

Identification and roles of the different active sites in supported vanadia catalysts by *in situ* techniques

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The roles of the different sites and structures of supported vanadium oxide catalysts have been studied by *in situ* spectroscopic techniques (UV-Vis-DRS and Raman) as well as by the use of isotopic oxygen labeling, in order to propose a molecular understanding of the roles of the different oxygen sites. The remarkable effect of the different oxide supports on the activity per vanadium site (TOF) underlines the relevance of the bridging V-O-support bond as the active site. The reducibility of the support appears to correlate with the activity per vanadium site. *In situ* Raman studies employing isotopic oxygen labeling rule out the terminal V=O bond as the critical site involved in the rate determining step for the oxidation of ethane. The bridging V-O-V bonds appear to have a moderate participation and the bridging V-O-Support bonds appear to be the critical site for ethane oxidation. *In situ* UV-Vis-DRS and *in situ* Raman spectroscopy are complementary for the determination of the polymerization degree of the surface vanadium oxide species. Under reducing conditions, polymeric surface vanadia species are more reducible than isolated species and vanadia supported on reducible oxides (titania, zirconia, ceria) is more reducible than vanadia supported on less reducible oxides (silica, alumina). However, the oxidation state under reaction conditions does not depend on the reducibility of the surface vanadia species, but on the average oxidation state under steady-state oxidation of ethane.

Keywords: *in situ* Raman, *in situ* UV-Vis, isotopic oxygen study, surface active site, vanadia, support-effect, oxidation state, polymerization degree, ethane oxidation

1. INTRODUCTION

The activity of supported vanadium oxide catalysts is strongly affected by the interaction with the specific oxide support and by the textural and chemical properties of the oxide support [1,2]. The surface coverage of the vanadium oxide also influences the structure and activity of the catalysts because it affects the polymeric-to-monomeric population ratio of the supported vanadium oxide species. Both parameters determine the amount and nature of

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exposed oxygen sites that interact with the hydrocarbon molecule. Recent kinetic and isotopic tracer analyses identify the elementary steps and their reversibility in the oxidative dehydrogenation of propane on V_2O_5/ZrO_2 catalysts [3]. Despite this, there is no definitive assessment on the exact role of the different oxygen sites of the catalysts. Accordingly, this work was undertaken with the aim to address these fundamental questions, which in turn may help in the improved design of supported vanadia catalysts for the partial oxidation of ethane to olefins or oxygenates. The approach consisted in the use of *in situ* Raman and *in situ* UV-Vis spectroscopic techniques under different environments (reaction, reducing and oxidizing) along with ^{18}O -isotopic labeling techniques for the characterization of the structures in supported vanadia catalysts. The performance of the different active sites, isolated and polymeric surface V species as well as their impact on the selectivity for selective oxidation of ethane to ethylene are discussed.

2. EXPERIMENTAL

The vanadium oxide was supported on SiO_2 , Al_2O_3 , CeO_2 , TiO_2 , and ZrO_2 . The catalysts were prepared by incipient wetness impregnation with V-isopropanol in a glove box under nitrogen flow. The vanadia loading was selected to keep the surface coverage below monolayer.

The partial oxidation of ethane was run in a quartz micro-reactor where void volume is minimized to avoid homogenous reaction from the gas phase. The reaction feed consisted of a mixture $O_2:C_2H_6:He=2:1:8$ (molar ratio) and total flow rates of 40-70 mL (STP)/min. The effluents of the reactor were analyzed by an on-line GC (Hewlett-Packard 5890-II). The TOF numbers were calculated by assuming that all the vanadium was dispersed, as confirmed by Raman spectroscopy.

The *in situ* Raman and *in situ* UV-visible spectra were run with *in situ* cells. The samples used for the *in situ* measurements were in powdered form and the reaction stream consisted of $C_2H_6 + O_2 + He$ in the proportion used for the catalytic experiments; a stream of $O_2:N_2$ (20:70) was used for the oxidizing environment, and a stream of $C_2H_6:He$ (1:2) was used for the reducing environment on the UV-Vis-DRS cell. The total gas flow for *in situ* experiments was 30 mL (STP)/min. The samples were pretreated in $O_2:N_2$ at 723 K for 1 h, and the spectrum at this temperature corresponds to the "fresh" sample. For the *in situ* spectra under reaction conditions, the sample followed the same pretreatment. Once that the sample was cooled to ambient temperature the feed gas was switched to the reaction mixture and heated stepwise, following the same procedure indicated for the reduction experiments. Oxygen-18 exchange was accomplished by several cycles of reduction on the catalyst in 10% H_2/Ar and reoxidation in 5% $^{18}O_2/Ar$ at 773 K; however, a complete oxygen exchange was not possible. The *in situ* UV-Vis DRS experiments were conducted on Varian Cary 5E UV-Vis-NIR spectrophotometer. The vanadia loading was limited to 5% since higher vanadia loading values show low signal-to-noise ratios [4]. The study of vanadia supported on ceria, niobia or titania was not possible due to the intense LMCT transition of the cations of these support oxides in the same spectral window as the V (V) cations. *In situ* UV-Vis DRS spectra were taken in the range of 5000-12000 cm^{-1} . The experimental procedure to determine the extent of reduction of V (V) cations and the use of reference compounds by DRS is described elsewhere

[5]. The *in situ* Raman spectra were obtained with a Renishaw Micro-Raman System 1000 equipped with a CCD detector at 200 K and a holographic Notch filter. The samples were excited with the 514 nm Ar line in an *in situ* cell (Linkam, TS-1500). The spectra acquisition consisted of 5 accumulations of 60 seconds of each sample. Ethane oxidation and reduction ($C_2H_6/O_2/He = 1/2/8$ and $1/0/8$, respectively) were performed at 723 K with a total flow rate of 90 mL/min. The *in situ* temperature-programmed Raman (TP-Raman) spectra were obtained by heating the samples stepwise (50 K each) with a spectrum collected at each temperature. The evolution of the oxygen-18-exchanged samples under reaction conditions was followed as a function of time by spectra of 1 spectrum collected every 60 seconds at constant reaction temperature.

3. RESULTS AND DISCUSSION

The Raman spectra of all the catalysts under dehydrated conditions do not exhibit the Raman bands of crystalline V_2O_5 , but the Raman band near 1030 cm^{-1} , which is characteristic of the terminal $V=O$ bond of the surface vanadia species. Therefore, all the supported vanadium oxide in these catalysts is 100% dispersed as a two dimensional overlayer.

The catalytic activity data underline the strong dependence of the partial oxidation activity on the specific oxide support. The support determines activity, as measured by TOF numbers to ethylene at 803 K, which changes by an order of magnitude: $2\%V_2O_5/ZrO_2$ ($1.5 \cdot 10^{-2} s^{-1}$) > $2\%V_2O_5/TiO_2$ ($1.3 \cdot 10^{-2} s^{-1}$) \geq $2\%V_2O_5/CeO_2$ ($1.1 \cdot 10^{-2} s^{-1}$) > $5\%V_2O_5/Al_2O_3$ ($4.4 \cdot 10^{-3} s^{-1}$) > $2\%V_2O_5/SiO_2$ ($9.9 \cdot 10^{-4} s^{-1}$), which corresponds in part with the reducibility of the support. This has a direct dependence on the Sanderson electronegativity of the cation of the support. The surface vanadia coverage on the support has much less of an effect on the catalytic performance. TOF values change to a much lower extent and the selectivity shows a slight decrease of selective partial oxidation products in favor of non-selective CO.

The *in situ* Raman spectra of the oxygen-18-exchanged $2\%V_2O_5/SiO_2$ and $10\%V_2O_5/Al_2O_3$ under reaction conditions are illustrated in Figure 1. Each supported-vanadia catalyst initially shows a Raman band at 1031 or 1017 cm^{-1} that correspond to the $V=O^{16}$ bond vibration of dehydrated surface vanadia on silica and on alumina, respectively. New Raman bands appear near 988 and 976 cm^{-1} upon exchange with $^{18}O_2$ that correspond to the $V=O^{18}$ bond vibration on silica and alumina, respectively. Alumina-supported vanadia presents a broad Raman band near 860 cm^{-1} that corresponds to the bridging V-O-V bond. A shoulder near 900 cm^{-1} is evident after oxygen-18 exchange, which corresponds to the vibration of the exchanged V-O 18 -V bond. The *in situ* Raman spectra in Figure 1 show that the supported vanadia is not reduced during ethane oxidation. The intensities of the 988 and 1031 cm^{-1} Raman bands of the $2\%V_2O_5/SiO_2$ catalyst are followed against time-on-stream during ethane oxidation (Fig. 1A). The Raman band of the $V=O^{18}$ bond decreases rather fast during the first minutes under reaction conditions at 863 K , however, it is not fully eliminated, even after more than 11 minutes time-on-stream, which corresponds to ca. 8 catalytic cycles. The exchanged $10\%V_2O_5/Al_2O_3$ shows a similar behavior (Fig. 1B), the intensity of the $V=O^{18}$ Raman band is weak but still evident even after 26 min on-stream, which corresponds to ca. 11 catalytic cycles. If the terminal $V=O$ bond were involved in the rate determining step, it should be eliminated within a catalytic cycle. Since is not fully eliminated within 10 catalytic cycles it must not be the critical active site of supported-vanadia catalysts. This is in agreement with

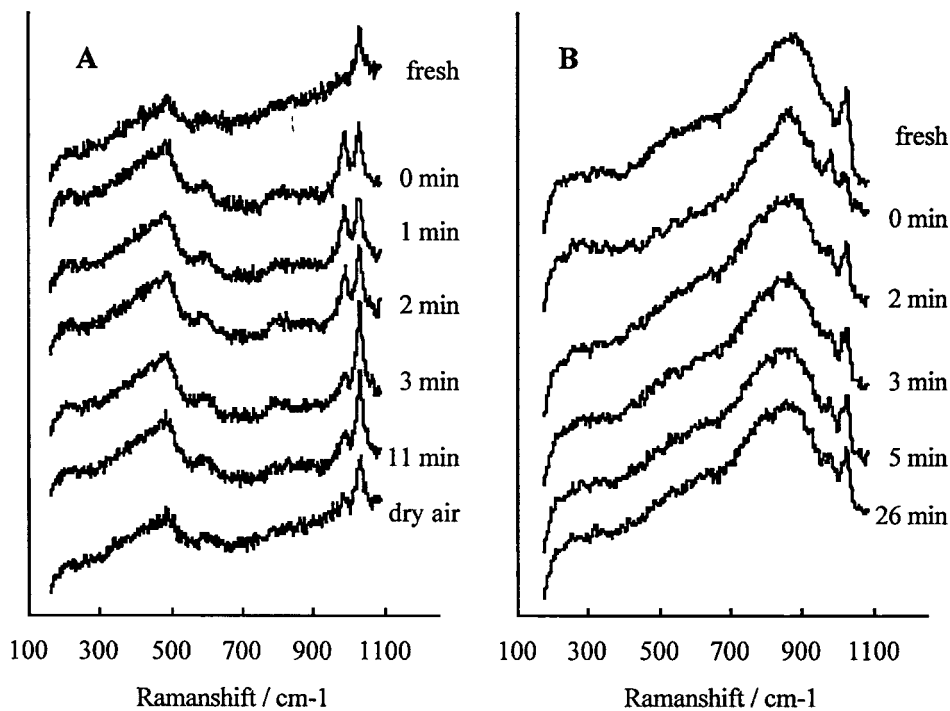


Figure 1. *In situ* Raman spectra of oxygen-18-exchanged supported vanadia catalysts under ethane oxidation reaction conditions. (A), 2% V_2O_5/SiO_2 at 863 K ($TOF = 1.2 \cdot 10^{-2} s^{-1}$); (B), 10% V_2O_5/Al_2O_3 at 783 K ($TOF = 6.9 \cdot 10^{-3} s^{-1}$).

preliminary studies where no correlation was found between the V=O bond Raman band position and the TOF number [6]. The V-O¹⁸-V bond appears to exchange faster than the terminal V=O¹⁸ bond, thus it appears that bridging V-O-V bonds may have a stronger relevance than the terminal V=O bond. However, its relevance must be moderate since any increase in vanadia surface coverage on alumina has only a minor effect on the TOF to ethylene numbers ($4.4 \cdot 10^{-3} s^{-1}$ for 5% V_2O_5/Al_2O_3 and $4.0 \cdot 10^{-3} s^{-1}$ for 15% V_2O_5/Al_2O_3 at 803 K). Therefore, the bridging V-O-support oxygen must be directly involved in the rate-determining step of the supported vanadium oxide catalysts. The relevance of the bridging V-O-Support is also underlined by the remarkable effect of the different supports on the reducibility of the supported vanadia species and the activity per supported vanadia site (TOF) that changes by an order of magnitude.

The *in situ* TP-Raman spectra of 1% V_2O_5/CeO_2 (Fig. 2) shows Raman bands at 1017 and 860 cm^{-1} that correspond to the polymeric surface vanadia species while the band at 1034 cm^{-1} corresponds to isolated surface vanadia sites. Under a reducing atmosphere (C_2H_6+He) the polymeric surface vanadia are more easily reduced than the isolated vanadium sites, as reflected by the preferential decrease of the two Raman bands characteristic of polymeric surface vanadia species during the TP-Raman experiment (Fig. 2A). Under reaction conditions ($C_2H_6+O_2+He$), however, only a small fraction of the sites were reduced since at 723 K the

Raman spectra remain essentially identical to the fresh sample. *In situ* UV-Vis DRS spectroscopy measures no significant reduction for the silica- and alumina-supported vanadia catalysts during ethane oxidation. The 1% V_2O_5/ZrO_2 catalyst shows a slight vanadia reduction during ethane oxidation and only 5.5 % reduction is observed during ethane reduction. Thus, 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 rates of the catalytic cycle.

UV-Vis spectroscopy is also sensitive to the degree of polymerization of surface vanadia species. The edge energy values are sensitive to the changes in the oxidation/coordination states of the surface vanadium oxide species. Any increase of the edge energy values reflects a shift from polymeric to isolated vanadia species [5]. During ethane oxidation the edge energy values are essentially unchanged on silica- or alumina-supported vanadia, but increase on more reducible supports like zirconia. The polymerization degree of surface V (V) cations increases from 1% to 4% V_2O_5/ZrO_2 catalyst due to the higher surface vanadia density [7]. The polymerized surface vanadia species on 4% V_2O_5/ZrO_2 is more easily reduced under ethane reduction conditions at 723 K (23.0 % reduction vs. 5.5 %). A similar trend is expected for ceria-supported vanadia. Unfortunately, V_2O_5/CeO_2 is not suitable for UV-Vis-DRS studies (see section 2), but the *in situ* TP-Raman spectra of 1% V_2O_5/CeO_2 provides evidence for the preferential reduction of polymeric vanadia. However, the polymerization degree of the surface V (V) species seems to only have a minor effect on the extent of reduction during ethane oxidation conditions since 4% V_2O_5/ZrO_2 is only reduced 3.6 %, as determined by *in situ* UV-Vis-DRS. *In situ* Raman shows the same trend for 1% V_2O_5/CeO_2 . The modest effect of surface vanadia coverage on activity and selectivity is in agreement with the slight effect measured by *in situ* UV-Vis-DRS and Raman spectroscopy on the average oxidation state and polymerization degree during catalytic oxidation of ethane.

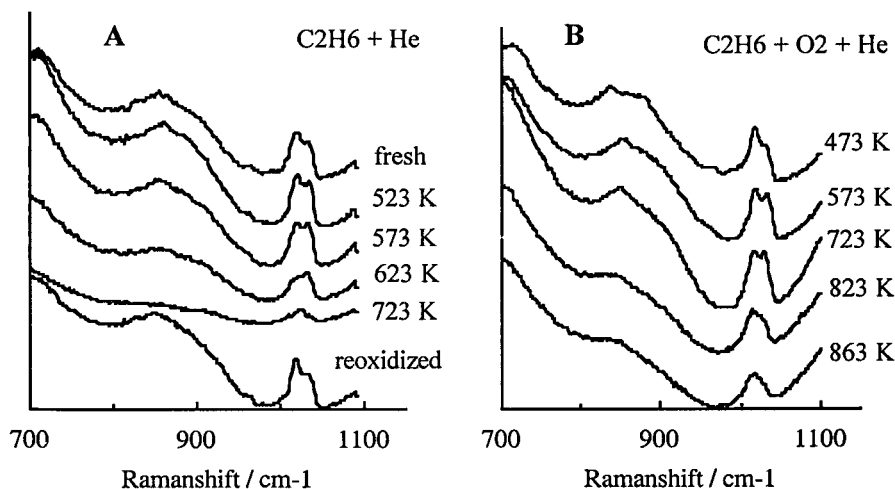


Figure 2. (A); representative *in situ* Raman spectra of 1% V_2O_5/CeO_2 catalyst under reducing atmosphere ($C_2H_6 + He$) and (B); representative *in situ* Raman spectra of 1% V_2O_5/CeO_2 catalyst under reaction conditions ($C_2H_6:O_2:He = 1:2:8$) at different temperatures.

4. CONCLUSIONS

The reactivity (TOF) of the supported vanadia catalysts for ethane oxidation is a strong function of the specific oxide support that changes an order of magnitude according to: $ZrO_2 > TiO_2 > Al_2O_3 > CeO_2 > SiO_2$. The reducibility of the oxide support seems to correlate with the activity per surface vanadium site for ethane oxidation. Although the polymerized surface vanadia species are more reducible than the isolated surface vanadia species, both species show a similar extent of reduction during ethane oxidation. *In situ* UV-Vis-DRS and *in situ* Raman spectroscopic techniques were shown to be complementary for the determination of the polymerization degree of the supported vanadium oxides. *In situ* spectroscopic (UV-Vis-DRS and Raman) studies of the supported vanadia catalysts during ethane reduction indicate that the polymeric surface vanadia species is more reducible than isolated surface vanadia species. Interestingly, they also show that during ethane oxidation only a small fraction of surface V (V) sites are reduced and that the polymerization degree of the surface vanadia is relatively unaffected under the ethane oxidation reaction conditions. Consequently, 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 rates of the catalytic cycle. The oxygen isotopic *in situ* Raman spectra underlines that the terminal V=O bond is not the critical site for the oxidation of ethane and that the bridging oxygen (V-O-V and V-O-Support) must be the active sites for ethane oxidation. The moderate effect of vanadia surface coverage on TOF values to ethylene and the pronounced effect of the support indicate that the bridging V-O-Support bond must be the critical site for this reaction.

ACKNOWLEDGEMENTS

This research was partially supported by the EU Commission under grant JOU2-CT92-0040 and CICYT (Spain) under projects 95-0894. The CICYT Grant (Spain) IN96-0053 funded the acquisition of the Raman spectrometer. This work was also supported by the U.S. Department of Energy - Basic Energy Sciences, Grant DE-FG02-93ER14350.

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