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# Dynamic behavior of supported vanadia catalysts in the selective oxidation of ethane
## In situ Raman, UV–Vis DRS and reactivity studies

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## Abstract

The coordination and oxidation states of surface vanadia species on different oxide supports were studied by in situ UV–Vis DRS and in situ Raman spectroscopy. Surface vanadia species remain essentially oxidized during the steady-state ethane oxidation reaction. Polymeric surface vanadia species are more reducible than isolated ones, but this has only a minor effect on the ethane oxidation reactions. It appears that only one surface V site is involved in the rate-determining step for ethane oxidation. The reducibility of supported vanadium oxide species corresponds with the TOF values, but not with the average oxidation state under steady-state reaction. Ceria- and niobia-supported vanadia catalysts do not follow this trend due to solid-state reaction between the surface vanadia species and the oxide support that decreases the number of exposed vanadia sites. This solid-state reaction does not appear to affect the nature of the active site, which is associated with the V–O–Support bond rather than with the terminal V=O bond. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* In situ Raman; In situ UV–Vis DRS; Ethane oxidation; Vanadia; Support effect; Oxidation state; Polymerization degree; Solid-state reaction

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## 1. Introduction

Supported metal oxides are widely used in many industrial applications. Vanadium oxide is a major component in the formulation of catalysts for selective oxidation reactions [1–6]. However, the state of the supported oxides and their transformations under catalytic oxidation reaction conditions are not fully understood. This contribution presents the use of in situ Raman and UV–Vis DRS spectroscopic techniques to study the changes in the molecular structure, coordination geometry/ligands and oxidation state of surface vanadium oxide cations on various supports ($Al_2O_3$, $ZrO_2$, $CeO_2$, $Nb_2O_5$, $TiO_2$, and $SiO_2$) during ethane oxidation. The relative extents of the reduction of $V^{5+}$ cations during ethane oxidation reaction and under anaerobic hydrocarbon reduction were analyzed.

## 2. Experimental

The oxide supports were: $SiO_2$ (Cabot), $Al_2O_3$ (Engelhard), $CeO_2$ (Engelhard), $TiO_2$ P-25 (Degussa), $ZrO_2$ (Degussa), and $Nb_2O_5$ (Niobium Products). The

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catalysts were prepared according to the experimental procedure described elsewhere [5]. The catalysts are referred to as "*x*VS", where "*x*" represents the weight percent of $V_2O_5$ and "S" stands for the cation of the specific oxide support.

The UV–Vis DRS experiments were conducted on Varian Cary 5E UV–Vis NIR spectrophotometer. The vanadia loadings on all samples used in the present work are 5% $V_2O_5$ or less since higher vanadia loading samples show high noise-to-signal ratios [6]. The study of vanadia supported on ceria, niobia or titania was not possible due to the intense LMCT transition of the cations of these oxide supports in the same spectral window as the V(V) cations. In situ UV–Vis DRS spectra were taken in the range 5000–12 000 $\mathrm{cm}^{-1}$. Ethane oxidation ($C_2H_6/O_2/He=2.4/8/81.6$) and reduction (4.12% $C_2H_6$ in He) were performed at 723 K with a total flow rate of 90 $\mathrm{cm}^3$/min. The samples were in powder form to prevent diffusion problems and ensure that all the catalyst in the cell is exposed to the flowing gases. This affords more accurate measurements than other in situ studies that used the catalysts pressed as wafers. The experimental procedure to determine the extents of reduction of V(V) cations and the use of reference compounds by DRS can be found elsewhere [7]. The spectra of the dehydrated vanadia supported samples were obtained after the samples were calcined at 773 K under $O_2$/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 under a 30 $\mathrm{cm}^3$/min stream of 10% $H_2$/Ar.

The in situ Raman spectra were run with a Renishaw Micro-Raman System 1000 equipped with a cooled CCD detector (200 K) and a holographic super-Notch filter that removes the elastic scattering. The samples were excited with the 514 nm Ar line in an in situ cell (Linkam, TS-1500), which allows temperature treatments up to 1773 K under flowing gases. Like the UV–Vis DRS experiments, the samples were in powder form to prevent diffusion problems and ensure that all catalyst in the cell is exposed to the flowing gases. The spectra acquisition consisted of five accumulations of 60 s of each sample. All the samples for the in situ measurements were pretreated in $O_2$/He at 723 K for 1 h before any further treatment. Ethane oxidation ($C_2H_6/O_2/He=1/2/8$) and reduction (1/0/8) were performed at 723 K with a total flow rate of 90 $\mathrm{cm}^3$/min.

The hydrogen temperature programmed reduction (TPR) experiments were run on a Micrometrics equipment model TPR/TPD-2900 fitted with a TCD detector. Samples of ca. 20 mg each were used. The TPR experiments were run in a 10% $H_2$/Ar stream, with a heating rate of 10 K/min with a flow rate of 80 $\mathrm{cm}^3$/min.

Ethane oxidation was carried out in an isothermal fixed-bed differential reactor. The catalysts (∼20 mg) were tested at various temperatures at atmospheric pressure. The reactant gas mixture of $C_2H_6/O_2/He$ (1/2/8) was used with a total flow rate of 30 $\mathrm{cm}^3$/min. The experimental details are described elsewhere [5]. The TOF values are calculated assuming that all the vanadia is dispersed, as confirmed by Raman spectroscopy.

## 3. Results and discussion

The Raman spectra of the dehydrated supported vanadia catalysts show the Raman bands characteristic of the different supports along with those from the supported oxide. The Raman band near 1030 $\mathrm{cm}^{-1}$ is the only band observed from the vanadium oxide and no Raman bands of crystalline vanadia are observed. Therefore, all the supported vanadium oxide is completely dispersed.

The in situ UV–Vis DRS spectra of the representative 1 and 4% $V_2O_5/ZrO_2$ samples under $O_2$/He, ethane oxidation and ethane reduction environments are presented in Fig. 1. The LMCT bands of V(V) are above 25 000 $\mathrm{cm}^{-1}$, while V(IV)/V(III) possess the d–d electronic transitions in the 10 000–30 000 $\mathrm{cm}^{-1}$ window [7,8]. Unfortunately, these d–d electronic transitions are broad and weak, and lie in the same

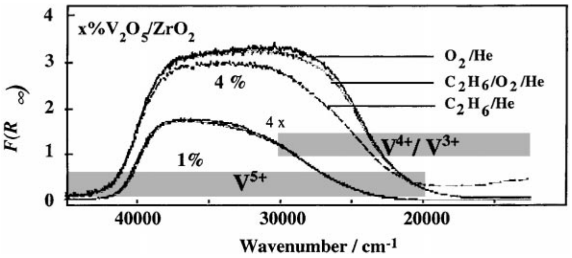

Fig. 1. In situ UV–Vis DRS spectra of 1 and 4% $V_2O_5/ZrO_2$ (1VZr and 4VZr) catalyst under oxidizing and reducing conditions.

Table 1
Relative extents of reduction and the edge energy shifts of supported vanadia catalysts (relative to the oxidized catalysts) during ethane oxidation/reduction

| Catalyst | Reduction at 723 K (%) | | Eg (eV), $O_2$/He | ΔEg | |
|---|---|---|---|---|---|
| | $C_2H_6/O_2$/He | $C_2H_6$/He | | $C_2H_6/O_2$/He | $C_2H_6$/He |
| 1VSi | 0.0 | 0.0 | 3.50 | 0.00 | 0.00 |
| 5VSi | 0.0 | 4.4 | 3.48 | 0.00 | 0.00 |
| 1Val | 0.0 | 0.0 | 3.89 | 0.00 | 0.00 |
| 5Val | 0.3 | 6.1 | 3.61 | 0.00 | 0.01 |
| 1VZr | 2.8 | 5.5 | 3.38 | 0.00 | 0.01 |
| 4VZr | 3.6 | 23.0 | 2.89 | 0.01 | 0.13 |

region, which makes them hard to distinguish. 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 determined by UV–Vis DRS spectroscopy have been calculated from the total area of the LMCT bands of V(V) and are listed in Table 2. This method provides a very accurate determination of the reduction of vanadium species [7]. No appreciable reduction of V(V) could be recorded for 1VSi and 1VAl under ethane oxidation. These in situ UV–Vis DRS results demonstrate that the surface V(V) cations dominate on these oxide supports during ethane oxidation reaction and that the extents of reduction during ethane oxidation/reduction strongly depend on the oxide support: 1 and 4% $V_2O_5/ZrO_2$>5% $V_2O_5/Al_2O_3$≥5% $V_2O_5/SiO_2$.

The extents of reduction for the 1 and 4% $V_2O_5/ZrO_2$ samples during ethane oxidation are only slightly different, while a more significant difference in the extents of reduction is observed during ethane reduction (see Table 1). The 1 and 4% $V_2O_5/ZrO_2$ samples possess different surface densities (2.0 vs. 8.2 V atoms/nm$^2$, respectively) and polymerization degree of surface V(V) cations (predominantly $VO_4$ monomer vs. $VO_4$ polymerized species, respectively). Thus, the polymerized surface $VO_4$ species on 4% $V_2O_5/ZrO_2$ sample is more easily reduced in the reducing environment. However, the polymerization degree of the surface V(V) species seems to have only a minor effect on the extents of reduction during steady-state oxidation of ethane. The same effects are observed under butane oxidation/reduction [7]. The average oxidation state under 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.

The edge energy shift due to the reduction of the surface V(V) species can provide further information about the oxidation/coordination state changes of the surface vanadium oxide species under different environments [7,8]. The edge energy of the 4VZr sample is the lowest (Table 1), which corresponds to the presence of polymerized surface $VO_4$ species. The lower

Table 2
TPR results of the supported vanadium oxide catalysts

| Support | Low vanadia coverage | | | High vanadia coverage | | |
|---|---|---|---|---|---|---|
| | Catalyst | V atom/nm$^2$ | $T_{max}$ (K) | Catalyst | V atom/nm$^2$ | $T_{max}$ (K) |
| $ZrO_2$ | 2VZr | 4.1 | 625 | 4VZr | 8.2 | 664 |
| $TiO_2$ | 3VTi | 4.7 | 711 | 6Vti | 9.4 | 721 |
| $Al_2O_3$ | 10VAl | 5.4 | 756 | 25VAl | 13.4 | 754 |
| $SiO_2$ | 5VSi | 0.9 | 792 | 12VSi | 2.1 | 806 |
| $CeO_2$ | 2VCe | 3.8 | 744+991 | 4Vce | 7.6 | 824+986 |
| $Nb_2O_5$ | 3VNb | 3.7 | 978+1167 | 5VNb | 6.1 | 779+762+1107 |

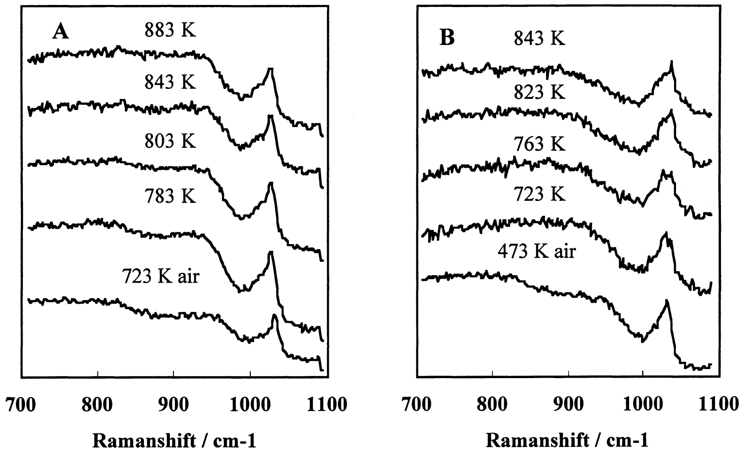

Fig. 2. In situ Raman spectra of 4VZr catalyst: (A) under ethane oxidation; (B) under reduction by ethane.

edge energy values are usually associated with the higher polymerization degree [9] or the larger domain size of the surface vanadium oxide species [10]. For the other samples, their edge energies are in the range 3.38–3.62 eV, which are associated with the presence of predominantly isolated surface $VO_4$ species [9]. During ethane oxidation/reduction, the edge energies of the catalysts are essentially unchanged. However, the edge energy for 4VZr slightly shifts upward during ethane oxidation and significantly shifts upward under the ethane reduction environment (Table 1). The upward shift of the edge energy must be associated with the reduction of the polymerized surface vanadia species. Similar results are observed for *n*-butane oxidation and reduction over these catalysts [7]. These results are consistent with the previous conclusion that the polymerized surface vanadia species are more easily reduced than the isolated surface vanadia species in the reducing environment [11].

The Raman spectra of 1VSi and 1VAl under $C_2H_6/He/O_2$ and $C_2H_6/He$ conditions are the same as those of the dehydrated samples with Raman bands at 1039 and 1026 $cm^{-1}$ for 1VSi and 1VAl, respectively. The 5VSi, 4VZr and 5VAl catalysts also exhibit no appreciable change in their Raman spectra under ethane oxidation conditions (Figs. 2A and 3A).

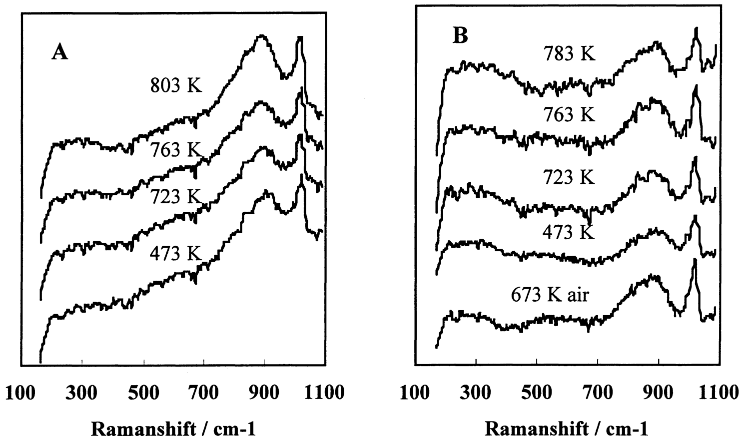

Fig. 3. In situ Raman spectra of 5VAl catalyst: (A) under ethane oxidation; (B) under reduction by ethane.

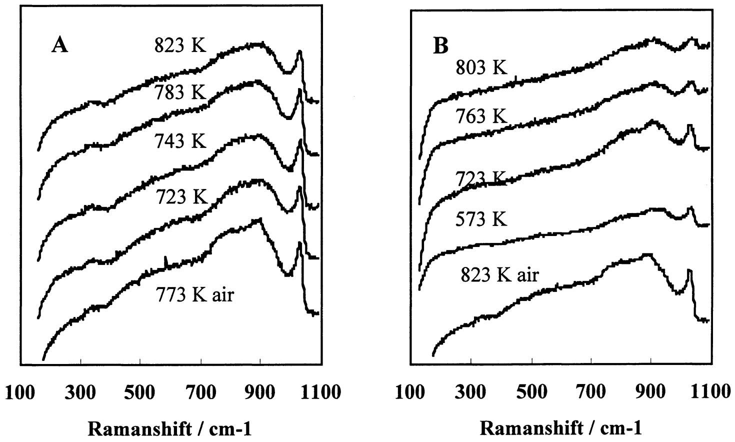

Fig. 4. In situ Raman spectra of 15VAl catalyst: (A) under ethane oxidation; (B) under reduction by ethane.

This trend closely parallels the data from the in situ UV–Vis DRS spectra discussed above. 4VZr shows a loss of surface polymeric species under $C_2H_6$/He feed, suggested by the decrease of the V–O–V Raman band (Fig. 2B), which parallels the conclusions from in situ UV–Vis DRS spectroscopy under reducing feed ($C_2H_6$/He) (23.0% reduction and 0.13 eV increase for Eg, Table 1). 5VAl shows no appreciable change in its Raman spectra under $C_2H_6$/He. This is in agreement with the slight reduction of these V sites under reducing conditions (6.1% and no change in Eg) (Table 1). The in situ Raman spectra of 15VAl show no appreciable change under ethane oxidation conditions (Fig. 4A); however, a moderate decrease of the V=O and V–O–V Raman bands is evident under $C_2H_6$/He feed (Fig. 4B). This trend is in agreement with an extrapolation of the UV–Vis DRS measurements since the coverage increases the polymerization of surface vanadia species, which are more reducible than the isolated species. As we indicated in Section 2, the V loading for this catalyst does not allow the UV–Vis measurements and no direct comparison could be made with in situ UV–Vis DRS.

The $H_2$-TPR profiles of the supported vanadia catalysts exhibited only one reduction peak, except for the ceria- and niobia-supported vanadia series (Table 2). $CeO_2$ and $Nb_2O_5$ present several reduction maxima with the highest temperature corresponding to the reduction of the corresponding oxide support. Thus, the temperature for the maximum reduction peak ($T_{max}$) has a strong dependence on the specific oxide support and follows the trend: $ZrO_2 < TiO_2 < CeO_2 < Al_2O_3 < Nb_2O_5 < SiO_2$. This trend parallels the variation of the Sanderson electronegativity of the cation of the support, except for $CeO_2$ that has the lowest Sanderson electronegativity. This trend underlines the relevance of the V–O–Support bond on the properties of the supported vanadium oxide. The values and trends of $T_{max}$ for ceria-supported vanadia series must be indicative of some important alteration of the nature of the surface vanadium sites on this system. The value of $T_{max}$ increases moderately as the vanadia loading increases. This result appears to contradict the spectroscopic in situ reducibility measurements that show an increase of reducibility of the surface vanadia species due to an increase of polymeric species. However, the $T_{max}$ value depends on the number of phenomena, mainly related to the removal of the water formed [12]. As vanadia loading increases, the production of water upon reduction increases. This raises the value of $T_{max}$ in the TPR experiments [12]. The strong effect of water vapor on the $T_{max}$ value and the total reduction for other supported oxides has also been reported very recently for other supported oxide catalysts [13]. On the other hand, the in situ (UV–Vis and Raman) experiments show a system under steady state that is not affected by these parameters and would provide a closer view to the real features of the catalyst.

The catalytic results for ethane oxidative dehydrogenation to ethylene are presented in Table 3. These results also show that the polymerization degree of

Table 3
Ethane oxidation on supported vanadia catalysts[a]

| Support | Catalyst | TOF at 823 K ($s^{-1}$) | 8% conversion | | | | |
|---|---|---|---|---|---|---|---|
| | | | Temperature (K) | Selectivity | | | |
| | | | | CO | $CO_2$ | $C_2H_4$ | $C_2$-oxygentes |
| $SiO_2$ | 5VSi | 0.008 | 851 | 20.5 | 5.8 | 61.1 | 12.7 |
| | 12VSi | 0.004 | 835 | 23.9 | 9.2 | 62.8 | 4.0 |
| $Al_2O_3$ | 5VAl | 0.013 | 816 | 25.7 | 4.1 | 70.2 | 0.0 |
| | 10VAl | 0.021 | 760 | 22.8 | 5.6 | 71.5 | 0.0 |
| $ZrO_2$ | 2VZr | 0.073 | 774 | 42.2 | 21.2 | 36.4 | 0.2 |
| | 4VZr | 0.066 | 769 | 50.5 | 4.4 | 45.1 | 0.0 |
| $TiO_2$ | 3VTi | 0.123 | 732 | 45.9 | 5.5 | 45.2 | 0.0 |
| | 5VTi | 0.135 | 738 | 52.0 | 4.8 | 42.5 | 0.7 |
| $Nb_2O_5$ | 3VNb | 0.021 | 859 | 41.4 | 11.7 | 46.8 | 0.0 |
| | 5VNb | 0.009[b] | 843 | 53.3 | 7.0 | 39.6 | 0.0 |
| $CeO_2$ | 1VCe | 0.042 | 834 | 20.4 | 54.4 | 25.2 | 0.0 |
| | 4VCe | 0.005[b] | 866 | 49.1 | 7.7 | 42.9 | 0.0 |
| | $CeVO_4$ | NA | 883 | 52.1 | 21.5 | 26.4 | 0.0 |

[a] Reaction conditions: $F$=30 $cm^3$/min; $W$=20 mg; feed, $C_2H_6/O_2/He$: 1/2/8 (mol).

[b] Apparent TOF since the solid-state reaction to form $CeVO_4$ removes surface vanadia sites.

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 loading. If the TOF value is moderately affected by V coverage, this means that the change of V species from isolated to surface polymeric has little effect on the rate and thus, the proximity of the vanadium sites is not critical for the reaction. If the increase of V coverage triggers the TOF values, it strongly suggests that the active site requires more than one V site. These results imply that only one surface V site is involved in the rate-determining step for ethane oxidation. The existence of a single active site present on the $V_2O_5/Al_2O_3$ catalysts for propane oxidative dehydrogenation has already been proposed [14,15]. The reactivity, represented as turnover frequency (TOF), of the supported vanadia catalysts for ethane oxidation is strongly dependent on the specific oxide support: $V_2O_5/ZrO_2 > V_2O_5/Al_2O_3 > V_2O_5/SiO_2$. More reducible oxides afford higher TOF numbers, which strongly suggest that the support effect plays a major role in determining the reactivity and the extent of reduction of the surface vanadia species during ethane oxidation. However, $V_2O_5/CeO_2$ and $V_2O_5/Nb_2O_5$ catalysts do not follow this trend. The decrease of the TOF value with vanadia loading must be indicative of some structural modification of the surface vanadia species. The in situ Raman spectra of a 4% $V_2O_5/CeO_2$ catalyst (monolayer) in dry air at different temperatures show that the disappearance of the band of surface vanadia (1022 $cm^{-1}$) is accompanied by the concomitant formation of new intense Raman bands, which are characteristic of the $CeVO_4$ phase (146, 215, 259, 369, 458, 768, 774 and 840 $cm^{-1}$). The selectivity at 8% conversion of the $V_2O_5/CeO_2$ series after the solid-state reaction is intermediate between $V_2O_5/CeO_2$ and that of pure $CeVO_4$.

## 4. Conclusions

In situ spectroscopic studies of the supported vanadia catalysts during ethane oxidation indicate that only a small fraction of surface V(V) sites are reduced to V(IV)/V(III) under steady-state reaction conditions. The extents of reduction of the surface V(V) species are strongly dependent on the specific oxide support. The average oxidation state under 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. The surface polymerized vanadia species are more easily reduced than the isolated surface vanadia species; however, no significant differences in the extents of reduction during steady-state ethane oxidation are observed. 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 involved in the rate-determining step for ethane oxidation. The reactivity (TOF) of the supported vanadia catalysts for this alkane oxidation is also strongly related with the specific oxide supports: $ZrO_2>TiO_2>Al_2O_3>SiO_2$. The reducibility seems to correlate with the reactivity of the catalyst. The unexpected low activity of some catalysts is related to the solid-state reaction between the surface vanadia layer and the underlying support (ceria or niobia). The in situ Raman and UV–Vis DRS results are very informative for elucidating the structure of the surface vanadium oxide species under reaction conditions.

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