

Adsorbate Bonding and the Selection of Partial and Total Oxidation Pathways

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The oxidation reaction of ethane has been studied on a series of well-characterized samples of vanadium oxide supported on silica. At low concentrations the vanadium species are isolated vanadyl groups, while at high concentrations they form small V_2O_5 crystallites. Oxygen chemisorption is used to measure the number of surface vanadium atoms on both types of species. At low conversions the oxidation of ethane is selective, producing mostly ethylene and acetaldehyde via structure-insensitive reactions. Intermediates for these are probably bonded to vanadium through an oxygen atom. In contrast the CO_x reaction is structure-sensitive, and probably involves intermediates bonded directly to vanadium. © 1991 Academic Press, Inc.

INTRODUCTION

In the investigation of hydrocarbon partial oxidation reactions the study of the factors that determine selectivity has been of paramount importance. A fundamental question is whether an intermediate bonds to a metal oxide directly to the metal or through an oxygen atom. A further question is whether this has any effect on selectivity. The question of bonding is not new: it was raised twenty years ago by Sachtler (1) who at the time concluded that there were insufficient data for a definitive answer. Since that time this question has not been directly addressed; much of the mechanistic work has concentrated on the nature of the surface sites or on the organic chemistry of the hydrocarbon (2). Nevertheless, considerable work relevant to this topic has been published.

Based on extensive adsorption work, Matsuura and Schuit identified two types of adsorption sites responsible for selective oxidation that were associated with different kinds of oxygen anions (3). Later, Keulks *et al.* assigned these sites to bridging and terminal oxygens (4). They also noted the buildup of very strongly held hydrocar-

bon fragments on bismuth molybdate that could only be removed by oxidation to CO and CO_2 , but did not speculate on their mode of bonding. Grasselli and Burrington depicted intermediates in propylene oxidation that lead to selective products as being bonded through oxygen atoms (5). Dadyburjor *et al.* suggested that olefins initially bind directly to coordinatively unsaturated metals, but in subsequent steps transfer to adjacent oxide sites to produce partial oxidation products (6). Kung and Kung established that for the oxidation of butenes on ferrite catalysts there are two types of sites that are independently responsible for selective and unselective oxidation (7). However, no bonding attributes were given. Although in the above studies not much is said about the unselective sites, for the selective products the implicit consensus seems to be that oxygen bonded intermediates are involved.

In this work the effects of oxide structure on the selective and unselective products of ethane oxidation are examined. The evidence suggests that selective oxidation occurs through oxygen bound intermediates and that total oxidation occurs through metal bound intermediates.

The analysis is made possible by the measurement of turnover rates. Turnover rates represent the most fundamental measure of intrinsic activity and are routinely reported in catalytic studies on metals. They are less frequently used with oxides because of the difficulty in measuring active sites on the more labile oxidic surfaces. Recently a high-temperature oxygen chemisorption method was developed that yields the number of vanadium atoms on the surface of unsupported and supported V_2O_5 (8). Using this technique it was shown that ethanol oxidation was a structure-insensitive reaction (9), confirming the findings of others (10, 11), and establishing the validity of the method. In this study results on the oxidation of ethane are presented.

EXPERIMENTAL

Details of the experimental procedures are reported elsewhere (9). Briefly, the catalysts were in the form of supported powders obtained by impregnating silica (Cabosil 90 m^2g^{-1}) with vanadium oxalate and calcining at 773 K. Reactivity measurements were carried out with 7.0 mg of V_2O_5 in a packed bed flow reactor using $P_{CH_3CH_3} = 13$ kPa, $P_{O_2} = 28$ kPa, $P_{H_2O} = 10$ kPa, $P_{He} = 50$ kPa at a flow rate of 73–74 $\mu mol s^{-1}$. Analysis was by GC using dual FID and TCD detectors to obtain C and O balances of $100 \pm 5\%$. The catalysts were pretreated at the maximum temperature used during rate measurements and the stability of the catalysts was checked by going up and down in temperature. Blank measurement with silica showed that it had insignificant activity at the conditions of this study. Turnover rates for the reaction of ethane to various products are reported based on oxygen chemisorption at 640 K after reaction.

RESULTS

The products of ethane oxidation were ethylene, acetaldehyde, CO, and CO_2 . Average conversions at 770, 800, 825, and 870 K were 0.34%, 0.82%, 2.2%, and 13%. The higher-temperature conversion and se-

lectivity values are reported in detail elsewhere (9). Values at 770 K are given in Table 1. For completeness, results for unsupported V_2O_5 are also included, but are discussed in (9).

A summary of turnover rates versus vanadium oxide concentration shows different trends for the various products (Fig. 1). For ethylene the rates first increase and then decrease slightly with active phase concentration (Fig. 1b). For acetaldehyde the rates increase steadily (Fig. 1c). In both cases the variations are of factors of 3–5, occur smoothly, and are highest at the lowest temperatures. A very different behavior is found for the carbon oxides (Fig. 1d). At low temperatures the lowest concentration samples have very high rates for CO_x production, but in going to the higher loading samples the activity drops precipitously, by a factor of ~ 30 . The sudden drop decreases in magnitude in going to higher temperatures and is leveled completely at 870 K. Overall, for the total rate of ethane oxidation the contributions of ethylene, acetaldehyde, and CO_x partially cancel and the total rate shows only moderate variations with active phase loading (Fig. 1a).

DISCUSSION

Earlier Raman spectra (8) unequivocally show that the silica-supported vanadium oxide is in two forms. At low concentrations (0.3 and 1.4 wt.%) the vanadium oxide species is molecular, consisting of monomeric $V=O$ units anchored to the surface by three $V-O-Si$ links (Fig. 2). These surface vanadyls are analogous to the vanadyl trihalides, $O=VF_3$, $O=VCl_3$, and $O=VBr_3$ (12). At higher concentrations (3.5 to 9.8 wt.%) the vanadium oxide nucleates into small V_2O_5 crystallites, of size $< 4nm$, but identical to bulk V_2O_5 (Fig. 2). Throughout this region of concentration there is a considerable change in dispersion, the ratio of surface atoms to total atoms, and these samples are ideal for studying the effect of structure on reactivity.

For the reactions of ethane to ethylene

TABLE I
Conversion and Selectivity Values in Ethane Oxidation ($T = 770$ K)

Sample	Conversion (%)	$S_{\text{CH}_3\text{CHO}}$ (%)	$S_{\text{CH}_2\text{CH}_2}$ (%)	S_{CO} (%)	S_{CO_2} (%)	v_t (10^3 s^{-1})
SiO_2	0	—	—	—	—	—
0.3% $\text{V}_2\text{O}_5/\text{SiO}_2$	0.65	4	16	3	77	1.2
1.4% $\text{V}_2\text{O}_5/\text{SiO}_2$	0.70	1	10	2	87	2.4
3.5% $\text{V}_2\text{O}_5/\text{SiO}_2$	0.17	17	70	6	8	0.49
5.6% $\text{V}_2\text{O}_5/\text{SiO}_2$	0.14	9	80	5	6	0.80
7.7% $\text{V}_2\text{O}_5/\text{SiO}_2$	0.20	12	68	3	17	1.1
9.8% $\text{V}_2\text{O}_5/\text{SiO}_2$	0.20	15	60	3	22	0.75
100% V_2O_5	5.5	0.2	28	32	40	4.0

and acetaldehyde the small magnitude and the smoothness in the variation in rates suggests that the reaction does not depend highly on surface structure. Since the lowest-concentration samples consist of monomeric vanadia species, only a single vanadium center is necessary for the reaction. The reactions are thus structure-insensitive (13).

The production of carbon oxides shows

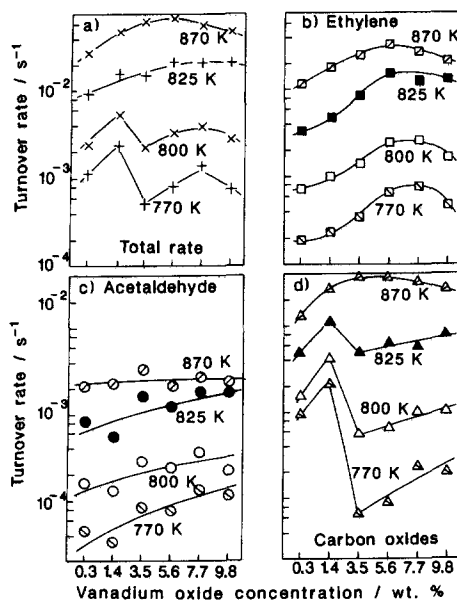


FIG. 1. Turnover rates in the oxidation of ethane.

considerable variation with vanadium concentration. At low temperatures the occurrence of two distinct regions of activity is consistent with the existence of two structural types as indicated by laser Raman spectroscopy (Fig. 2). Interestingly, the big drop in turnover rate for CO_x between the two regions has little effect on the rates of ethylene and acetaldehyde production. This strongly suggests that the reactions proceed by independent pathways. Thus, in the high-activity region the CO_x is not produced by a consecutive reaction involving the same intermediates leading to ethylene or acetaldehyde. If this were so, suppression of that pathway should lead to a jump in ethylene

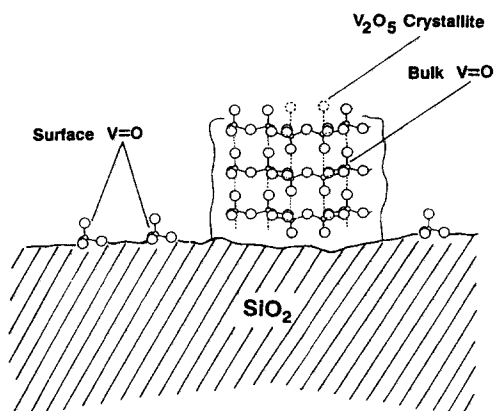


FIG. 2. Structure of the vanadium oxide catalysts.

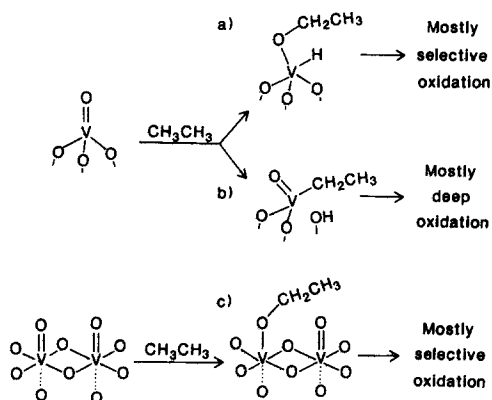


FIG. 3. Possible modes of adsorption of intermediates in ethane oxidation.

and acetaldehyde production, which is not observed. What is strongly indicated is that there are different intermediates for the selective and unselective reaction pathways (Fig. 3).

The initial interaction of ethane with the monomeric $V=O$ units can result in two intermediates. First, the ethane can add to the $V=O$ double bond to form an adsorbed ethoxide species (Fig. 3a). This intermediate can react by an α -elimination to produce acetaldehyde or by a β -elimination to produce ethylene. Similar intermediates have been suggested for the oxidation of ethanol on V_2O_5 (14). Only one vanadium center is involved, in agreement with the lack of structure-sensitivity.

A second intermediate may be formed by addition of ethane to the surface $V-O-Si$ bond to form an adsorbed ethyl species (Fig. 3b). This is a likely reaction as both the organometallic and $Si-OH$ species are stable and the $V-O-Si$ link is weak (12). The H atom has the additional option of being located on the vanadyl oxygen to form a $V-OH$ species. The formation of the $Si-OH$ species is more likely because the $V=O$ bond is strong and because bridging oxygens are more basic than terminal oxygens and are better able to accommodate the protons.

It is surmised that the ethyl species can

only be released through its complete oxidation to carbon oxides. There are two reasons for this. First, as will be discussed later, the ethyl species is very stable and, thus, can not desorb. Second, because of the formation of the $M-C$ bond there are no ready decomposition pathways such as α - or β -elimination to produce selective oxidation products. Reductive elimination does not yield a stable product.

It must be recognized that intermediates other than the ethyl species may also form in the course of CO_x formation; for example, di- σ -adsorbed species or carboxylates. However, it is difficult to picture how these species would form by interacting with the very simple vanadyl monomer. The ethyl species remains the most likely initial intermediate.

Assuming that formation of the ethyl intermediate leads primarily to carbon oxides formation, selectivity values on the 1.4% V_2O_5 sample (Table 1) indicate that activation by formation of the ethyl species is favored 9 to 1 over the ethoxide.

In the case of the V_2O_5 crystallites it is likely that ethane can only adsorb through the intermediacy of an oxygen atom. Although V in the crystallites is also in the +5 oxidation state, it is now octahedrally coordinated (Fig. 3c) and the ethyl group is sterically prevented from bonding directly to the vanadium. If it were to bond to vanadium, an unlikely 7-coordinate species would be formed. The formation of the ethoxide leads to lower rates for the crystallites but higher selectivities to partial oxidation products (Table 1 and Fig. 1). This supports the idea that it is the formation of the ethyl species that leads to high rates and CO_x formation.

In the reaction schemes presented above the interaction of the hydrocarbon reactant occurs with fully oxidized surface species. These may be represented by $M^{n+}O^{2-}$, where the M^{n+} represents the LUMO and the O^{2-} represents the HOMO of the surface site. Because the surface site is in its highest oxidation state, adsorption cannot occur by

oxidative addition to the metal center alone; instead reaction proceeds by heterolytic cleavage of a C—H bond due to interaction with the HOMO and LUMO. Another type of site that can occur on the surface of oxides is a partially reduced metal center, M_{red} . This site may be associated with coordinative unsaturation. However, in selective oxidation the hydrocarbon reactant is more likely to react with fully oxidized $M^{n+}O^{2-}$ sites than with M_{red} . This certainly occurs in the case of all known stoichiometric oxidation reagents like KMnO_4 (15, 16), OsO_4 (17, 18), or Cl_2CrO_2 (19) through well-established pathways. In a catalytic cycle involving the Mars–van Krevelen mechanism it is likely that a reactant would also react with an oxidized site. The site would be reduced and would be eventually reoxidized by O_2 . This view is supported by kinetics, which indicate independent hydrocarbon oxidation and site reoxidation steps. The alternative possibility of interaction with a reduced site requires oxidation by O_2 or lattice oxygen at the time of site occupation and is inconsistent with redox kinetics. However, there are examples in which this does occur, as in the case of oxidation on the Zn-rich surfaces of ZnO (20, 21).

Presently there exist only limited thermochemical data for high-valent vanadium compounds to support the thesis that the species bound directly to the metal is strongly held (22, 23). However, in the related systems comprising high-valent chromium and molybdenum compounds, theoretical valence bond calculations indicate that the formation of alkyl groups is favored over the formation of alkoxide species (24). The results are illustrated in Fig. 4 which reports the ΔG_{300} (kcal mol^{-1}) for various reactions. For the addition of ethane to chromyl chloride the ethyl product is favored over the ethoxide by 16 kcal mol^{-1} (Fig. 4a). However, here the comparison is unfair because the ethyl-bearing complex also contains a so-called spectator oxygen group which greatly increases its stability. A more fair comparison is provided for the

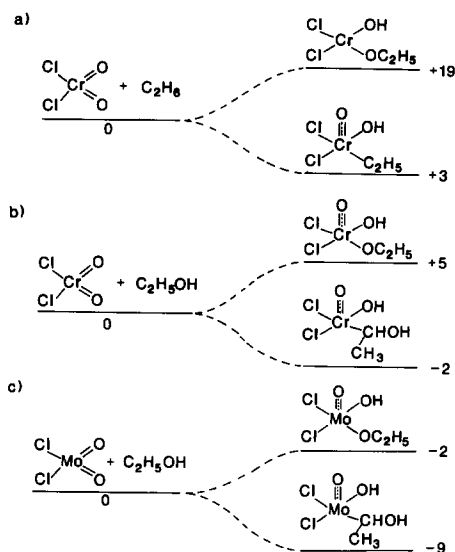
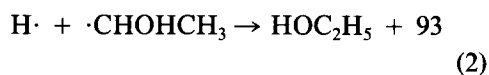
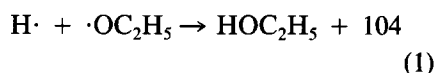
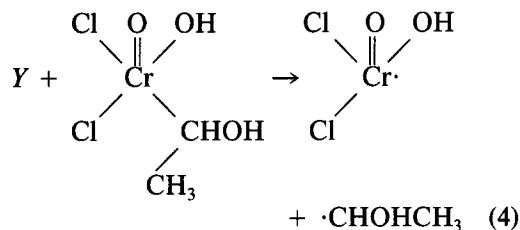
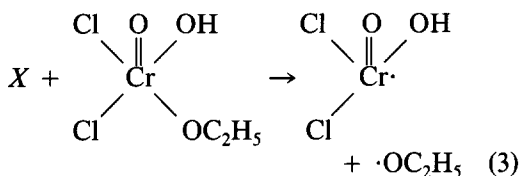


FIG. 4. Formation of alkyl and alkoxide complexes of high-valent metal oxides. Quantities given are ΔG_{300} values in kcal mol^{-1} . Adapted from Ref. (24).

additions of ethanol to chromyl and molybdenyl chlorides (Fig. 4b and 4c). In these cases the products have identical structures, all of them containing the spectator oxygen, and differ only in having the $\text{C}_2\text{H}_5\text{O}$ group attached directly to the metal or through the oxygen atom. For both the chromium and molybdenum complexes the directly-bonded species is more stable than the oxygen-bonded species by 7 kcal mol^{-1} .

It must be noted that although the alkyl species is more stable than the alkoxide species, the $M\text{—C}$ bond energy is slightly less than the $M\text{—O}$ bond energy. This can be verified by carrying out a Hess' law summation. For example, for the chromium case the following two sets of reactions are employed together with the reactions shown in Fig. 4b (because only pairs of similar reactions are taken it is assumed that entropic differences cancel out):





In reactions (3) and (4) above, X and Y represent the homolytic dissociation energies of the $M-O$ and $M-C$ bonds, respectively. From the dissociation energies (25) of reactions (1) and (2) and the values in Fig. 4b it is possible to calculate the relative magnitudes of X and Y :

$$\begin{aligned} X - Y &= (104 - 93) - (5 + 2) \\ &= 4. \end{aligned}$$

Thus, the $M-O$ bond is only 4 kcal mol⁻¹ stronger than the $M-C$ bond. $M-O$ bond energies for alkoxy derivatives of vanadium and chromium are 90 and 77 kcal mol⁻¹, respectively (22). The greater overall stability of the alkyl versus the alkoxide species is a consequence not of the strengths of the $M-O$ and $M-C$ bonds alone, but of the overall structure of the molecules. In terms of the fundamental thesis of this paper, the greater stability of alkyls coupled to their lack of ready decomposition pathways is responsible for their complete oxidation.

The finding that structural effects tend to disappear at higher temperatures may be due to the enhancement of total oxidation reactions on the crystallites. These reactions have higher activation energies on the crystallites than on the monomers (9) and would be favored on the crystallites at elevated temperatures. Also higher conversions would lead to higher rates of secondary oxidation of products which would tend to equalize differences between catalysts.

As far as is known this is the first time that the mode of adsorption of an intermediate, oxygen-bonded versus metal-bonded, has been suggested to relate to selectivity in an oxidation reaction. This view is radically different from the classical theory that lattice oxygen is responsible for selective products and adsorbed electrophilic oxygen is responsible for deep oxidation. It will be interesting for further work to uncover whether adsorbate bonding directs selectivity for oxides other than V_2O_5 .

If indeed for oxidation by the redox mechanisms bonding of intermediates by direct $C-M$ bonds leads to the formation of carbon oxides, it would be expected that partially reduced oxides would be less selective. However, this would be true only if these oxides exposed metal atoms on the surface. Solids that accommodate partial reduction by the formation of shear structures would not fall under this category. Multi-component oxides based on bismuth molybdate are examples of this type of solid. The very high selectivities in propylene oxidation to acrolein found on these oxides may thus be due to the lack of coordinatively unsaturated sites on the surface. It also must be recognized that the $C-M$ bond must be strong for deep oxidation to be the only means of releasing the intermediate. For weak $C-M$ bonds other alternatives may be possible.

The picture presented here for the relationship between mode of adsorption and selectivity pertains to primary selectivity in the absence of secondary reactions. In this study this is attained because of the low conversion (<1%) conditions. In most studies of partial oxidation at higher conversions it is likely that overall selectivity will be affected by secondary reactions (26).

The availability of turnover rates makes it interesting to compare the behavior of the V_2O_5 crystallites to that of platinum (27), one of the most active metallic oxidation catalysts. Table 2 compares the performance of the two materials. It is seen that

TABLE 2

Comparison of Activity in Ethane Oxidation at 770 K

Catalyst	Turnover rate (s ⁻¹)	Selectivity (%)		
		CH ₃ CHO	CH ₂ CH ₂	CO _x
7.7% V ₂ O ₅ /SiO ₂	1.1 × 10 ⁻³	12	68	20
Pt	6.0 × 10 ⁵	—	—	100

platinum has over eight orders of magnitude higher activity than V₂O₅, but is unable to produce the selective oxidation products.

CONCLUSIONS

(1) The oxidation of ethane to ethylene and acetaldehyde occurs with high selectivity on high-loading vanadium oxide on silica.

(2) The selective reactions to form ethylene and acetaldehyde are structure-insensitive. They proceed at similar turnover rates on monomeric vanadyls and on the surface of crystallites, possibly through intermediates bonded to vanadium through oxygen atoms.

(3) The reaction to form CO_x is structure-sensitive. It occurs faster on monomeric species of low coordination, possibly through the formation of intermediates with direct metal-carbon bonds.

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