* transitions appear in the region 8000–30,000 cm⁻¹ [19,500(sh), 17,400, and ∼9000 cm⁻¹]. These bands are most likely associated with V(III) cations (8), in agreement with the TPR results. The absorption bands remained above 30,000 cm⁻¹ after H_2 reduction should be assigned to the LMCT transitions of V(III)/V(IV) cations (8, 16) since no V(V) cations should be left according to the above TPR experiments. The band maxima of the *d–d* transitions of all the H_2-reduced samples are listed in Table 1. The band maximum, intensity, and shape of these *d–d* transitions are a strong function of the support, as shown in Fig. 2. All reduced samples exhibit a broad and weak band around 9000 cm⁻¹, suggesting that
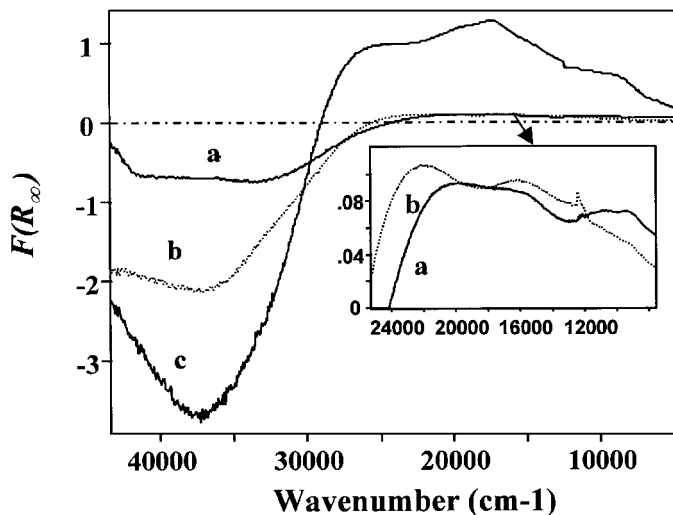
FIG. 2. Difference spectra of the supported vanadia catalysts after H_2 reduction (relative to the oxidized catalysts): (a) 1% V_2O_5/ZrO_2, (b) 1% V_2O_5/Al_2O_3, (c) 1% V_2O_5/SiO_2.

V(III) cations are probably dominant on these supports, in agreement with the TPR results.

For partially reduced vanadium oxide catalysts during alkane oxidation, however, V(IV) cations could be present in a greater concentration than V(III) cations (9). The V(IV) and V(III) $d-d$ transition bands are difficult to distinguish since these bands are located in the same region and tend to be broad and weak. Broadbands due to V(IV) and/or V(III) were observed during ethane and *n*-butane oxidation/reduction, as shown in Fig. 3. Therefore, the area of the reduced LMCT bands of the V(V) cations after H_2 reduction is considered as the reference area to relatively quantify the extent of 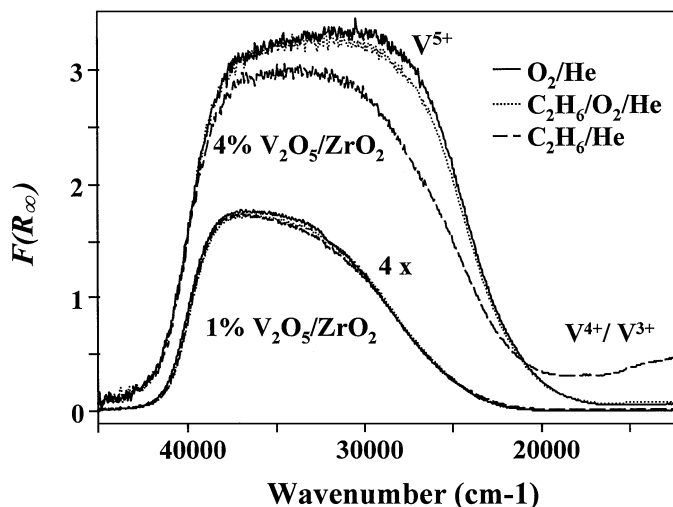reduction of the V(V) cations. Use of the area instead of the intensity of the LMCT bands is preferred because these broadbands tend to be mixed contributions from different electronic transitions of different surface vanadium oxide species (e.g., monomer and polymerized species) (15). No calibration curve for V(V) cations [intensity or area of the LMCT transitions as a function of the V(V) concentration] was obtained since this type of calibration curve usually loses its linearity at a metal concentration above 1 wt% (11).

The spectral difference between the reduced and oxidized spectra of the 1% V_2O_5/SiO_2 sample is also presented in Fig. 1. The area of the reduced LMCT bands of V(V) after H_2 reduction (the negative area in spectrum c) was used as the reference area [100% reduction of all V(V) cations to V(III)/V(IV) cations] to determine the relative reduction of surface V(V) species during *in situ* alkane oxidation/reduction. However, the area of the reduced LMCT bands depends on the support (see Fig. 2) and the vanadia loading. Thus, the area of the reduced LMCT band for each sample is used as its own reference area. The relative intensity change [$F(R_\infty)$ value] at a single wavenumber (17,000 cm^{-1}) in the region of $d-d$ transitions of V(IV)/V(III) cations has also been considered. Unfortunately, it is not possible to establish a more reliable estimate of the extent of reduction during oxidation reactions due to the extremely weak intensity in this region for low-vanadia-loading samples. For the 4% V_2O_5/ZrO_2 sample, however, the two methods [i.e., the relative intensity ($F(R_\infty)$ value)] at a single wavenumber (17,000 cm^{-1}) and the relative LMCT reduction area] are compared in Table 2 and are in reasonable agreement. This suggests that the comparison of the relative reduction areas can be used to estimate the relative extent of reduction during alkane oxidation reactions.

FIG. 3. *In situ* UV–vis diffuse reflectance spectra of 1 and 4% V_2O_5/ZrO_2 catalysts at 450°C under various environments. (The 1% V_2O_5/ZrO_2 sample was multiplied by 4.)

TABLE 2

Comparison of the Extents of Reduction of 4% V_2O_5/ZrO_2 Estimated by Two Different Methods

Reaction condition	Method 1[a] (%)	Method 2[b] (%)
$C_2/O_2/He$, 450°C	3.6	1.1
C_2/He, 450°C	23.0	22.3
$C_4/O_2/He$, 230°C	9.6	6.5
C_4/He, 230°C	20.1	15.8

[a] The relative decrease in the LMCT band area $= (1 - A_{rxn}/A_0')/(1 - A_{red}/A_0)$, where A_0 or A_0' is the LMCT band area of the corresponding oxidized catalyst before reduction or reaction, respectively; A_{red} is the area of the H_2-reduced reference catalyst; and A_{rxn} is the area of the catalyst during alkane oxidation/reduction.

[b] The relative increase in $F(R_\infty)$ intensity at 17,000 cm$^{-1} = (F(R_\infty)_{rxn} - F(R_\infty)_0')/(F(R_\infty)_{red} - F(R_\infty)_0)$, where $F(R_\infty)_0$ or $F(R_\infty)_0'$ is the intensity of the corresponding dehydrated, oxidized catalyst before reduction or reaction, respectively; $F(R_\infty)_{red}$ is the intensity of the H_2-reduced reference catalyst, and $F(R_\infty)_{rxn}$ is the intensity of the catalyst during alkane oxidation/reduction.

TABLE 3

Comparison of the Relative Extents of Reduction during Ethane and *n*-Butane Oxidation/Reductions

Catalyst	$C_2/O_2/He$, 450°C (%)	C_2/He, 450°C (%)	$C_4/O_2/He$, 230°C (%)	C_4/He, 230°C (%)
5% V_2O_5/SiO_2	∼0	4.4	∼0	0.2
5% V_2O_5/Al_2O_3	0.3	6.1	0.2	0.4
1% V_2O_5/ZrO_2	2.8	5.5	8.0	13.5
4% V_2O_5/ZrO_2	3.6	23.0	9.6	20.1

TABLE 4

Edge Energy Shifts of Supported Vanadia Catalysts (Relative to the Oxidized Catalysts) during Ethane Oxidation/Reduction

Catalyst	E_g (eV) O_2/He, 450°C	ΔE_g (eV) $C_2/O_2/He$, 450°C	ΔE_g (eV) C_2/He, 450°C
5% V_2O_5/SiO_2	3.48	0.00	0.00
5% V_2O_5/Al_2O_3	3.61	0.00	0.01
1% V_2O_5/ZrO_2	3.38	0.00	0.01
4% V_2O_5/ZrO_2	2.89	0.01	0.13

The *in situ* diffuse reflectance spectra of the 1 and 4% V_2O_5/ZrO_2 samples under oxidizing, ethane oxidation, and ethane reduction environments are presented in Fig. 3. Only a small fraction of the surface V(V) cations are reduced to V(IV)/V(III) cations during ethane oxidation. Additional surface V(V) cations are reduced under an ethane reduction environment (in the absence of O_2). The estimated relative extents of reduction during ethane oxidation/reduction are listed in Table 3, together with the results for *n*-butane oxidation/reduction. The extents of reduction for the 1% V_2O_5/SiO_2 and 1% V_2O_5/Al_2O_3 samples were not obtained since the areas of their LMCT band reduction are too small to estimate (within experimental error). These *in situ* UV–vis DRS results demonstrate that the surface V(V) cations dominate on these oxide supports during ethane and *n*-butane oxidation reactions. This is in agreement with the recent *in situ* EXAFS/XANES results for the 17.5% V_2O_5/Al_2O_3 monolayer catalyst during *n*-butane oxidation, which shows that the structure of the surface vanadium oxide species under steady-state conditions is very similar to the structure in the fully oxidized state (17). *In situ* Raman spectroscopic studies of supported vanadia catalysts also confirm that only a small fraction of surface V(V) sites are reduced during ethane oxidation (18). Comparison of the results in Table 3 indicates that the extents of reduction during both ethane and *n*-butane oxidation/reduction are a strong function of the oxide support: 1 and 4% V_2O_5/ZrO_2 > 5% V_2O_5/Al_2O_3 ≥ 5% V_2O_5/SiO_2. This trend is consistent with the reducibility order of these catalysts obtained by the TPR experiments, which is inversely proportional to the T_{max} values listed in Table 1.

The extents of reduction for the 1 and 4% V_2O_5/ZrO_2 samples during ethane oxidation are only slightly different, while a significant difference in the extents of reduction is observed during ethane reduction (see Table 3). Similar results are obtained for these two samples during *n*-butane oxidation/reduction. The 1 and 4% V_2O_5/ZrO_2 samples possess different surface densities (2.0 vs 8.1 V atoms/nm², respectively) and polymerization degrees of surface V(V) cations (predominantly VO_4 monomer vs VO_4 polymerized species, respectively). Thus, the 4% V_2O_5/ZrO_2 sample with predominantly polymerized surface VO_4 species is more easily reduced in the reducing environment (ethane or *n*-

butane). However, the polymerization degree of the surface V(V) species seems to have only a minor effect on the extent of reduction during steady-state oxidation of ethane and *n*-butane. Thus, it appears that both polymerized and isolated surface V sites are involved in these alkane oxidation reactions. The average oxidation state under present steady-state oxidation conditions does not rely on the reducibility of the catalyst, but on the equilibrium of the reduction and reoxidation of the catalytic cycle.

Some recent studies show that the edge energies (E_g) of the LMCT transitions could be very informative in elucidating the local structures (coordination and domain size) of the transitional metal cations, such as V(V) and Mo(VI) (15, 19–21). Thus, the edge energy shift due to reduction of the surface V(V) species can provide further information about the oxidation/coordination state changes of the surface vanadium oxide species in the different reactive environments. The edge energies for the oxidized supported vanadia catalysts and the edge energy changes due to ethane and butane oxidation/reduction are listed in Tables 4 and 5. Comparison of E_g values in the two tables indicates that the edge energies of some catalysts in the oxidized state are slightly different at different temperatures, which may be associated with the temperature shift of the band-gap energy of vanadium oxide (22). Nevertheless, the edge energy of the 4% V_2O_5/ZrO_2 sample is the lowest, which corresponds to the presence of predominantly polymerized surface VO_4 species. The lower edge energy value is usually associated with a higher polymerization degree (15) or larger domain size of the surface vanadium oxide species (5). For the other samples, their edge energies are in the range

TABLE 5

Edge Energy Shifts of Supported Vanadia Catalysts (Relative to the Oxidized Catalysts) during *n*-Butane Oxidation/Reduction

Catalyst	E_g (eV) O_2/He, 230°C	ΔE_g (eV) $C_4/O_2/He$, 230°C	ΔE_g (eV) C_4/He, 230°C
5% V_2O_5/SiO_2	3.62	0.00	0.00
5% V_2O_5/Al_2O_3	3.61	0.01	0.01
1% V_2O_5/ZrO_2	3.38	0.00	0.01
4% V_2O_5/ZrO_2	3.14	0.04	0.10

3.38–3.62 eV and are associated with the presence of predominantly isolated surface VO_4 species (15). During ethane oxidation/reduction, the edge energies of the catalysts remain essentially unchanged. For the 4% V_2O_5/ZrO_2 sample (see Table 4), however, the edge energy slightly shifts upward during ethane oxidation and significantly shifts upward in the ethane reducing environment. The upward shift of the edge energy must be associated with reduction of the polymerized surface vanadia species. Similar results are obtained for n-butane oxidation and reduction over these catalysts, as shown in Table 5. These results are consistent with the previous conclusion that polymerized surface vanadia species are more easily reduced than isolated surface vanadia species in reducing environments.

The catalytic results for ethane oxidative dehydrogenation to ethylene are presented in Table 6. The reactivity, represented as TOF, of the supported vanadia catalysts for ethane oxidation is a strong function of the specific oxide support: $V_2O_5/ZrO_2 > V_2O_5/Al_2O_3 > V_2O_5/SiO_2$. These results also show that the polymerization degree of the surface vanadia species does not significantly affect the reactivity of the catalysts since only very minor reactivity differences are observed for these catalysts with different vanadia loadings. These results strongly suggest that only one surface V site is needed for ethane oxidation. Eon et $al.$ (9) have also postulated that a single active site is present on V_2O_5/Al_2O_3 catalysts for propane oxidative dehydrogenation. This is in agreement with the in $situ$ DRS results that both polymerized and isolated V sites are involved in alkane oxidation reactions and that the polymerization degree of the surface vanadium oxide species has only a minor effect on the extent of reduction during ethane oxidative dehydrogenation.

The reactivity (TOFs) of the supported vanadia catalysts for n-butane oxidation at $221°C$ has been previously reported (2) and follows the order 4% V_2O_5/ZrO_2 (4.5×10^{-5} s^{-1}) > 17.5% V_2O_5/Al_2O_3 (0.9×10^{-5} s^{-1}) > 7% V_2O_5/SiO_2 (0.4×10^{-5} s^{-1}). These results are also consistent with the present in $situ$ DRS results, which strongly suggest that

the support effect plays a major role in determining the reactivity and extent of reduction of the surface vanadia species during n-butane oxidation.

CONCLUSIONS

In $situ$ UV–vis DRS studies of the supported vanadia catalysts during ethane and n-butane oxidation indicate that only a small fraction of surface V(V) sites (less than 10%) are reduced to V(IV)/V(III) cations under present steady-state reaction conditions. The extents of reduction of the surface V(V) species are a strong function of the specific oxide support: $V_2O_5/ZrO_2 > V_2O_5/Al_2O_3 > V_2O_5/SiO_2$. The surface polymerized vanadia species are more easily reduced than the isolated surface vanadia species in reducing environments (ethane or n-butane); however, no significant differences in the extents of reduction during the present oxygen-rich steady-state ethane/butane oxidation are observed. Both polymerized and isolated surface V species appear to be the active sites for these alkane oxidation reactions. The reactivity, TOF, of the supported vanadia catalysts for these alkane oxidation reactions is also a strong function of the specific oxide supports: $V_2O_5/ZrO_2 > V_2O_5/Al_2O_3 > V_2O_5/SiO_2$. The catalytic results indicate that the polymerization degree of the surface vanadia species does not significantly affect the reactivity (TOF) of the catalysts for ethane oxidation. It appears that only one V site is needed for ethane oxidation.

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TABLE 6

Activity and Selectivity of Supported Vanadia Catalysts for Ethane Oxidation

Catalyst	TOF (s^{-1})[a] at 550°C	C$_2$H$_4$ selectivity (%)[b] (8.0% ethane conversion)
2% V_2O_5/ZrO_2	7×10^{-2}	36
4% V_2O_5/ZrO_2	8×10^{-2}	45
5% V_2O_5/Al_2O_3	1×10^{-2}	70
10% V_2O_5/Al_2O_3	2×10^{-2}	71
2% V_2O_5/SiO_2	5×10^{-3}	77
5% V_2O_5/SiO_2	7×10^{-3}	63

[a] TOF is calculated on the basis of the total V atoms in the catalysts.
[b] C$_2$H$_4$ selectivity is obtained at 8% ethane conversion.

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