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Active Sites of V_2O_5/γ-Al_2O_3 Catalysts in the Oxidative Dehydrogenation of Ethane

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The oxidative dehydrogenation (ODH) of ethane to ethylene was studied on V_2O_5/γ-Al_2O_3 catalysts (1–20 wt% V_2O_5). The reducibility of the catalysts by hydrogen, ethane, and ethylene and their reoxidation by oxygen were determined by thermogravimetry linked to differential scanning calorimetry and by a pulse catalytic test linked to a microcalorimeter. Ammonia and sulphur dioxide microcalorimetry adsorptions were carried out on all catalysts to characterize their acid–base properties. In ethane ODH reaction at the steady state at 823 K, 60% ethylene selectivity was obtained at 28% ethane conversion. The improved catalytic properties for such reaction on vanadia/γ-alumina catalysts compared to vanadia/silica and bulk vanadium pentoxide catalysts appear to be related in the first place to the dispersion and coordination degree of the vanadium cations of the active sites, and in the second to the development of their acidic properties. The active sites are suggested to be oxidized vanadate dimers composed of tetrahedrally coordinated and oxygen-bridged vanadium cations operating according to a redox mechanism involving very probably transient radicals generated via one-electron transfer. Such dimers undergo a relatively high rate of reduction by ethane. The population of vanadate dimers was estimated in the case of the sample with 20 wt% V_2O_5 loading. The number and strength of active sites are described. More than silica, γ-alumina induces the dispersion of such active sites for ethane ODH.

INTRODUCTION

There is nowadays a major incentive for the selective oxidation of light hydrocarbons into more valuable compounds. Ethane is usually thermally cracked into ethylene at 1073 K in the presence of steam (0.5 volume ratio steam to ethane), at short residence time (1 s or less). This steam cracking is performed at 80% yield (40% per pass) and is an energetically costly process.

Vanadium oxide is an important component of catalysts that are used for selective oxidations of hydrocarbons, for example, the oxidations of orthoxylene to phtalic anhydride on V_2O_5/TiO_2, of *n*-butane to maleic anhydride on $(VO)_2P_2O_7$, and of acrolein to acrylic acid on V_2O_5-MoO_3. This metal cation exhibits both redox and Lewis type acidic properties which are involved in the general mechanism of selective oxidation (1, 2). Hydrogen abstraction from the hydrocarbon may be performed by an oxygen ion attached to a vanadium cation (e.g., vanadyl V=O bond). The resulting alkyl carbanion may be adsorbed on the vanadium cation which acts as a Lewis acid center. According to this approach, active sites for selective oxidation should exhibit a dual redox and acid–base function (1, 2).

Bulk vanadium pentoxide and V_2O_5/SiO_2 catalysts have been studied for the oxidative dehydrogenation (ODH) of ethane (3–6). A low activity and medium ethylene selectivity were observed on bulk vanadium pentoxide, a weakly acidic metal oxide. Spreading vanadium cations on silica results in the creation of a moderate acidity, attributable to isolated vanadate VO_4^{3-} units. Improvements of ethane conversion and ethylene selectivity have been related to the generation of these vanadate species which are absent on bulk vanadium pentoxide.

γ-alumina is known to allow the dispersion of vanadium cations as vanadium oxide monolayer, i.e., as interconnected tetrahedral vanadate VO_4^{3-} units (7, 8) sharing corners (7), forming a two-dimensional layer, or sharing one oxygen atom (8), thus, building isolated dimeric pyrovanadate-type $V_2O_7^{4-}$ species.

In the present work, the reactivity of V_2O_5/γ-Al_2O_3 catalysts and the role of their acid–base properties in ethane ODH reaction have been investigated. For this aim a series of V_2O_5/γ-Al_2O_3 catalysts, which vanadium content varies in the 1 to 20 wt% V_2O_5 range, has been studied in this reaction. The catalytic performances of these samples have been compared with those of V_2O_5/SiO_2 and bulk vanadium pentoxide catalysts. The reducibility of the V_2O_5/γ-Al_2O_3 catalysts has been studied by thermoprogrammed reduction using thermogravimetry linked to differential scanning calorimetry (TG-DSC equipment), and with a pulse catalytic test linked to a microcalorimeter. Adsorptions of acidic and basic probe molecules have been performed

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before and after catalytic run using the microcalorimetry method. The experimental results have been gathered to try to gain more insight into the mechanism and the nature of the active sites for the ethane ODH reaction over vanadia/γ-alumina catalysts.

EXPERIMENTAL

The preparations and physicochemical characterizations of the $V_2O_5/\gamma\text{-}Al_2O_3$, V_2O_5/SiO_2, and bulk vanadium pentoxide catalysts, the adsorption microcalorimetry equipment have been described in previous papers (5, 6, 9).

Activity Measurements

The activity of the $V_2O_5/\gamma\text{-}Al_2O_3$, catalysts in ethane ODH reaction has been investigated in the 573–823 K temperature range using the pulse and steady-state methods.

Pulse-Mode Experiments

A quartz microreactor placed in a microcalorimeter and used in the pulse mode allowed us to study the ability of the catalysts to use lattice oxygen for reacting with ethane. The microreactor was flushed by a continuous flow of helium ($15\ cm^3 \cdot min^{-1}$, purity 99.99%). The outlet of the microreactor was connected to a gas chromatograph equipment (a Porapak Q column and a thermal conductivity detector). A pulse ($0.3\ cm^3$, 13.5 μmol) of pure ethane was admitted every 15 min on the catalyst (50 mg) placed in the microcalorimeter cell. For every pulse of pure ethane, the degree of reduction of the catalyst (expressed in oxygen atoms converted per vanadium atom) and the enthalpy of reaction (expressed in kilojoule per mole of oxygen converted) were determined from the chromatography analyses of the products and thermograms. The following reactions with O^{2-} representing the lattice oxygen ions of the catalyst and the electrons used for the reduction of the V cations

$$C_2H_6 + O^{2-} \rightarrow C_2H_4 + H_2O + 2e^- \qquad [1]$$

$$C_2H_6 + 5O^{2-} \rightarrow 2CO + 3H_2O + 10e^- \qquad [2]$$

$$C_2H_6 + 7O^{2-} \rightarrow 2CO_2 + 3H_2O + 14e^- \qquad [3]$$

and the chromatography analyses of the products have been considered to calculate for each pulse p of pure ethane, the number of oxygen ions consumed in the reduction of the catalyst, $n_p(O)$, and the reduction degree of the catalyst, r_p,

$$n_p(O) = n_p(C_2H_4) + 5/2\, n_p(CO) + 7/2\, n_p(CO_2) \qquad [4]$$

$$r_p = (n_p(O)/n^o(V)), \qquad [5]$$

where $n^o(V)$ is the amount of vanadium atoms of the catalyst. The reduction degree of the catalyst after N pulses, R_N was determined according to Eq. [6]:

$$R_N = \sum r_p \qquad [6]$$

Steady State Experiments

Activity measurements at the steady state in ethane ODH reaction were performed in the 0–100% conversion range using a quartz plug-flow microreactor (70 mm in length, 3.1 mm inner diameter). Variation of the conversion was obtained by changing the flow rate, ($20\text{–}60\ cm^3 \cdot min^{-1}$), and weight of catalyst (250–750 mg). Contact time was in the $0.2\text{–}1.5\ g \cdot s^{-1} \cdot cm^{-3}$ range. Oxygen : ethane molar excess was 3 : 1. Helium (99.5% purity) was used as dilutent in the gas mixture. The catalyst was mixed with quartz chips (3 weight-equivalents) to avoid hot spots in the microreactor.

A fixed-bed continuous flow microreactor was used for kinetic measurements (at 5% ethane conversion) and for ethane conversion at low contact time (less than $0.2\ g \cdot s^{-1} \cdot cm^{-3}$). Gas flow rates were regulated using Brooks mass flow controllers. The temperature of the microreactor was monitored and regulated by an automatic program. A hot box at 373 K was placed directly at the outlet of the microreactor to prevent condensation. Two injection valves ($0.3\ cm^3$) were placed in the hot box for chromatography analyses. Hydrocarbon products were separated on the Porapak Q column (N_2, 373 K, 4 m) and analyzed by flame ionization detector. Oxygen, carbon monoxide, and carbon dioxide were separated on a Carbosieve G column (H_2, 333 K, 3 m), and analyzed by a thermal conductivity detector.

Thermoprogrammed Measurements

The reducibility of the $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts was studied by thermoprogrammed measurements using a microbalance linked to a differential scanning microcalorimeter (TG-DSC apparatus). The catalyst power (20 mg), placed in the sample holder of a symetrical microbalance, was set in a vertical microcalorimeter cell. Ethane, ethylene, and hydrogen were used as reducing agents. Helium (99.99% purity, $25\ cm^3 \cdot min^{-1}$) was used as carrier gas. The catalyst was flushed by the diluted gas reducer (10 vol%) and subjected to a temperature programmed treatment between 298 K and 773 K for the reductions by ethane and ethylene, between 298 K and 873 K for the reduction by hydrogen. The heating rate was $5\ K \cdot min^{-1}$. At 773 K carbonaceous deposition was checked to be negligible in the reductions of the $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst by ethane and ethylene. Mass changes, corresponding heat flows, and programmed temperature were recorded by microcomputer. After the reduction the catalyst was cooled to room temperature under helium before being reoxidized under an oxygen–helium flow at $5\ K \cdot min^{-1}$.

RESULTS

Catalytic Activity Using the Pulse Mode

Catalytic performances in ethane ODH at 823 K of the 5.2 wt% $V_2O_5/\gamma\text{-}Al_2O_3$ (2.20 μmol $V_2O_5 \cdot m^{-2}$) and of bulk

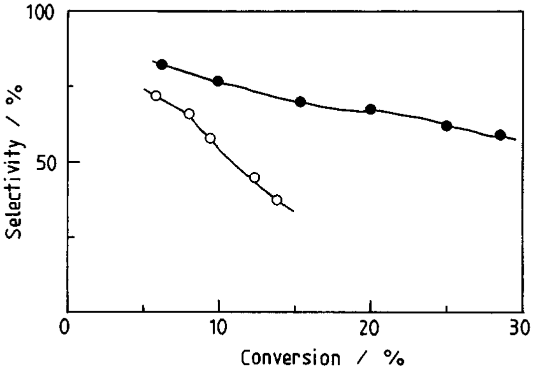


FIG. 1. Ethylene selectivity as a function of ethane conversion at 823 K in pulse mode conditions on: (●) 5.2 wt% V_2O_5/γ-Al_2O_3; (○) unsupported vanadium pentoxide. One pulse of ethane (0.3 cm^3, 13.5 μmol) every 15 min; m(cat) = 50 mg.

vanadium pentoxide, using the pulse mode, are compared in Fig. 1. Ethane conversion decreased as pulses of ethane were admitted on the catalysts every 15 min. The better catalytic properties in this reaction of the $V_2O_5/\gamma Al_2O_3$ catalyst are demonstrated by a couple of facts: first, at isoconversion, a higher selectivity is obtained on the V_2O_5/γ-Al_2O_3 catalyst than on bulk vanadium pentoxide and, second, the selectivity to ethylene decreases less rapidly with increasing ethane conversion of the V_2O_5/γ-Al_2O_3 catalyst than on bulk vanadium pentoxide. Under the same conditions the 10.7 wt% V_2O_5/SiO_2 catalyst gave 82% ethylene selectivity at 3% ethane conversion. The dispersion of vanadium cations on γ-alumina affords higher turnovers. On each catalyst additional products were carbon oxides. No oxygenated products were detected. Homogeneous ODH reaction was checked to be negligible below 873 K.

Catalytic Activity at the Steady State

The performances of the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst at the steady state are depicted in Fig. 2. Ethylene selectivity decreases with increasing ethane conversion because ethylene is further oxidized to carbon monoxide and carbon dioxide. No oxygenated products were detected. At 823 K, 60% ethylene selectivty was observed at 28% ethane conversion. Ethylene selectivity raised to 75% at 10% ethane conversion or less. Deactivation did not occur. Ethylene yield of 15–20% can be reached if the ethane ODH is performed at 823 K at low conversion (<30%). At isoconversion of ethane, increasing the temperature from 773 K to 823 K resulted in a gain of 5 to10 points in ethylene selectivity. At the end of every catalytic run the color of the catalyst had turned from yellow to pale green.

The influence of the vanadium content of the V_2O_5/γ-Al_2O_3 catalysts on the rates of ethane conversion and ethylene formation at 753 K is shown in Fig. 3. The diagram clearly shows that ethane ODH reaction is sensitive to the structure of the vanadium oxide phase. The rates of ethane conversion (dashed lines) and ethylene formation (full lines) are constant at very low vanadium oxide content (<2.0 wt% V_2O_5, 0.8 μmol $V_2O_5 \cdot m^{-2}$). At such a low vanadium loading, only vanadate monomers are present (10)–(12). Their catalytic activity is low and comparable or hidden by that of vanadium-free γ-alumina. On the blank carrier initial ethylene selectivity was 66%. It raised to 76% on the 1.0 wt% V_2O_5/γ-Al_2O_3 catalyst.

Between the 2.9 and 9.8 wt% V_2O_5 contents, the rates of ethane conversion and ethylene formation, expressed per square meter, rise linearly, due to the interconnection of these tetrahedral vanadate units building a

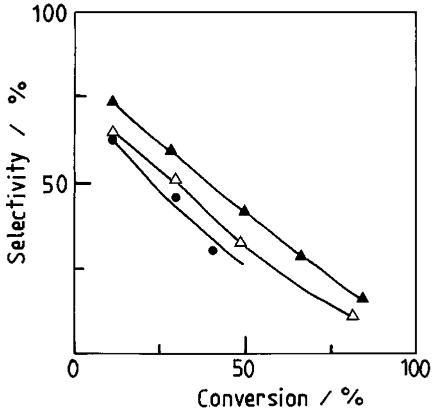


FIG. 2. Ethylene selectivity as a function of ethane conversion in steady state flow rate conditions on the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst at 703 K (●); at 773 K (△); at 823 K (▲). p(ethane) = 9 kPa, p(oxygen) = 27 kPa.

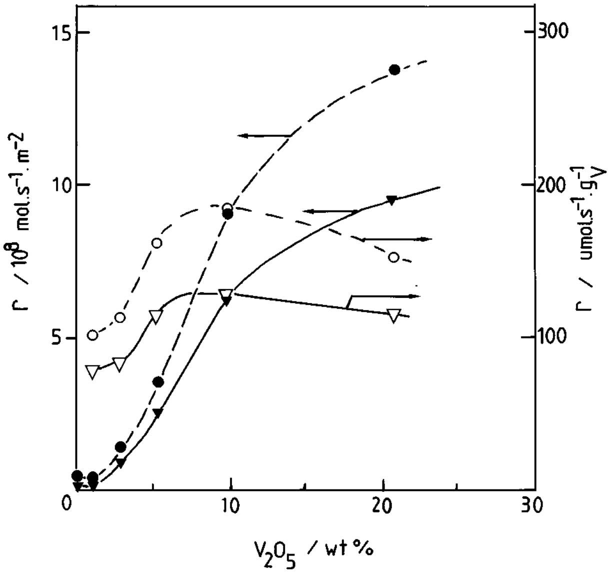


FIG. 3. Rates of ethane conversion (dashed lines) and ethylene formation (full lines) at 753 K as a function of the vanadia content of the V_2O_5/γ-Al_2O_3 catalysts. m(cat) = 35 mg-Ft = 65 cm^3 min^{-1}-p(ethane) = 11.3 kPa-p(oxygen) = 2.0 kPa. Steady state flow rate conditions.

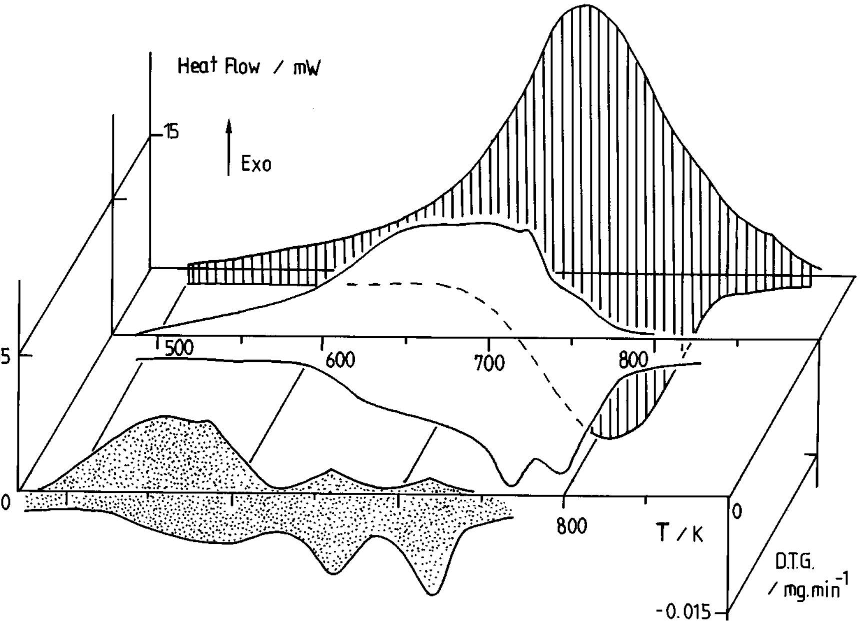


FIG. 4. Enthalpy of reduction of the 20.9 wt% V_2O_5/γ-Al_2O_3 catalysts and associated derivative of the thermogravimetric curve as a function of the temperature for various reducing agents: (vertical lined) hydrogen; (medium plane) ethane; (frontal plane) ethylene. Heating rate of 5 K $\cdot$ min^{-1} -F(helium) = 25 cm^3 $\cdot$ min^{-1}, F(reducer) = 5 cm^3 $\cdot$ min^{-1}, m(cat) = 20 mg.

bidimensional array (7) or dimeric species (8). These rates, expressed per gram of vanadium, reach a plateau for the 5.2–9.8 wt% vanadia range, and then slightly decrease, above the 9.8 wt% V_2O_5 loading, as a result of the condensation of vanadium as vanadium pentoxide (9, 13, 14), which is less reactive in ethane ODH (5). Figure 3 shows that the variations of ethane conversion and ethylene formation are similar so that there are no drastic changes in ethylene initial selectivity. It remains in the 70–75% range. At 10% ethane conversion and 753 K, it decreased from 72% (over the 2.9 wt% V_2O_5/γ-Al_2O_3 catalyst) to 67% (over the 20.8 wt% V_2O_5/γ-Al_2O_3 sample).

In summary it can be concluded that on V_2O_5/γ-Al_2O_3 catalysts, a vanadate layer is mainly responsible for ethane conversion and ethylene selectivity, whereas monomeric vanadate compounds and bulk vanadium pentoxide play minor roles in this reaction. This is a new example of the catalytic activity attributable to vanadium oxide layers (2).

Reducibility of Vanadium Cations on V_2O_5/γ-Al_2O_3 Catalysts

TG-DSC Measurements

Temperature-programmed reduction and reoxidation is a suitable technique to get information on the reducibility of oxide phases, which can be related to their behavior in oxidation reactions. It has been proven to be correct with respect to quantitative analyses (13, 14).

The thermograms and the associated derivatives of the thermogravimetric curves (DTG) of the temperature-programmed reductions of the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst by hydrogen, ethane, and ethylene are displayed in Fig. 4. Weight variations, enthalpies, and temperatures of the maxima $T_{\max}$ of the reductions and reoxidations are reported in Table 1. The constant loss of water that occurred on the catalyst between 473 K and 873 K has been substracted from the observed mass variations.

It is observed that each calorimetric signal is associated with a thermogravimetric peak. The temperatures $T_{\max}$ of each thermoprogrammed reduction are 50 K lower on the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst than on bulk vanadium pentoxide (5). It is known that the $T_{\max}$ temperature can determine the ease of oxygen removal from the catalyst and consequently that the oxidation activity can be inversely related to the $T_{\max}$ temperature (15). Referring to the $T_{\max}$ temperatures, ethylene is only somewhat better than ethane as a reducing agent. In each reduction, the loss in oxygen atoms on the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst is always less important than that observed in the reduction of bulk vanadium pentoxide, which is reduced to vanadium trioxide by hydrogen, ethane, and ethylene (corresponding to one oxygen atom converted per vanadium cation) (5). Our 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst is composed of vanadate species and of particles of vanadium pentoxide (9). It is suggested that the vanadate species are less easily reduced by hydrogen than the crystallites of vanadium pentoxide and that ethane and ethylene reduce the vanadate species less deeply than hydrogen does. Depending on the reducer, enthalpies of reduction, expressed per mole of vanadium, are 2 to 12 times more important on the V_2O_5/γ-Al_2O_3 catalyst

TABLE 1

TG-DSC Data of the Reduction by Hydrogen (up to 873 K), Ethane and Ethylene (up to 773 K) and of Reoxidation by Oxygen (up to 773 K) of the 20.9 wt% V_2O_5/γ-Al_2O_3 Catalyst

20.9 wt% V_2O_5/γ-Al_2O_3	Reduction Δm (at. O / at. V)	Reduction ΔH ($kJ \cdot mol^{-1}$ V)	Reduction T_m (K)	Reoxidation Δm (at. O / at. V)	Reoxidation ΔH ($kJ \cdot mol^{-1}$ V)	Reoxidation T_m (K)
H_2	−0.64	−765	739	+0.45	−370	635
C_2H_6			717			614
	−0.45	−300		+0.35	−252	634
			739			640
C_2H_4	−0.30	−150	665	+0.25	−385	594
			724			637

than on bulk vanadium pentoxide (5). This phenomenon may be due to the presence of specific reactive vanadate species on the V_2O_5/γ-Al_2O_3 catalyst.

Each reoxidation of the reduced 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst starts at 460 K with a slow weight gain associated to an endothermal signal (see Fig. 5). This endothermal peak is followed by an exothermogram ($T_{max} = 637$ K). Each reoxidation is completed at 673 K, i.e. 100 K lower than the corresponding former reduction. It is thus suggested that at the steady state of ethane ODH, the V_2O_5/γ-Al_2O_3 catalyst works in an oxidized state. Note that a similar T_{max} of the exothermogram in reoxidation, at 370 K, is observed on the 20.9 wt% V_2O_5/γ-Al_2O_3 and bulk vanadium pentoxide catalysts (5). For each reoxidation of the reduced 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst the weight gain balances only at 70–80% the weight loss of the corresponding reduction. Such an irreversibility in weight loss was not observed on bulk vanadium pentoxide (5). Enthalpies of reoxidation of the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst are similar, whatever the reducing agent was.

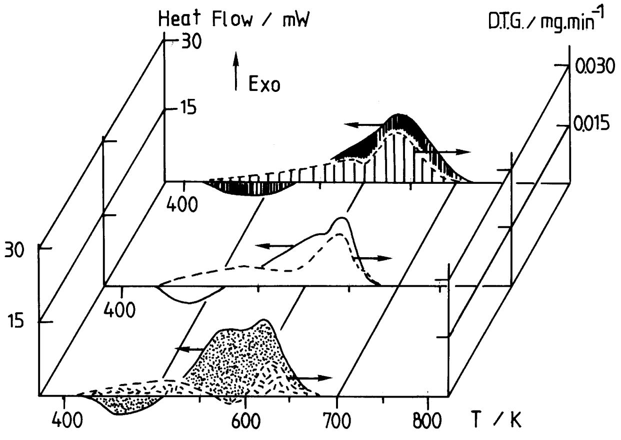


FIG. 5. Enthalpy of reoxidation of the 20.8 wt% V_2O_5/γ-Al_2O_3 catalysts and associated derivative of the thermogravimetric curve as a function of temperature. Previous reduction in: (vertical lined) hydrogen; (medium plane) ethane; (frontal plane) ethylene-F(helium) 25 $cm^3 \cdot min^{-1}$-F(oxygen) = 25 $cm^3 \cdot min^{-1}$ -Heating rate of 5 $K \cdot min^{-1}$.

In summary the TG-DSG measurements show that the improved catalytic activity of the V_2O_5/γ-Al_2O_3 catalyst in ethane ODH can be related to its enhanced reducibility, probably afforded by the structure of the vanadate phase of the V_2O_5/γ-Al_2O_3 catalyst.

Pulse Measurements

The reducibility of the V_2O_5/γ-Al_2O_3 catalyst was also investigated with a pulse catalytic test linked to a microcalorimeter. Figure 6 displays the conversion of ethane, the ethylene selectivity, and the enthalpy of reaction (per mole of oxygen consumed) against the number of pulses on the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst at 823 K. The ethane conversion slightly decreases for the five first pulses of ethane and more rapidly for the following pulses.

The conversion drop from 28% to 6% is associated with the increase from 59% up to 82% in ethylene selectivity. Additional products were carbon monoxide and carbon dioxide.The enthalpy of reaction varies strongly with the number of pulses. The enthalpy is constant and exothermic in the first couple of pulses. It collapses at the third pulse and reaches a plateau at the fourth pulse. An endothermal signal emerges at the fourth pulse and is constant in intensity in the following pulses. Thus the thermograms contain a couple of successive signals, a first exothermal peak and a second endothermal, which cannot be separated (see Fig. 6). The global measured enthalpy does not appear correlated to the enthalpies of reactions [1], [2], and [3] (see Experimental) and to the variations of product selectivities. More likely it is related to phenomena happening at the active sites of the catalyst by contacting pulses of ethane at 823 K.

The reduction degree at 823 K of the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst and of bulk vanadium pentoxide are compared versus the number of pulses in Fig. 7. After 25 pulses of ethane, 3.8 and 0.06 oxygen atoms have been converted per vanadium atom respectively on the 5.2 wt%

V_2O_5/γ-Al_2O_3 and V_2O_5 catalysts, confirming the relative higher reduction rate of the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst. The reduction degree of 3.8 oxygen atoms per vanadium atom on the vanadia–alumina catalyst is higher than the theoretical reduction degree corresponding to the reduction of V^{5+} cations to V^{4+} cations (0.5 oxygen atom per vanadium atom) and to V^{3+} cations (1.0 oxygen atom per vanadium atom) as a result of the intrinsic activity of γ-alumina. After 25 pulses of ethane, 4% of lattice oxygen atoms from γ-alumina have been consumed.

We also note that under the same conditions, after 20 ethane pulses, only 0.20 oxygen atoms were consumed per vanadium atom on the 10.7 wt% V_2O_5/SiO_2 catalyst (0.034 oxygen atom per vanadium atom per pulse, 174 kJ · mol^{-1} O converted, per pulse). The reduction degree of the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst rises lineary during the five first pulses, then it increases following a logarithmic function. This deviation is also observed on bulk vanadium pentoxide although its reduction degree is very low (<0.03 oxygen atom per vanadium atom). This feature must be related to the drops in the ethane conversion and enthalpy of reaction, and also to the threshold of an endothermal signal in Fig. 6. These variations suggest that after a few pulses, a change in the rate limiting step of the ODH reaction is taking place: in the first pulses, the rate limiting step of the ODH reaction would be the reduction of the surface active sites by ethane, after a few pulses, it would be the regeneration of the active surface sites by lattice oxygen atoms.

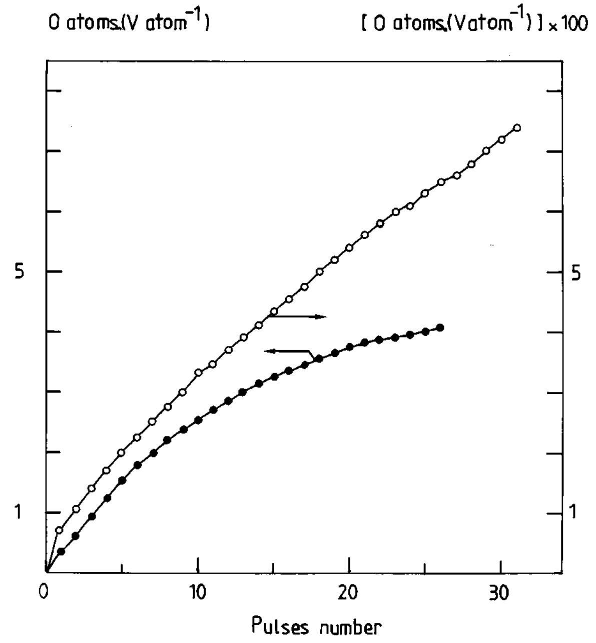


FIG. 7. Reduction degree (oxygen atoms consumed per vanadium atom) at 823 K as a function of the number of pulses of ethane on: (●) 5.2 wt% V_2O_5/γ-Al_2O_3; (○) unsupported vanadium pentoxide. m(cat) = 50 mg – 1 pulse of ethane (0.3 cm^3, 13.5 μmol) every 15 min.

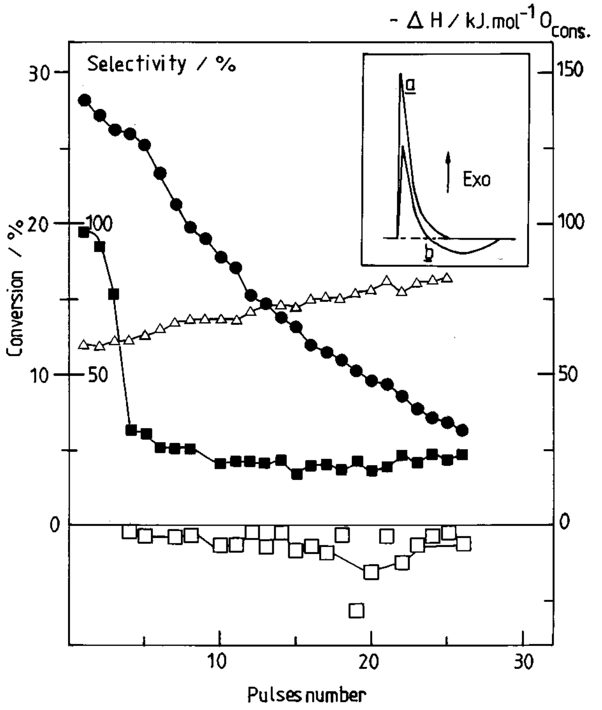


FIG. 6. Ethane conversion at 823 K (●); ethylene selectivity (△); and enthalpy of reaction: (■), exothermal signal; (□), endothermal signal, as a function of the number of pulses of ethane on the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst. m(cat) = 50 mg^{-1} – 1 pulse of ethane every 15 min. Inside: Thermogram of ethane pulses on the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst at 823 K: (a) third pulse (single exothermal signal); (b) tenth pulse (exothermal + endothermal contributions).

In summary, the pulse data show the higher reduction rate by ethane of vanadia-alumina catalysts compared with those of vanadia-silica and unsupported vanadium pentoxide, and the ability of γ-alumina to supply oxygen atoms to the active sites.

The Relationship between the Acid–Base and Catalytic Properties of V_2O_5/γ-Al_2O_3 Catalysts

Catalytic activity in selective oxidation of hydrocarbons has been related to the cooperative action of an oxidizing and of an acidic function (1, 2, 16).

The acid–base properties of the V_2O_5/γ-Al_2O_3 catalysts have been studied on the 833 K-calcined samples (9) but also after catalytic run by microcalorimetry adsorptions of ammonia and sulphur dioxide at 353 K. Before the microcalorimetry measurements, the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst has been subjected overnight to an ethane/oxygen/helium gas mixture at 683 K in a continuous flow microreactor, applying a low conversion of ethane (<5%). The used catalyst was cooled and outgassed at 623 K for 2 h before the adsorption measurements. Figure 8 displays the acidic (right-hand side) and basic (left-hand side) features of the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst before and after the catalytic run. The acid–base features of γ-alumina

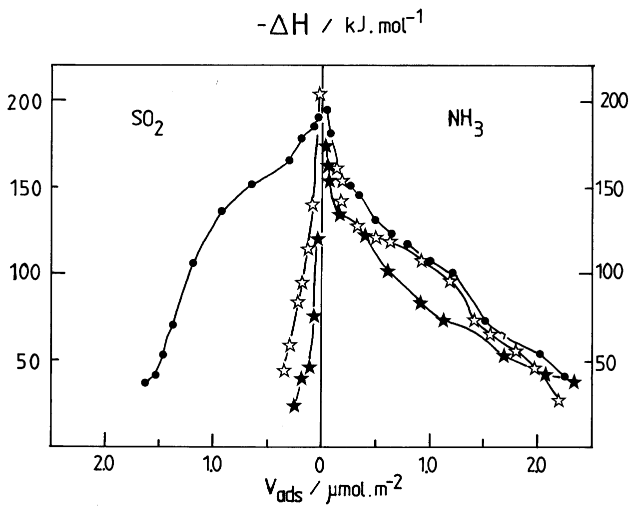


FIG. 8. Differential enthalpy of ammonia adsorption (right-hand side) and of sulphur dioxide adsorption (left-hand side) at 353 K on the 5.2 wt% $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst: (★), fresh catalyst; (☆), after catalytic run at 683 K; and (●) on the blank carrier.

are also reported for reference. It is observed that some acid sites (0.1 μmol · m^{-2}, 70–180 kJ · mol^{-1}) have emerged after the catalytic run. This amount corresponds to 5% of the overall acidic sites of this catalyst. It is interesting to note the same increase in basic sites (0.1 μmol · m^{-2}, 50–200 kJ · mol^{-1}). These features are consistent with the restoration of some acid–base pairs of γ-alumina and show the overall stability of the acid–base character of the vanadium oxide layer.

Figure 3 shows that a vanadate oxide layer is mainly responsible for the ethane conversion and the ethylene selectivity on the $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts. Such a vanadate layer grows in the 2–10 wt% V_2O_5 range. In a previous paper (9) we showed the threshold and growth of acidic sites in this 2–10 wt% vanadia range.

Most acid sites of the vanadia-alumina catalysts with vanadia coverage higher than 3 wt% were attributable to the vanadate layer. The variations of the rates of ethane conversion, ethylene formation and of the amount of acidic sites, against the vanadia loading are similar (9). However, the density of acid sites decreases by a factor 2 from the 5.2 wt% to the 9.8 wt% vanadia coverage (9), whereas the rates of ethane conversion and ethylene formation, expressed per gram of vanadium, are constant (see Fig. 2). Thus, although the vanadate phase includes a population of acidic sites that would be most reactive in ethane ODH, this reaction does not take place exclusively on Lewis acid vanadium centers. Consequently, the mechanism of ethane ODH involving transfers of unshared electron pairs (ethyl carbanions) to Lewis acid vanadium centers cannot account for the experimental results of Fig. 3. A redox mechanism, i.e., one-electron transfer in generating radicals, is more likely to occur.

DISCUSSION

Catalytic Properties of the $V_2O_5/\gamma\text{-}Al_2O_3$ Catalysts

$V_2O_5/\gamma\text{-}Al_2O_3$ catalysts can convert significantly ethane into ethylene between 673 K and 823 K. At the steady state at 823 K, they afford an ethylene selectivity of 60% at 28% ethane conversion. Initial ethylene selectivity is in the 70–76% range. Little deactivation is observed. The pale green color of the catalyst at the end of the reaction may suggest that it is reduced to some extent. ESR analysis of a used sample (5.2 wt% $V_2O_5/\gamma\text{-}Al_2O_3$) revealed the threshold of an ill-resolved hyperfine structure attributable to some V^{4+} cations. These V^{4+} cations are probably incorporated in the matrix since they were not detected by XPS spectroscopy.

No acetaldehyde, acetic acid, or other oxygenated products were detected between 673 K and 823 K. In a previous paper (17) we showed the formation of adsorbed acetate species on $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst resulting from the coadsorption of an ethylene–oxygen continuous cofeed at 398 K. The coadsorption of an ethane-oxygen continuous cofeed resulted in the formation of formate and carbonate adsorbed species at 573 K. The acetates, formates and carbonates were the precursors of carbon oxides, due to their strong adsorption.

Activation energies for ethane conversion and ethylene formation on $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts are reported in Table 2. Depending on the vanadium content, they are 40 to 80 kJ · mol^{-1} lower than those calculated for vanadia/silica samples (6).

The catalytic properties of the $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts are comparable to those of chromium phosphates (18), tin oxide (19), boron-aluminium oxide (20), Mg-VAPO-5 (21), and nickel-vanadium-tin-aluminium oxides (22). Some catalysts are reported to produce a substantial ethylene yield at lower temperatures for example, $(VO)_2P_2O_7$ (60–80% ethylene selectivity at 50–70% ethane conversion at 673 K) (23), and Mo-V-Nb-O (100% ethylene selectivity at 10% ethane conversion at 573 K) (24). On the above-mentioned catalysts, as well as on $V_2O_5/\gamma\text{-}Al_2O_3$, ethylene

TABLE 2

Summary of the Activation Energies for Ethane Conversion and Ethylene Formation over Vanadia/Alumina Catalysts

$V_2O_5/\gamma\text{-}Al_2O_3$ catalysts V_2O_5/wt%	Ea (C_2H_6) kJ · mol^{-1}	Ea (C_2H_4) kJ · mol^{-1}
0	88 ± 7	95 ± 5
1.0	113 ± 15	108 ± 15
2.9	101 ± 7	97 ± 4
5.2	96 ± 13	102 ± 3
9.8	69 ± 5	68 ± 10
20.8	119 ± 8	101 ± 10

selectivity is a function of ethane conversion. At high conversion of ethane, ethylene, due to its reducing properties, is partially converted to carbon oxides and selectivity into C_2 diminishes. Ethane ODH occurs over a number of catalysts at higher temperature, i.e., between 873 K and 973 K (25, 26). For examples the Li-Mg-Cl catalyst (25) gives 58% yield of ethylene (75% ethane conversion and 77% ethylene selectivity) at 893 K, and mixed lithium–titanium oxide is reported to produce 90–95% ethylene selectivity at 25% ethane conversion at 973 K (25).

The selective formation of ethylene by contacting pulses of ethane on the V_2O_5/γ-Al_2O_3 catalyst strongly suggests that ethane ODH may proceed via the Mars–van Krevelen mechanism (27). At low and isoconversion of ethane (6%) at 823 K, ethylene selectivity is some points higher on the reduced catalyst (82%; see Fig. 1) than on the oxidized catalyst (75%; see Fig. 2). At high ethane conversion (28%) at 823 K, the same ethylene selectivity (60%) is obtained whether the pulse or the steady-state method is used, demonstrating that gaseous oxygen is well directed to the active sites.

γ-alumina makes possible the dispersion of active sites for ethane ODH. This inductive effect is much less developed with silica as support. In addition to the role of the support, V_2O_5/SiO_2 and V_2O_5 catalysts, present isolated tetrahedral monomers and octahedrally coordinated vanadium cations. These local environments for vanadium atoms, result in relatively low reaction rates in ethane ODH on these catalysts: at 753 K, in similar experimental conditions, the rates of the ethane conversion and ethylene formation measured on V_2O_5/SiO_2 catalysts (expressed per vanadium atom) only represent 2% of those measured on V_2O_5/γ-Al_2O_3 catalysts (6).

TG-DSC Measurements

The supported vanadate species and the particles of vanadium pentoxide of the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst can be distinguished from their behavior in thermoreductions by ethane and ethylene and a more detailed structure of the vanadate phase can be proposed.

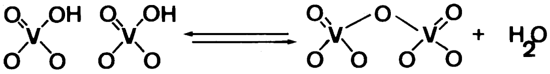
During these thermoprogrammed reductions (see Fig. 4), three exothermal peaks were detected. The first and broad exothermal peak occurred at 573 K in the reduction by ethane, at 523 K in the reduction by ethylene, and it was not detected in the case of the reduction of bulk vanadium pentoxide (5). The sharp second and third DTG peaks of the reductions by ethane and ethylene in Fig. 4 were not detected on V_2O_5/γ-Al_2O_3 catalysts with vanadia content less than 5.2 wt% V_2O_5, and appeared for the 9.8 wt% V_2O_5/γ-Al_2O_3 catalyst which contains V_2O_5 particles. It is therefore suggested that these two DTG peaks correspond to the reduction of particles of vanadium pentoxide, while the first and broad TG-DSC peak is attributable to the sole reduction of surface vanadate species. Following this approach, on V_2O_5/γ-Al_2O_3 catalysts, the vanadate species are reduced by ethane and ethylene at temperatures lower than that for the particles of vanadium pentoxide. Such particles of vanadium pentoxide are reduced at a lower temperature than bulk vanadium pentoxide (5), presumably because of their smaller crystal size (13, 28).

The relative estimation of the surface vanadate species and of the particles of vanadium pentoxide present on the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst can be drawn from the temperature-programmed reduction of this catalyst by hydrogen (see Fig. 4 and Table 1). On this catalyst, one can write the balance in removed lattice oxygen atoms by hydrogen as

$$1 \cdot N_{\mathrm{Vp}} + M \cdot N_{\mathrm{Vd}} = 0.64 \tag{7}$$

$$N_{\mathrm{Vp}} + N_{\mathrm{Vd}} = 1. \tag{8}$$

N_{Vd} and N_{Vp} are the atomic fractions of vanadium cations (atom%) of the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst that are respectively part of vanadate species and of particles of vanadium pentoxide. At the end of the reduction by hydrogen at 873 K, one can make the tentative assumption that the particles of vanadium pentoxide are completely reduced to particles of vanadium trioxide, i.e., one oxygen atom is converted per vanadium atom (5, 13) while vanadate species are less completely reduced. If M oxygen atoms are converted per vanadium atom of the vanadate species ($M < 1$), the vanadate compounds of the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst can be described as follows (2, 8) by dehydroxylation into dimers:


[9]

The reduction of the vanadate species by hydrogen can be formulated according to Eq. [10]


[10]

where one oxygen atom would be consumed per two vanadium atoms corresponding to the reduction of V^{5+} in V^{4+}. Thus the value $M = 0.5$ would be valid for Eq. [7], in accordance with other workers (8, 14, 29). Consequently the resolution of Eqs. [7] and [8] lead to the solution of $N_{\mathrm{Vd}} = 0.72$ as the fraction of vanadium atoms incorporated as vanadate species in the 20.9 wt% V_2O_5/γ-Al_2O_3 catalyst.

Active sites for alkane oxydehydrogenation on vanadium oxide-containing catalysts are generally regarded as tetrahedral vanadate species. The intrinsic activity of these units is largely dependent on the structure of their nearest surrounding (30). Our TG-DSG data support the concept of vanadate dimers units as most surface active sites in the ethane ODH on V_2O_5/γ-Al_2O_3 catalysts. Vanadate dimers units have been proposed as active sites of V_2O_5/γ-Al_2O_3

and other vanadium-containing catalysts in the selective oxidation of higher hydrocarbons (31, 32).

Number and Strength of Active Sites of V_2O_5/γ-Al_2O_3 Catalysts in Ethane ODH

Figure 9, which is obtained from Figs. 6 and 7, displays the enthalpy of ethane ODH (using the pulse mode) and the conversion at 823 K of ethane on the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst (2.20 μmol $V_2O_5 \cdot m^{-2}$) versus the amount of consumed oxygen atoms (expressed per vanadium atom). This diagram is instructive on the number and strength of active sites of the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst in this reaction.

The enthalpy of reduction is initially 95 ± 2 kJ per mol of consumed oxygen atoms. Based on the amount of oxygen atoms consumed per vanadium atom (0.65), this plateau may correspond to the reduction of V^{5+} cations to V^{4+} cations. The enthalpy of reduction drops afterwards to 77 kJ per mol of consumed oxygen atoms. This second plateau may represent the reduction of V^{4+} cations to V^{3+} cations. At this stage the whole population of vanadium cations V^{5+} has been reduced to V^{3+} species (1.0 oxygen atom converted per vanadium atom). Reoxidation of the active sites is now the limiting step. The enthalpy of migration of oxygen atoms is assumed to be measured. Oxygen conversion takes place on reduced vanadium cations and on the vanadia-free carrier and decreases as less and less mobile lattice oxygen atoms are available. The threshold of an endothermal signal when the reduction degree of the catalyst reaches 1.0 oxygen atom per vanadium atom was confirmed by repeating these pulse experiments at 723 K and 773 K.

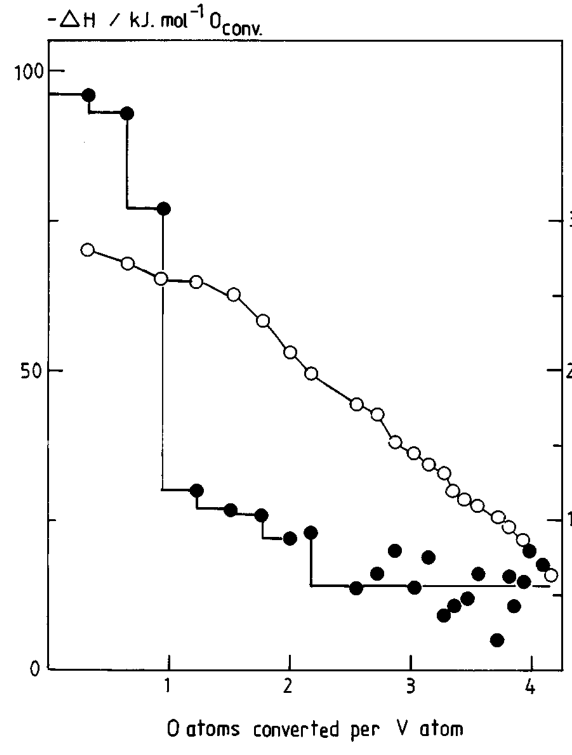


FIG. 9. Enthalpy of reaction, (●) and conversion of ethane, (○) at 823 K as a function of the amount of consumed oxygen atoms on the 5.2 wt% V_2O_5/γ-Al_2O_3 catalyst. One pulse of ethane (0.3 cm^3, 13.5 μmol) every 15 min m(cat) = 50 mg.

In summary, the experimental data of Fig. 9 shows the different populations of active sites of the vanadia/alumina catalyst. The activity per active site depends on its reduction degree. The enthalpies of reaction show that the strength of vanadium-oxygen bonds of active sites is heterogeneous.

CONCLUSION

V_2O_5/γ-Al_2O_3 catalysts are active and selective for the dehydrogenation of ethane into ethylene in the presence of oxygen. At the steady state, 60% ethylene selectivity was obtained at 28% ethane conversion at 823 K. The improved catalytic properties in ethane ODH of vanadia/γ-alumina catalysts referred to vanadia/silica and bulk vanadium pentoxide appear to be related first to the dispersion and coordination of the vanadium cations of the active sites, more than to the development of their acidic properties. The active sites can be regarded as vanadate dimers and its population and strength can be estimated. More than silica, γ-alumina induces the dispersion and activation of such sites. The active sites of the V_2O_5/γ-Al_2O_3 catalysts are thus described as dimers of two tetrahedrally coordinated and oxygen-bridged vanadium cations which are reduced by ethane more easily than those of vanadia silica which are tetrahedral vanadate monomers and than those of bulk vanadium pentoxide which are octahedrally coordinated vanadium cations.

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