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The impact of redox properties on the reactivity of V_2O_5/Al_2O_3 catalysts

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ABSTRACT

The redox properties of 5 and 15 wt.% V_2O_5/Al_2O_3 catalysts calcined at 753 and 973 K were characterized by measuring their composition as a function of P_{O_2} at 748 K using coulometric titration. The redox isotherms showed that the 5 wt.% catalyst calcined at 753 K underwent gradual reduction from V^{+5} to V^{+4} at P_{O_2} between 10^{-4} and 10^{-19} atm, and stepwise reduction from V^{+4} to V^{+3} at a P_{O_2} of 10^{-24} atm corresponding to a ΔG_{red} of 343 kJ/mol of O_2. This sample was also found to exhibit relatively high thermal stability. The redox isotherm for a 15 wt.% catalyst calcined at 753 K was similar to that obtained for a 5 wt.% catalyst. This sample was much less thermally stable, however, and recrystallized upon calcination at 973 K, forming a highly reducible $AlVO_x$ species that underwent reduction from V^{+5} to V^{+3} in a single step at a P_{O_2} of 10^{-6} atm at 748 K with a ΔG_{red} of 86 kJ/mol. In spite of the differences in the redox properties, all the catalysts were found to exhibit a similar reactivity for the selective oxidation of methanol. The catalysts also exhibited a similar propane ODH activity except for the 15 wt.% catalyst calcined at 973 K which had a lower activity, was unselective, and produced only CO_2.

1. Introduction

Many selective oxidation reactions proceed via a Mars-van Krevelen mechanism [1,2] in which surface lattice oxygen is the active oxygen species. This oxygen is removed from the catalyst during one of the steps in the catalytic cycle and is then replenished via reaction with gas-phase oxygen in a separate step. Based on this mechanism the activity and selectivity of the catalyst are expected to depend on its redox properties. For example, one might anticipate an easily reducible catalyst to have a high oxidation activity. If oxygen removal is too facile, however, the catalyst may not be very selective for the partial oxidation products, instead producing CO or CO_2. These principles are widely recognized and many attempts to correlate catalytic activity with the catalyst redox properties can be found in the literature [3–20]. The majority of these studies, however, have relied on temperature-programed reduction (TPR) data to provide a measure of the relative reducibility of the catalysts. While such studies are useful, TPR provides a measure of the kinetics of reduction and it is difficult to directly relate these data to oxygen binding strength or thermodynamic variables such as ΔG and ΔH of reduction.

In order to provide more quantitative relationships between redox properties and catalytic activity, we have been using a coulometric-titration technique to directly measure redox isotherms, i.e. the oxygen composition of the sample as a function of P_{O_2} above the sample at a constant temperature, for a range of selective oxidation catalysts and then relating these thermodynamic data to their reactivity [21–26]. ΔG values for oxidation and reduction can be deduced directly from the isotherm, and ΔH and ΔS can be obtained by collecting data at multiple temperatures [24]. Supported-vanadia catalysts are active for both the selective oxidation of alcohols [27–31] and the oxidative dehydrogenation (ODH) of alkanes to produce alkenes [3,4,19,29,32–34] and are therefore of some interest. We have previously reported redox isotherm data for monolayer vanadia species on both TiO_2 and ZrO_2 supports [35]. For low coverages where the vanadia was present in the form of isolated vanadates, the redox isotherms for both supports showed that reduction from V^{+5} to V^{+3} occurred in a single step at a P_{O_2} of $\sim 10^{-20}$ atm at 748 K corresponding to a ΔG_{red} of 300 kJ/mol of O_2. In contrast, for a higher weight loading V_2O_5/ZrO_2 sample which contained predominantly polyvanadates, reduction proceeded in a stepwise fashion, V^{+5}–V^{+4}–V^{+3}, over a wide P_{O_2} range (10^{-2}–10^{-28} atm) at 748 K. In spite of these variations in the redox properties with vanadia coverage the catalysts exhibited similar activities and selectivities for the oxidation of methanol to formaldehyde and propane ODH suggesting that V–O bond scission is not rate limiting for these reactions on these catalysts and that the V–O bond strength does not affect the rate of these reactions.

In the work reported here we have expanded our previous studies of supported-vanadia catalysts to include vanadia supported on alumina. V_2O_5/Al_2O_3 catalysts have been reported to be less active for the selective oxidation of methanol compared to vanadia on more reducible supports, such as ceria and titania [27], but are widely used as a model system for studying structure–activity

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relationships for ODH reactions [32–34,36,37]. Redox isotherms for both low and high coverages of vanadia on γ-Al_2O_3 are reported and, as in our previous studies, are compared to the reactivity of the catalysts for both methanol oxidation and propane ODH.

2. Experimental

The γ-Al_2O_3-supported-vanadia catalysts used in this study were synthesized using the incipient wetness technique. Prior to adding vanadia, the γ-Al_2O_3 support (Alfa-Aesar) was calcined in air at 973 K for 8 h in order to stabilize the surface area. Vanadia was then deposited onto the supports by the impregnation of a solution of ammonium metavanadate (NH_4VO_3, Sigma) and oxalic acid ($C_2H_2O_4$, Aldrich). After drying in air at 400 K the samples were ground with a mortar and pestle and were calcined at 753 K in air for 4 h. Some samples were also calcined at 973 K in air for 10 days in order to induce reaction between the vanadia and the support. Catalysts were prepared with various vanadia loadings but only the samples with 5 and 15 wt.% vanadia were characterized in detail. As will be shown below, these weight loadings correspond to sub-monolayer and slightly greater than one monolayer vanadia coverage.

Raman spectra were obtained at room temperature under ambient conditions using a Renishaw RM1000 VIS Raman Microspectrometer with 514.5 nm Ar laser (9 mW) as the excitation source. A 50× objective was used on the microscope that collected the reflected Raman signal. XRD patterns were collected using a Rigaku Geigerflex diffractometer with a Cu(Kα) radiation source ($l = 1.5405$ Å). The surface areas for all samples were determined using the BET method with N_2 adsorbent.

Coulometric titration was used to measure redox isotherms, i.e. the sample composition as a function of P_{O_2} at a constant temperature, for each catalyst. The coulometric-titration technique has been described in detail previously [23,24,38]. A schematic of the experimental apparatus used in the current study is shown in Fig. 1 and consisted of an yttria-stabilized zirconia (YSZ) tube with Ag electrodes that were painted on the inside and outside. The sample to be analyzed was contained in a ceramic crucible that was inserted into the tube. The sample size was chosen so as it contained ~100 μmoles of vanadium. The ends of the tube were sealed using Cajon fittings and the center portion of the tube was placed in a tube furnace allowing the tube to be heated up to 1100 K. The external surface of the tube was exposed to air during the measurement. YSZ is an oxygen ion conductor and during the measurement of redox isotherms the P_{O_2} in the tube was determined from the open-circuit potential between the electrodes using the Nernst equation:

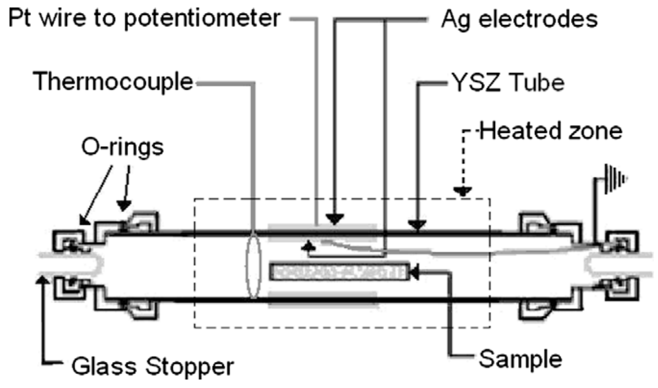

Fig. 1. Schematic diagram of coulomb-titration apparatus.

$$V = \frac{RT}{4F} \ln\left[\frac{P_{O_2}}{0.21\ \text{atm}}\right] \qquad (1)$$

where F is Faraday's constant.

Controlled amounts of oxygen could be pumped into or out of the YSZ tube via the application of a voltage across the electrodes using a Gamry Instruments potentiostat. The amount of oxygen transferred was quantified by integrating the current.

For the measurement of each redox isotherm a mixture of 2.5% O_2, 50% CO_2, and 50% Ar was initially flowed over the sample for 1 h at 748 K to insure that the sample was fully oxidized at the beginning of the measurement. After this treatment the ends of the YSZ tube were sealed and the sample was allowed to equilibrate with the gas phase at the temperature of interest. For this set-up it is important to recognize that at the low P_{O_2} values at which the samples equilibrated, the effective oxygen pressure is determined by the equilibrium between CO and CO_2 and that the oxidation or reduction for the samples occurs via reaction with these molecules. After each addition or removal of oxygen from the cell, the sample was allowed to equilibrate until the sample composition changed by less than 0.005 micromoles of O_2 per hour. Due to the slow kinetics of the reaction of the supported vanadia with CO and CO_2 it typically took between 2 and 15 days for equilibrium to be established. It should be noted that the ΔG of oxidation/reduction of the vanadia depends only on the initial and final states of the oxide and not the identity of the buffer gas used to maintain the P_{O_2} during the measurement as long as this gas does not react with the vanadia to form new compounds, e.g. carbonates. We have previously demonstrated that this is not a problem for vanadium oxides when using CO/CO_2 gas mixtures by measuring redox isotherms for bulk V_2O_5 and showing that the ΔG of reduction obtained from the isotherm was consistent with those reported in the literature for the reduction of V_2O_5–V_2O_4 and V_2O_4–V_2O_3 [24]. It should also be noted that the Al_2O_3 support does not undergo redox reactions for the conditions used in this study; thus, the measured isotherms can be attributed solely to the vanadium ions in the catalyst.

Rates for the selective oxidation of methanol and oxidative dehydrogenation (ODH) of propane were measured using a flow reactor equipped with an online gas chromatograph (SRI-8610C) with a TCD detector. The feed gas for methanol oxidation contained He, O_2, and CH_3OH in a 22.5:2:1 M ratio and the total flow rate was maintained at 125 cm^3/min. The feed for propane ODH consisted of He:O_2:C_3H_8 in a 7.6:1.6:1 M ratio a total flow rate of 100 cm^3/min. In both cases, the conversion was kept well under 20% so that differential reaction conditions could be assumed. The reaction rates were normalized to the vanadium content of each catalyst, except for the samples containing $AlVO_x$ compounds where the exposed surface vanadium was used, and are reported as turnover frequencies (TOFs).

3. Results

3.1. Catalyst characterization – XRD

The surface areas of the various V_2O_5/Al_2O_3 catalysts as determined using the BET method are listed in Table 1. The surface areas were measured for both the as-prepared samples that were calcined in air at 753 K and after calcining each sample in air at 973 K for 10 days. The latter treatment was chosen in order to induce reaction of the vanadia with the alumina support and to form a surface layer of $AlVO_4$ [39,40]. The calculated vanadia coverage for each sample, assuming that the vanadia forms a film on the surface, is also given in the table. For the samples calcined at 753 K, the surface areas were somewhat less than that of the bare support (180 $m^2\ g^{-1}$) and decreased with increasing vanadia weight load-

Table 1
BET surface areas and vanadia coverages.

wt.% of V_2O_5	Surface area, m^2/g, calcined at 753 K	Surface area, m^2/g, calcined at 973 K	% Reduction in surface area	Vanadia coverage V/nm^2 calcined at 753 K	Vanadia coverage, V/nm^2 calcined at 973 K
0	180	163	9.7	0	0
3.6	151	128	15.3	1.6	1.9
5	180	124	31.2	1.8	2.7
6.36	139	80	42.4	3.0	5.3
8.3	132	75	43.7	4.2	7.4
14.5	131	35	73.4	7.3	28
15	137	22	83.6	7.3	44
100 (bulk)	192	–	–	7	n/a

ing. For the 15 wt.% V_2O_5/Al_2O_3 sample which had a vanadia coverage of 7.3 V nm^{-2}, a value close to that reported for monolayer coverage of polyvanadates in the literature [30], the surface area, 137 $m^2\ g^{-1}$, was 24% less than that of the bare alumina support. This decrease is primarily due to the added mass of the sample and indicates that the overall morphology of the alumina support is preserved.

Upon calcination at 973 K for 10 days, the BET surface areas of all the samples decreased, with much larger decreases observed for the higher weight loading samples. For example, for the 3.6 wt.% V_2O_5/Al_2O_3 sample the surface area decreased by only 15% but the decrease was 84% for the 15 wt.% sample. Obviously major structural changes occur upon the calcination of the high vanadia coverage samples at high temperatures, while the low vanadia coverage samples remain largely unchanged. These differences between the low and high vanadia coverage samples are also reflected in the XRD data presented in Figs. 2 and 3.

Fig. 2 displays XRD data for the 5 wt.% vanadia sample. The XRD pattern for the bare alumina support is also shown for reference. Note that the XRD pattern for the 5 wt.% vanadia sample after calcining at 753 K contains only features indicative of the alumina support. This is consistent with the vanadia being present as a well-dispersed surface species. For this sample calcination at 973 K did not cause any significant changes in the XRD pattern. As shown in Fig. 3, for the 15 wt.% sample calcined at 753 K, small peaks at 20.4, 26.3, and 31.2 2θ, which can be attributed to bulk V_2O_5, are present in the XRD pattern in addition to the features indicative of γ-Al_2O_3. This demonstrates the presence of V_2O_5 crys-

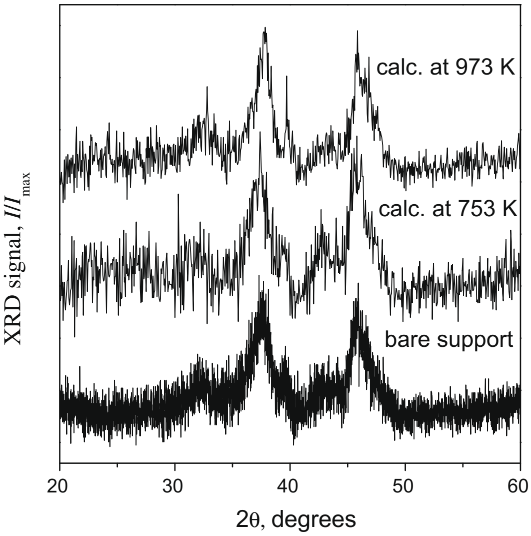

Fig. 2. XRD patterns for the 5 wt.% V_2O_5/Al_2O_3 sample as a function of the calcination temperature. For comparison the XRD pattern of the bare γ-Al_2O_3 support is also included in the figure.

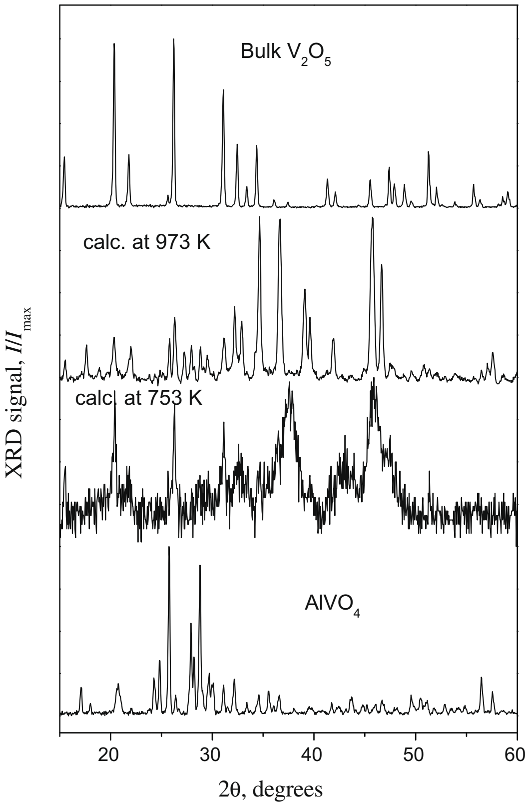

Fig. 3. XRD patterns for the 15 wt.% V_2O_5/Al_2O_3 sample as a function of the calcination temperature. For comparison the XRD patterns of bulk $AlVO_4$ and V_2O_5 are also included in the figure.

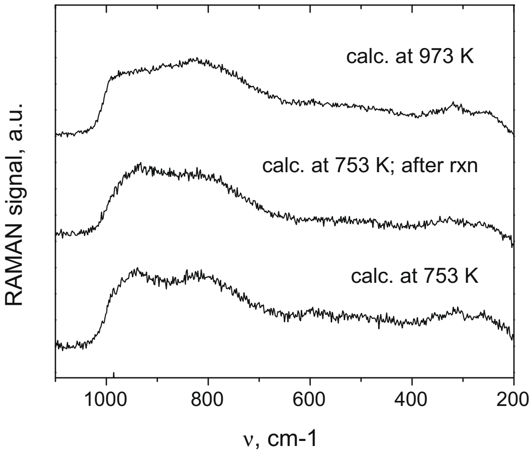

Fig. 4. Raman spectra of the 5 wt.% V_2O_5/Al_2O_3 sample as a function of the pretreatment conditions.

tallites and that the vanadia coverage was slightly greater than one monolayer. After calcination at 973 K, the 15 wt.% sample transforms into a new highly crystalline phase whose XRD pattern resembles that of the monoclinic phases of alumina. Diffraction peaks indicative of $AlVO_4$ or V_2O_5 could not be identified for this sample, but the surface is presumably covered with an $AlVO_x$ species. Vanadia has a relatively low melting point of only 963 K and is a well-known sintering aid [41–43]. It is likely that this may have contributed to the dramatic loss of surface area and recrystallization of the 15 wt.% V_2O_5/Al_2O_3 sample upon calcination at 973 K.

3.2. Catalyst characterization – Raman

Analogous trends were observed using Raman spectroscopy. Raman spectra of the 5 and 15 wt.% vanadia samples as a function of pretreatment conditions are shown in Figs. 4 and 5, respectively. The Raman spectra for the 5 wt.% vanadia catalyst after calcination at 753 (both before and after use as an methanol oxidation catalyst) and 973 K were nearly the same and contained broad peaks at 810 and 950 cm^{-1} which can be assigned to polymeric vanadia [44]. Peaks indicative of monomeric vanadia species were not observed, but this may be due to the fact that the spectra were collected in air and the surfaces were likely to be hydrated. These results are consistent with the XRD results and indicate that high-temperature calcination had little effect on the structure of the catalyst.

The Raman spectrum of the 15 wt.% sample (Fig. 5) calcined at 753 K is also consistent with the XRD results and is dominated by peaks indicative of bulk V_2O_5 [44]. The features associated with polymeric dispersed vanadia are not observed but could be obscured by the more intense peaks due to the crystalline vanadia. Calcination at 973 K resulted in significant changes in the Raman spectrum including a large decrease in the intensity of the peaks associated with bulk V_2O_5, and a new broad peak has emerged at 760 cm^{-1}. The origin of this feature is not clear. As shown by the reference spectrum of $AlVO_4$ which is also included in the figure, it does not correspond to bulk aluminum vanadate.

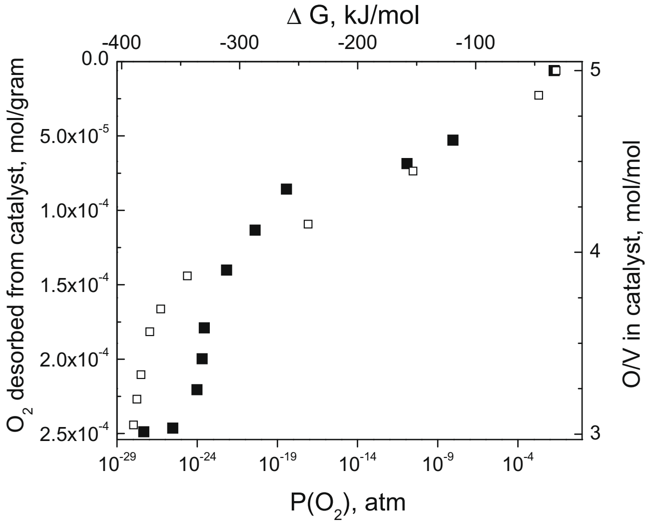

Fig. 6. Redox isotherms for 5 wt.% V_2O_5/Al_2O_3 at 748 K: (■) 5 wt.% V_2O_5 calcined at 753 K, and (□) 5 wt.% V_2O_5 calcined at 973 K.

3.3. Catalyst characterization – redox isotherms

Redox isotherms were measured for each sample at 748 K. The isotherms for the 5 wt.% sample calcined at both 748 and 973 K are displayed in Fig. 6. The isotherm for the 753 K calcined sample shows that reduction from V^{+5} to V^{+4} is gradual and occurs for P_{O_2} values between 10^{-4} and 10^{-19} atm corresponding to a ΔG_{red} range of 57–272 kJ/mol. A sharper transition is observed for the reduction from V^{+4} to V^{+3} which occurs at a P_{O_2} of 10^{-24} with a ΔG_{red} of 343 kJ/mol. A similar isotherm was obtained for the sample calcined at 973 K except that the reduction of V^{+4}–V^{+3} occurred at a lower P_{O_2} of 10^{-28} atm and a ΔG_{red} of 401 kJ/mol, suggesting that some structural changes in the catalyst may have occurred during high-temperature calcination.

The isotherms for the 5 wt.% sample are significantly different from those observed for bulk V_2O_5. Previously measured redox isotherms [24,25] for bulk V_2O_5, corrected to 748 K, show stepwise reduction from V_2O_5 to VO_2 and then to V_2O_3 with the transitions occurring at P_{O_2} values of 10^{-12} and 10^{-26} atm corresponding to ΔG_{red} of 171 and 372 kJ/mol, respectively [24]. A more gradual transition from V^{+5} to V^{+3} like the one observed here for 5 wt.% vanadia on alumina has been observed, however, for vanadia on zirconia [25,35]. In that case the lack of a sharp transition in the isotherm was attributed to the presence of polyvanadates with a distribution of cluster sizes as well as some isolated species. This is also likely to be the case for the 5 wt.% V_2O_5/Al_2O_3 sample. It is

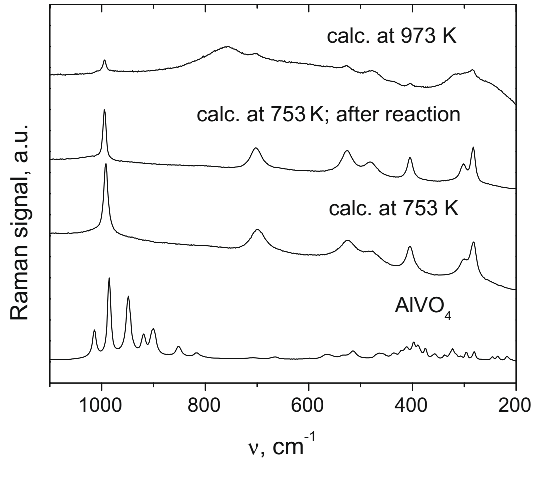

Fig. 5. Raman spectra of the 15 wt.% V_2O_5/Al_2O_3 sample as a function of the pretreatment conditions. For comparison the Raman spectrum of bulk $AlVO_4$ is also included in the figure.

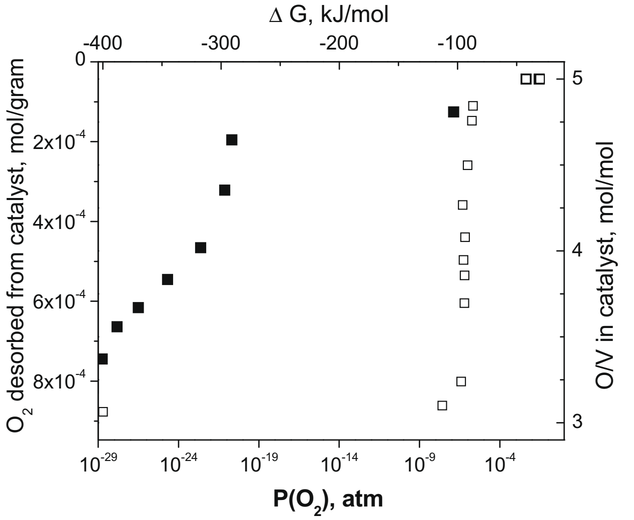

Fig. 7. Redox isotherms for 15 wt.% V_2O_5/Al_2O_3 at 748 K: (■) 15 wt.% V_2O_5 calcined at 753 K, and (□) 15 wt.% V_2O_5 calcined at 973 K.

noteworthy that for 973 K calcined sample that reduction from V^{+4} to V^{+3} occurred at a P_{O_2} lower than 10^{-27} atm. At such low oxygen pressures one needs to consider whether the reduction of the YSZ electrolyte is starting to occur. Nonetheless the redox isotherm clearly shows that for the 5 wt.% V_2O_5/Al_2O_3 sample it is very difficult to reduce V^{+4}–V^{+3}.

Somewhat different redox behavior was observed for the 15 wt.% sample as shown in Fig. 7. For the 753 K calcined sample the isotherm has some similarity to that obtained for the 5 wt.% sample although there is a significantly lower fraction of easily reduced species. The isotherm shows that ~25% of the V^{+5} cations undergo reduction to V^{+4} at P_{O_2} values between 10^{-4} and 10^{-19} atm with ΔG_{red} ranging from 58 to 274 kJ/mol. The remaining V^{+5} cations undergo reduction to V^{+4} at a P_{O_2} of 10^{-20} with a ΔG_{red} of 286 kJ/mol. Recall that the XRD and Raman results for this sample indicate that the vanadia coverage is slightly above one monolayer. Thus, the redox isotherm for this sample would be expected to have contributions from both the dispersed monolayer and the V_2O_5 crystallites. Since the reduction of bulk V_2O_5–VO_2 at 753 K occurs at a P_{O_2} of ~10^{-12} atm [24], some of the 25% of the vanadium cations that undergo reduction between 10^{-4} and 10^{-19} atm of O_2 may be in the V_2O_5 crystallites, with the remaining cations that undergo reduction to V^{+4} at 10^{-20} atm of O_2 being associated primarily with the dispersed polymeric species. The sharper reduction transition in the 15 wt.% sample compared to 5 wt.% sample may be a result of the higher vanadia coverage producing a more uniform polymeric species.

As was also the case for the 5 wt.% sample, the reduction of V^{+4}–V^{+3} was very difficult and incomplete for P_{O_2} values as low as 10^{-29} atm. It is noteworthy that in agreement with this a number of previous studies of supported-vanadia catalysts have also reported that a fraction of the vanadium cations appear to be either unreducible or inaccessible [20,25,35,39,45,46]. The reason for this, however, is not clear.

Calcining the 15 wt.% vanadia sample at 973 K caused dramatic changes in its redox behavior. The 748 K redox isotherm for this sample (Fig. 7) contains a single transition from V^{+5} to V^{+3} at a P_{O_2} of 10^{-6} atm corresponding to a ΔG_{red} of 86 kJ/mol. The amount of oxygen removed in this transition matches the V content. Thus, this sample is much more reducible than the 15 wt.% vanadia sample calcined at 753 K and the 5 wt.% sample calcined at either 753 or 973 K. In spite of the fact that the Raman and XRD data indicate that this sample still contains a small amount of bulk V_2O_5, the isotherm does not include the expected transitions at ~10^{-12} and ~10^{-26} atm of O_2 corresponding to V^{+5}–V^{+4} and V^{+4}–V^{+3}. Thus, the isotherm is dominated by a new surface species resulting from reaction between the vanadia and the alumina during the high-temperature calcination step. Unfortunately, the structure and composition on this species cannot be determined from the XRD and Raman results. The redox behavior of this species, however, does have some similarities to that of bulk $AlVO_4$ which also undergoes a one-step reduction from V^{+5} to V^{+3} at a relatively low P_{O_2} (10^{-6} atm at 948 K) [22].

In previous studies of the redox behavior of mixed oxides containing vanadium and a second less reducible cation, it has been shown that stepwise reduction, i.e. discrete transitions in the redox isotherm for V^{+5}–V^{+4} and for V^{+4}–V^{+3}, only occurs when the compound contains V–O–V bonds [22]. Thus, the single-step reduction of V^{+5}–V^{+3} observed for the 15 wt.% vanadia sample calcined at 973 K suggests that the surface species in this sample contains primarily Al–O–V linkages.

3.4. Reactivity studies

The TOF for the selective oxidation of methanol and the ODH of propane were measured as a function of temperature for each sample and are reported in Figs. 8 and 9, respectively. During methanol oxidation, the selectivity to formaldehyde was greater than 90% for all four catalysts in the temperature range for which rate data are reported (430–515 K). At higher temperatures dimethylether (DME) produced via reaction on the alumina support became a significant product. The TOF for the selective oxidation of methanol to formaldehyde (Fig. 8) are consistent with those reported in the literature [27,47] for similar catalysts. For example, Deo and Wachs report that the TOF for selective oxidation of methanol to formaldehyde over 15 wt.% V_2O_5/Al_2O_3 at 503 K is 0.02 [27]. The corresponding value in our study was 0.015. The measured TOF at each temperature varied by less than a factor of 4, which can easily be ascribed the experimental uncertainties associated with the surface area and coverage measurements. The activation energies were also found to be almost the same for each catalyst with a value of ~70 kJ/mol.

It is interesting that in spite of the range of thermodynamic properties exhibited by these catalysts, their reactivities for the selective oxidation of methanol are nearly the same. It is well established that C–H bond cleavage in the methyl group is the rate-limiting step for the oxidation of methoxide species on sup-

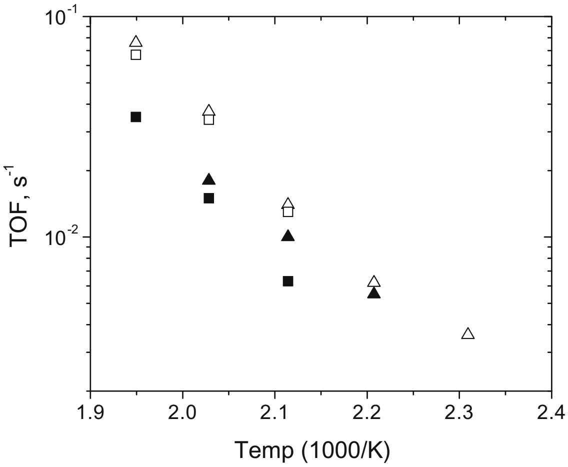

Fig. 8. TOF for the partial oxidation of methanol to formaldehyde on (▲) 5 wt.% V_2O_5 calcined at 753 K, (■) 15 wt.% V_2O_5 calcined at 753 K, (△) 5 wt.% V_2O_5 calcined at 973 K, and (□) 15 wt.% V_2O_5 calcined at 973 K.

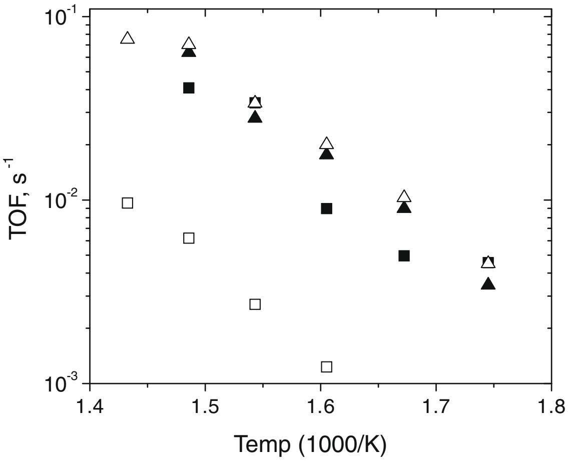

Fig. 9. TOF for propane consumption during propane ODH on (▲) 5 wt.% V_2O_5 calcined at 753 K, (■) 15 wt.% V_2O_5 calcined at 753 K, (△) 5 wt.% V_2O_5 calcined at 973 K, and (□) 15 wt.% V_2O_5 calcined at 973 K. Relative product yields are given in Table 2.

Table 2
Selectivities for propane ODH at 623 K.

	5 wt.% V_2O_5/Al_2O_3 calcined at 753 K	5 wt.% V_2O_5/Al_2O_3 calcined at 973 K	15 wt.% V_2O_5/Al_2O_3 calcined at 753 K	15 wt.% V_2O_5/Al_2O_3 calcined at 973 K
Selectivity to C_3H_6 (%)	69	63	40	–
Selectivity to CO_2 (%)	31	37	60	100

ported vanadia to produce formaldehyde [31,47]. The apparent lack of a dependence of this step on the redox properties suggests that this step does not involve cleavage of a V–O bond. This conclusion is also consistent with that obtained previously for V_2O_5/TiO_2 and V_2O_5/ZrO_2 catalysts [35].

More complex behavior was observed for the ODH of propane. Fig. 9 displays the TOF for propane consumption as a function of temperature for a reaction mixture consisting of He, O_2, and C_3H_8 in a 7.6:1.6:1 M ratio. The selectivities to propene and carbon dioxide for each catalyst at 623 K are listed in Table 2. The 5 wt.% V_2O_5/Al_2O_3 catalysts calcined at either 753 or 973 K both exhibited relatively high selectivities to propene, 69% and 63%, respectively, and nearly identical reaction rates and activation energies (90 kJ/mol). The propene selectivity for the 15 wt.% V_2O_5/Al_2O_3 catalyst calcined at 753 K was only 40%, but the propane consumption TOF and activation energy were nearly the same as that for the 5 wt.% samples; however, the 15 wt.% V_2O_5/Al_2O_3 catalyst calcined at 973 K exhibited dramatically different behaviors. For the reaction conditions studied, this catalyst was active only for the complete oxidation of propane to CO_2, and the propane consumption TOF was an order of magnitude less than those obtained for the other catalysts.

4. Discussion

There are a number of interesting conclusions that can be drawn from the present study. First, a comparison of the results obtained for V_2O_5/Al_2O_3 with those in our previous publications on V_2O_5/TiO_2 and V_2O_5/ZrO_2 [22,35] reveals that the equilibrium redox properties are similar for vanadia on all these supports. While there are subtle differences, the P_{O_2} where oxidation/reduction reactions occurred, and therefore the ΔG of reduction, were similar on each of the supports. The effects of increased vanadia loading, which in turn leads to V–O–V bonds, were typically larger than the effect of changing the support composition. Even with this and the inherent inhomogeneity of the surface sites on these support materials, the major portion of the reducible species is described by a ΔG of reduction at 748 K of 180 ± 50 kJ/mol on all the supports. This result is somewhat surprising given that the ΔG of reduction for bulk compounds made from vanadia and cations in typical support materials (e.g. Zr^{+4}, Ce^{+4}, and Al^{+3}) were found to vary significantly [22]. In comparing the series of bulk vanadates, from $LaVO_4$ to $AlVO_4$, ΔG of reduction at 973 K was observed to change from ~350 to 125 kJ/mol, depending on the electronegativity of the second cation. It was only after high-temperature treatment, which led to bulk compound formation, that the supported catalysts exhibited characteristics similar to the bulk compounds.

For V_2O_5/ZrO_2 catalysts, calcination above 873 K gave rise to samples that exhibited vibrational spectra and redox isotherms that were identical to that of ZrV_2O_7 [35]. For V_2O_5/Al_2O_3, the results are similar but slightly more subtle. For low vanadia coverages, heating to 973 K had minimal effect on the catalyst. For high vanadia coverages, high-temperature treatment led to a large loss in surface area but neither the diffraction data nor vibrational spectra could be identified with the bulk $AlVO_4$. However, as with the zirconia-supported catalyst, the isotherm changed in a way that suggests the formation of a compound like $AlVO_4$. The equilibrium P_{O_2} was shifted to much higher values, to a range similar to that observed with bulk $AlVO_4$. Furthermore, since the amount of reducible oxygen agreed quantitatively with the vanadium content of the sample, all of the vanadia in this sample was accounted for and was present in a similar environment.

Given that much of the oxygen on the supported-vanadia catalysts is described by a similar ΔG of reduction, it is perhaps not surprising that catalytic activities for vanadia/zirconia, vanadia/titania, and vanadia/alumina are similar for both methanol oxidation and propane ODH. However, the high-temperature form of the 15 wt.% vanadia/alumina sample provides an opportunity for understanding how large changes in the oxygen binding in a vanadia catalyst affect catalytic activity. For a selective oxidation of methanol, the ease of reduction of the catalyst had no effect on activity since the highly reducible $AlVO_x$ species in the high-temperature form of the 15 wt.% V_2O_5/Al_2O_3 sample exhibited essentially the same reactivity as the dispersed vanadia species on the alumina support. As pointed out earlier, this likely indicates that the rate-limiting C–H bond cleavage step for methanol oxidation does not involve the breaking of V–O bonds.

The results for propane ODH are more interesting. For this reaction, the more reducible form of vanadia on the high-temperature vanadia/alumina was completely unselective for the production of propene. We hypothesize that the surface species formed after the abstraction of hydrogen on this sample are oxidized quickly to CO_2 and H_2O by the loosely bound oxygen present in this catalyst. This in turn suggests that researchers looking for more selective vanadia catalysts for ODH consider investigating additives which strengthen the oxygen binding. In light of the ease of reduction of the high-temperature vanadia/alumina sample, it is reasonable to expect the catalyst to also exhibit higher oxidation rates. Instead, ODH activities on this catalyst were significantly lower. A possible explanation for the lower rates is that the working catalyst may be in a more highly reduced state under reaction conditions, with reoxidation of the catalyst being rate limiting.

Obviously, vanadia catalysts are not simply oxygen donors and oxygen bond strengths are only one aspect of these materials. There will be significant differences in the geometry of the sites and in the accessibility of the vanadium cations for the vanadia on the various supports and for the low- and high-temperature forms of vanadia/alumina. More work is required to understand the mechanisms for partial oxidation reactions and our results highlight only one aspect of these materials.

5. Conclusions

Redox isotherms for V_2O_5/Al_2O_3 catalysts were measured as a function of the vanadia weight loading and calcination temperature. The 5 wt.% V_2O_5/Al_2O_3 catalysts were found to be thermally stable and their redox isotherms at 748 K showed that reduction from V^{+5} to V^{+4} occurred for P_{O_2} values between 10^{-4} and 10^{-19} atm and reduction from V^{+4} to V^{+3} occurred at a P_{O_2} of 10^{-24} atm corresponding to a ΔG_{red} of 343 kJ/mol. The 748 K redox isotherm for a 15 wt.% V_2O_5/Al_2O_3 catalyst calcined at 753 K showed a sharper transition for reduction from V^{+5} to V^{+4} which occurred at a P_{O_2} of 10^{-20} atm with a ΔG_{red} of 286 kJ/mol. This sharper transition compared to the lower vanadia coverage sample may be the result of a more uniform polyvanadate species on this sample. In contrast to the 5 wt.% sample, the 15 wt.% sample was not thermally stable and underwent recrystallization upon calcination at 973 K resulting in a low surface area material whose surface was covered with a highly reducible $AlVO_x$ species.

In spite of the differences in redox properties, all the V_2O_5/Al_2O_3 catalysts were found to exhibit similar activity for the selective oxidation of methanol to produce formaldehyde suggesting that V–O bond cleavage does not occur in the rate-limiting C–H bond breaking step for this reaction. For propane ODH larger differences between the catalysts were observed. The 5 wt.% vanadia samples and the 15 wt.% vanadia sample calcined at 753 K all exhibited a similar activity for the ODH reaction. The highly reducible 15 wt.% V_2O_5/Al_2O_3 sample that was calcined at 973 K, however, was active only for the complete oxidation of propane to CO_2 and water.

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