

Calorimetric Study of Vanadium Pentoxide Catalysts Used in the Reaction of Ethane Oxidative Dehydrogenation

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Vanadium pentoxide catalysts have been studied in the partial oxidation reaction of ethane in the 723–843 K temperature range. The relationship between the acid–base properties and the catalytic behavior was investigated. The number and character of acidic sites of V_2O_5 catalysts were determined by studying the adsorption of a basic molecule using microcalorimetry. The reducibility level and the evolution of the surface state, as well as the heat evolved, were studied by using a pulse method with pure ethane only. The reaction of ethane oxidative dehydrogenation was studied by a continuous flow method and the activation energies for the formation of C_2H_4 and CO were calculated. The selectivity of the catalyst was interpreted in connection with the acid–base properties. The strong sites were observed to decrease rapidly with time on stream, although the catalysts were still active. Temperature-programmed reduction of V_2O_5 using a TG–DSC coupling was also investigated with hydrogen, ethylene, or ethane as reducers. The different heats of reduction are given. It was observed that C_2H_4 is a much more efficient reducing agent than H_2 and C_2H_6 . Following each reduction, reoxidation studies by oxygen were performed in the same equipment showing clearly different steps in the reoxidation process.

Metal oxides having high bonding energies of surface oxygen were shown to oxidize alkanes selectively by the action of surface oxygens of the oxides^{1,2} but their activity was low. Vanadium oxide was observed to be rather a selective catalyst in such reaction.³ However, very few studies have been devoted to the transformation of ethane into more valuable compounds.⁴ Using N_2O or O_2 as oxidant, Erdöhelyi and Solymosi⁵ recently showed that vanadium oxide supported on silica is an effective catalyst for the oxidative dehydrogenation of ethane to ethylene and to a low extent to acetaldehyde. However, most of the studies reported in the literature deal with N_2O as oxidant⁶ which is not a particularly attractive reactant for industrial purposes.

Two schools of thought regarding the mechanism of these catalysts exist. One postulate is that oxidation–reduction processes are responsible for the catalytic activity. This has led to extensive studies by a number of workers with techniques such as oxygen chemisorption, laser Raman spectroscopy, ESR and TPR studies.^{7–11} In contrast, the second school has firmly established that catalytic activity and selectivity in mild oxidations can be interpreted in terms of acid–base interaction between the catalyst and the reactant.¹² Indeed vanadium pentoxide contains V^{5+} ions with a d^0 electron configuration which are strong Lewis acids.

Further progress in the field, for example determining which school is correct, requires development of the theory and experimental investigations of mechanism and factors which determine activity and selectivity. It was earlier shown¹³ that for oxidation catalysis not only redox but also acid–base interactions of reagents (or products) with catalysts are essential. Typical redox steps are the reduction of the surface oxides $M^{m+}O^{2-}$ with the reactant and the reoxidation in their reduced form by O_2 . Acid–base interactions are broadly defined to include the formation of complexes with the Lewis or Bronsted active sites. The acidic properties of metal oxides have been determined systematically by Tanabe et al.¹⁴ by titration using Hammett's indicators. However, in the case of catalysts used for oxidations consisting mostly of transition metal oxides, the titration method cannot be used because of their colors. Specifically, in this study the following questions were addressed: do the measures of acidity obtained from adsorption microcalorimetry of a basic probe molecule such as NH_3 correlate to the catalytic activity and selectivity in the case of oxidative dehydrogenation reactions? A second question is, does the higher

valence state of vanadium take direct part in the dehydrogenation of ethane? In order to answer the above questions, the degree of reduction of vanadium oxide catalyst was measured directly in the course of the reaction by a pulse method, and the influence of this factor on the activity of the catalyst and on the course of catalytic conversion of ethane in absence of additive oxygen was analyzed. The results had to be compared to those obtained by a continuous flow method using ethane and molecular oxygen as reactants.

Another purpose of the present study was to try to measure the energy of the adsorbed or desorbed species during the reaction of ethane oxidative dehydrogenation generated by ethane pulses on bulk V_2O_5 .

Experimental Section

Materials. Vanadium pentoxide was prepared by stirring overnight about 10 g of vanadyl oxalate in methanol in order to achieve complete dissolution. Hydrolysis of the complex was carried out by addition of 3 mL of water. The solvent was then evacuated under hypercritical conditions of temperature and pressure for 1 h. The sample was then subjected to standard treatment, consisting of heating at 833 K in a current of air overnight. The catalyst was red-orange and the specific surface, measured by the BET method with nitrogen, was 12.8 m^2/g .

The gases used in this study were helium, oxygen, hydrogen, and ethane, from Alphagaz, whose purity was over 99.9%. Ammonia, from Alphagaz (purity > 99.9%) was purified and out-

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gassed by freeze-pump-thaw cycles and dried over molecular sieves before any acidity measurement.

Methods. Acidity Measurements. Differential heats of ammonia adsorption were measured using a Setaram heat flow microcalorimeter connected to a vacuum and gas line equipped with a Barocel type pressure gauge to maintain the gas pressure within the range 0–200 Pa as described elsewhere.¹⁵ The catalyst sample (0.1 mg) was pretreated overnight at 673 K under oxygen and then outgassed for 2 h at the same temperature under vacuum of ca. 1.33 mPa. The adsorption was carried out by introducing successive doses of known amounts of the adsorbate onto the samples. The experimental setup was monitored by a micro-computer so that the evolved heat and the residual gas pressure could be recorded continuously following admission of each dose. Identical doses of gas were repeatedly admitted into the calorimeter cell until a final equilibrium pressure of ca. 133 mPa was reached. The calorimeter was maintained at 353 K for the adsorption of ammonia in order to avoid too much physical adsorption. The calibration of the volumetric line and the calibration of the response of the calorimeter by Joule effect were performed in the same conditions of temperature and gaseous atmosphere as the acidity measurements.

Catalytic Runs. The investigations concerning the catalytic properties of vanadium pentoxide were conducted in a fixed bed continuous flow microreactor. The reacting gas mixture controlled using Brooks mass flow controllers, consisted of 8% ethane, 1% oxygen, and helium as diluent. A total flow rate of 50 mL min⁻¹ under 10⁵ Pa and 0.1 g of catalyst was used. The products were analyzed with an Intersmat gas chromatograph. Hydrocarbons such as C₂H₆, C₂H₄, CH₄ were separated on a Porapak Q column (4 m, 373 K) and analyzed by a flame ionization detector. Oxygen and carbon oxides were eluted on a Carbosieve G column (3 m, 333 K) and analyzed by a thermal conductivity detector. During each catalytic run the reactor temperature was changed by using an automatic program. The change of temperature was performed in a random manner in a range of about 50 K to control the absence of deactivation phenomena.

In order to study the degree of reduction of vanadium oxide together with the heat evolved when the catalyst is contacted by successive doses of pure ethane, a pulse chromatographic assembly was connected to a heat flow microcalorimeter.

The quartz reactor was set in the microcalorimeter which allowed a study of the energy related to the interaction of successive doses of ethane with the catalyst surface. The reactor was connected through a six-way valve, to the chromatograph equipped with a Porapak Q column (4 m, 323 K) and a thermal conductivity detector, which permitted the determination of unreacted ethane and secondary products. A description of the instrument combining both techniques, its operation and calibration have been presented elsewhere.¹⁶

Helium (purity > 99.99%) was used as carrier gas at a flow rate of 15 mL·min⁻¹ and was flowed through the reactor for 1/2 h to remove excess and physically adsorbed oxygen prior to the first pulse. Regular injections of pure ethane were performed every hour with a calibrated pulse volume of 0.3 mL. The reduction of the catalyst (≈90 mg) was studied at a constant temperature of 823 K.

Temperature-Programmed Reduction and Oxidation Experiments. A TG-DSC 111 from Setaram allows simultaneous monitoring of both heat and mass changes.¹⁷ The symmetrical microbalance is arranged in a sealed enclosure connected to the calorimeter in vertical position. The sample holders attached to the microbalance are placed in the microcalorimeter. The calorimetric measurements are performed with fluxmeters surrounding the tubes containing the sample holder but without physical contact. During the reduction the gas flows in the two tubes were balanced out to minimize disturbances. Calorimetric calibration was carried out over the whole temperature range by

DIFFERENTIAL HEAT OF ADSORPTION (kJ·mol⁻¹)

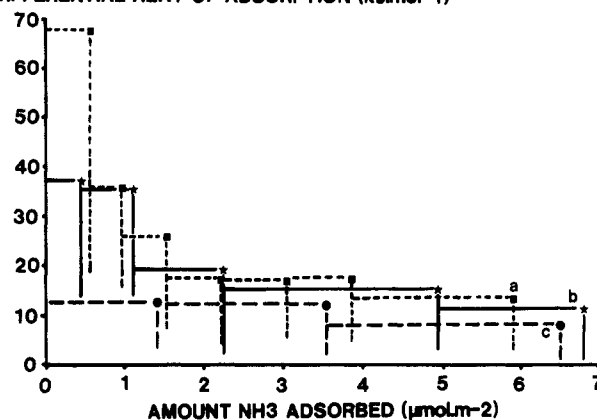


Figure 1. Differential heat of adsorption of ammonia adsorbed at 353 K on different samples of V₂O₅: (a) (□) fresh catalyst, (b) (*) after reaction with ethane-oxygen mixture at 823 K, and (c) ● after ethane pulses at 823 K.

use of the Joule effect. The sample weights were in the range 10–20 mg. The reductive gas was successively pure hydrogen, ethane, and ethylene; the catalyst was reoxidized by pure oxygen prior to another reduction.

Results and Discussion

The acidity of pure vanadium pentoxide, as determined by the amount of basic molecules irreversibly adsorbed, is given concomitantly with the heats evolved when ammonia doses contacted the catalyst. Figure 1a which represents the differential heats of adsorption of NH₃ (kJ·mol⁻¹) as a function of the ammonia coverage (expressed in μmol·m⁻²) clearly shows there are very few acid sites (<10⁻⁶ mol·m⁻²) able to strongly chemisorb ammonia with heats greater than 50 kJ·mol⁻¹. The total number of surface sites neutralized by ammonia represents approximately 0.6% only of the total number of vanadium atoms of the catalyst. Moreover, the strongest ones which irreversibly absorb ammonia represent 10% of the number of surface sites which adsorb ammonia molecules.

Figure 1b shows the differential heats of adsorption of ammonia on the same catalyst after it was subjected to the gas flow reaction of ethane conversion at a constant temperature of 823 K. The catalyst was held under reaction conditions for 8 h in the mixture of ethane, oxygen, and helium as described in the Experimental Section. The catalyst was still red-orange and was not submitted to any reoxidation treatment before acidity measurements. As shown by the figure, most of the strong acid sites have disappeared. Only the medium acid strength sites (40 kJ·mol⁻¹) are still present but are also still effective since the catalyst was still active after 8 h on stream.

Figure 1c shows the differential heats of adsorption of ammonia after fresh V₂O₅ was subjected to a reduction in a gas mixture of ethane and helium as diluent, in the absence of oxygen, at increasing temperature up to 873 K. The catalyst was black corresponding to V₂O₃ and about 7 wt % of coke (as determined by chemical analysis). In that case, we observed only reversible adsorption and very weak acid sites which confirms the basic tendency of V₂O₃.¹⁸

The same lack of acidity was observed on another sample catalyst after being submitted to 600 pulses of pure ethane which correspond to the reduction state of V₆O₁₃. In that case, most of the strong and medium strength surface sites have also disappeared and the surface area of the sample has decreased from 12.8 to 5.1 m²·g⁻¹. However, carbonaceous residues, determined by chemical analysis, represent less than 0.2 wt % of the catalyst.

Figure 2 represents the integral heats of adsorption of ammonia (in J·g⁻¹) on the same previous three catalysts (see Figure 1), as a function of the coverage, at the equilibrium pressure of 66.6

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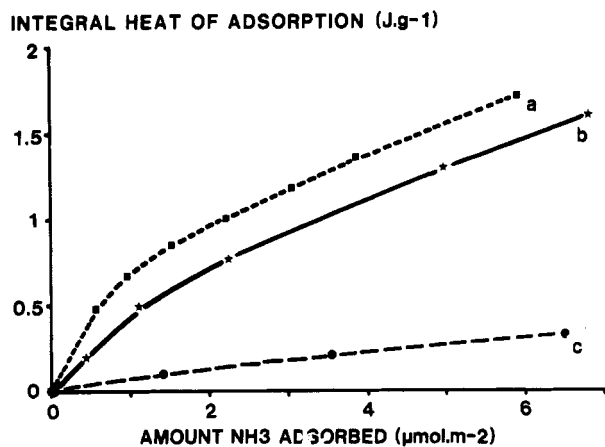


Figure 2. Integral heat of adsorption for ammonia adsorbed at 353 K on different samples of V_2O_5 : (a) fresh catalyst, (b) after reaction with ethane-oxygen mixture at 823 K, and (c) after ethane pulses at 823 K.

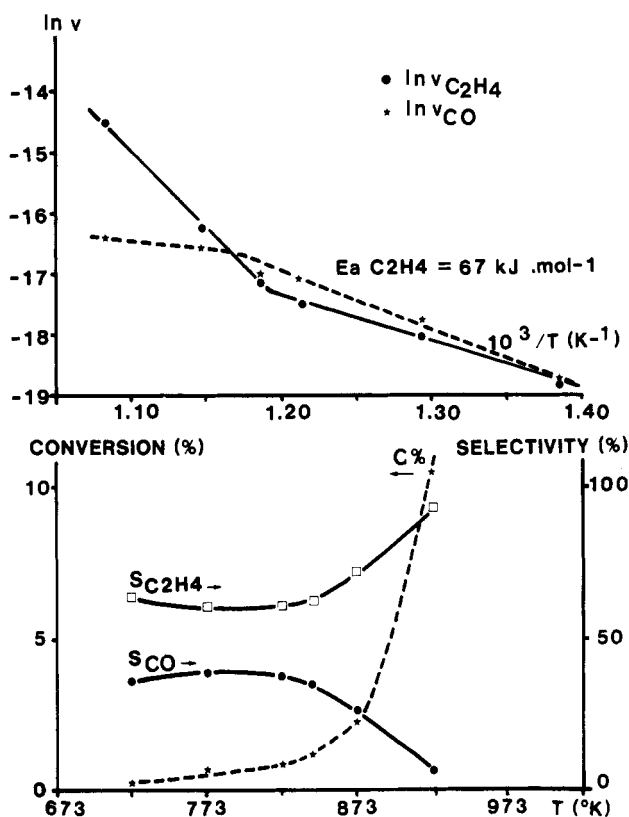


Figure 3. Ethane conversion and product distribution as a function of temperature: 100 mg of V_2O_5 , $F_v = 50$ mL/min, $P(C_2H_6) = 61$ Torr, $P(O_2) = 8$ Torr.

Pa. This figure clearly shows that it is primarily the strong acid sites that are first covered during the reaction, as curves a and b stay parallel at high coverage. Curve c is characteristic of the absence of acid sites.

Vanadium pentoxide subjected to the catalytic conditions of a mixture of ethane, oxygen, and helium as diluent (as described in the Experimental Section) gave rise mainly to ethylene, carbon monoxide, and water as products. The conversion of ethane and the product distribution as a function of temperature are depicted in Figure 3. The selectivities for both products C_2H_4 and CO appear to be nearly independent of the temperature till about 873 K but become strongly dependent above. The rate of C_2H_6 conversion, recorded for a random sequence of temperature over a period of 18 h, indicates that the catalyst was stable with respect to time on stream over the temperature range of 723–823 K.

Above 823 K, conversion increases exponentially with temperature and selectivity for ethylene increases at the expense of that for carbon monoxide. Around 873 K, homogeneous reaction

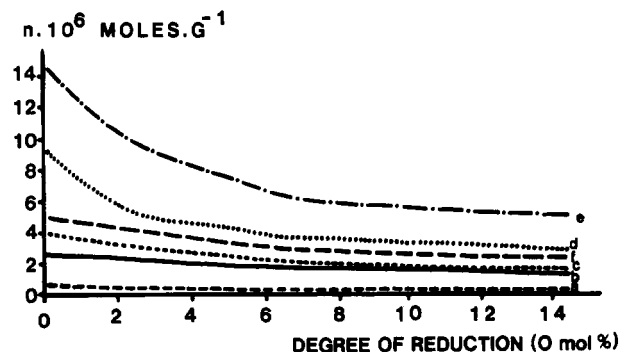


Figure 4. Amounts of products (micromol/g) formed in ethane pulse on V_2O_5 at 823 K: (a) CO_2 , (b) C_2H_4 , (c) CO, (d) H_2O , (e) lattice oxygen consumed, and (f) C_2H_6 consumed, as a function of the degree of reduction.

in the gas phase becomes more and more prominent and it can be assumed that around 923 K catalyst sintering begins to occur, resulting in its irreversible deactivation which is apparently caused by profound changes in its structure, and also by the proximity of the melting point of vanadium pentoxide (958 K). An Arrhenius plot of the rate of ethylene and carbon monoxide formation is also given in Figure 3. Below 873 K, we observe nearly the same value of apparent activation energy, 67 ± 6 kJ·mol $^{-1}$ for the formation of ethylene or carbon monoxide. Under our experimental conditions, oxygen of the gas phase is not completely consumed and does not limit the conversion of ethane; i.e., there is sufficient oxygen to maintain the vanadium oxide in its maximum valence state.

By the coupling method of volumetry and calorimetry as used for ammonia adsorption, we studied the adsorption of oxygen on the oxidized catalyst surface at 353 K and under an equilibrium pressure of 133 Pa. No adsorption was observed even after 24 h. In contrast, on the partially reduced catalyst surface by hydrogen at 673 K, oxygen was adsorbed irreversibly until complete oxidation of the catalyst occurred, but the rate of oxygen adsorption is extremely low at the end of the oxidation. This leads to the suggestion that the reaction takes place by a redox mechanism with the participation of the oxygen of the catalyst. The reduction step is more rapid than the stage involving the reoxidation of the catalyst as will be shown further.

Since adsorption of oxygen does not take place on an oxidized surface, it may be suggested that the catalytic reaction begins to take place with the participation of the oxygen of the catalyst, the loss of which is subsequently made good by adsorption from the gaseous phase. That is, lattice oxygen is a primary source of oxygen used in the reaction and this is against a Langmuir-Hinshelwood type mechanism in the whole range of oxygen pressure. It is inferred that the small amount of adsorbed oxygen prevents this oxide from lowering the reaction selectivity.¹⁹ But it is difficult to establish accurately the proportion of the surface operating actively, since the adsorption of oxygen from the gaseous phase cannot give information on the degree of coverage.

The ability of lattice oxygen to take part in the reaction was supported by experiments using ethane only, by a pulse method. The degree of reduction of the catalyst in the course of catalytic conversion of ethane was determined in the calorimetric cell linked to a chromatograph as described in the Experimental Section. Complete analysis of the reaction products made it possible to calculate the degree of reduction of the catalyst following each pulse, together with the heat evolved.

As shown in Figure 4, when pulses of pure ethane are sent regularly on the catalyst maintained at 823 K, the main products were CO_2 (a), C_2H_4 (b), CO (c), and H_2O (d). From the number of CO, CO_2 , and H_2O molecules that have been produced after each pulse of ethane sent on the catalyst, one can calculate the total amount of oxygen atoms evolved from the sample (curve e)

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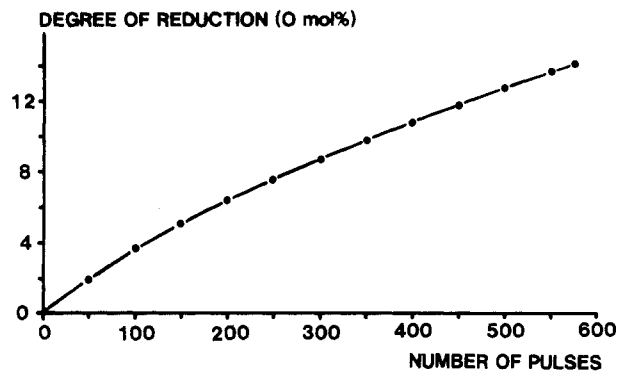


Figure 5. Degree of reduction of V_2O_5 at 823 K as a function of the number of ethane pulses.

and subsequently the degree of reduction of the catalyst.

Figure 4 also shows the dependence of the extent of ethane conversion and of the selectivity for carbon monoxide and ethylene on the number of pulses at 823 K. It can be seen from the figure that during the first pulses the ethane conversion is very high but it falls during the subsequent pulses, with a decrease of selectivity for carbon monoxide. The amount of product is higher in the first pulses due to the presence on the surface of vanadium ions in the highest valence state. Consumption of surface oxygen is accompanied by the formation of oxygen vacancies in the bulk which leads to the reduction of bulk vanadium cations. Then the amounts of products decrease but it can be seen from Figure 4 that the selectivity for ethylene slowly increases at the expense of carbon monoxide. The number of moles of ethane retained and converted by the catalyst is plotted in curve f.

The degree of reduction of the catalyst surface was tentatively calculated from the amounts of oxygen-containing products, based on the area occupied by an adsorbed oxygen molecule.²⁰ Monolayer coverage of 1 m^2 of the surface corresponds to 0.238 mL of molecular oxygen. So the degree of surface reduction of V_2O_5 corresponding to the first pulse is 5% of a monolayer. Subsequent pulses of ethane do not lead to drastic changes of the degree of reduction of the surface.

As lattice oxygen is a continuous source of surface oxygen, the degree of reduction plotted in Figure 4 is referred to the total amount of oxygen contained by the catalyst. As shown in Figure 5, after 575 pulses of pure ethane we reached only 14% of reduction of the catalyst and starting from about 4% the slope of the curve changes and the conversion of ethane tends to a limit which can correspond to the statement of an equilibrium in the oxygen migration and electronic transfer between the surface and the bulk of V_2O_5 . At the end of the experiment the catalyst corresponded to the formal reduction of V_2O_5 to V_6O_{13} .

The heat of the reaction taking place was determined by relating the calorific power measured in the calorimeter for each pulse to the quantity of converted ethane. Figure 6 represents the heat evolved in kilojoules per mole of consumed ethane for each pulse versus the number of pulses. For the first pulses, together with a higher amount of product evolved, we only observed a rapid exothermic peak (curve a) corresponding to a high rate of reaction on V_2O_5 . After the third ethane pulse, the exothermic thermogram decreased but it was immediately followed by an endothermic signal (curve b), corresponding to the reoxidation of the catalyst surface by oxygen diffusion from the lattice and to the desorption of the products. These two successive signals were found to interfere each other and the net endothermicity calculated from the thermobalance sheet takes into account both the catalytic reaction, which is overall exothermic, and the desorption of the products, which is endothermic. We tend to a process of equalization of the concentration of oxygen vacancies between the surface and the volume of the solid and the thermal balance sheet (curve C) becomes constant. Analysis of the data in Figure

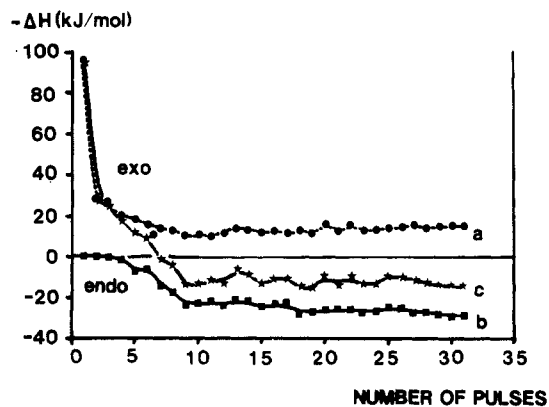


Figure 6. Heat of reduction of V_2O_5 at 823 K as a function of the number of ethane pulses: (a) exothermic signal, (b) endothermic signal, and (c) overall thermal balance sheet.

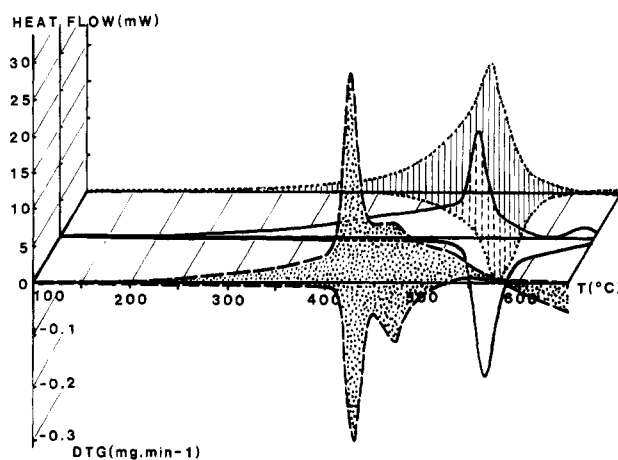


Figure 7. Heats of reduction of V_2O_5 and associated derivatives of the thermogravimetric curves as a function of the temperature, for various reducing agents: (vertical lined) hydrogen, (medium plane) ethane, (dotted) ethylene.

6 also shows that at the beginning of the reaction the weakly bound surface oxygen is rapidly removed. Then in the next pulses ethane and the firmly bound oxygen take part in the reaction.

Thermoprogrammed reductions of the catalyst may provide kinetic data of theoretical significance as well as an insight into the mechanism of the reduction processes. In order to compare the reducibility power of hydrogen, ethane, and ethylene, we have performed the reduction of fresh vanadium pentoxide by each of them (diluted in helium) in a TG-DSC (see Experimental Section). We have recorded simultaneously the heat flow signal, the loss or gain of weight, and the derivative of the weight (DTG) while temperature was increased from room temperature up to 893 K at a rate of 5 K/min.

Figure 7 shows the heats of reduction which are exothermic and the derivative of the thermogravimetric curves which are negative if associated with a weight loss occurring during the reduction. The DTG signal is more indicative than the TG signal of whether the heat evolved is associated or not to a weight variation. In the three cases, the catalyst was black at the end of the experiment. According to the weight loss, a similar reduction extent occurred whether hydrogen, ethane, or ethylene was used as reducing agent, which corresponds to the formation of V_2O_3 . In the case of reduction by C_2H_6 or C_2H_4 , an endothermic peak begins around 873 K corresponding to ethane cracking and resulting in some coke deposition. At 893 K the amount of coke, as determined by chemical analysis, were respectively 7 and 9 wt %.

After each reduction the catalyst was reoxidized in a flow of oxygen and helium at the same heating rate. Figure 8 displays the corresponding heat curves of reoxidation (exothermic) together with the DTG signals which are positive, corresponding to a weight

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TABLE I

reducing agent	reduction			reoxidation		
	heat evolved ΔH , kJ/g	mass variation Δm , %	peak maxima T , K	heat evolved ΔH , kJ/g	mass variation Δm , %	peak maxima T , K
H ₂	-1.2	-16.6	783	-5.9	16.6	513 548 643
C ₂ H ₆	-0.27	-16.2	794	-1.7	16.7	671
C ₂ H ₄	-0.56	-16.2	693 733	-2.1	16.0	598 628

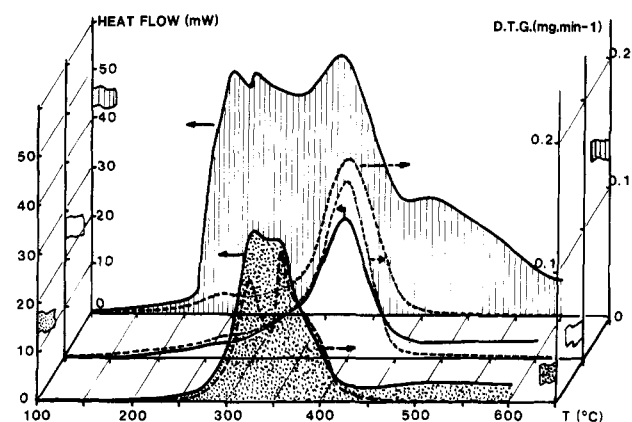


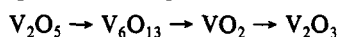
Figure 8. Heats of reoxidation of prereduced V₂O₅ samples and associated derivatives of the thermogravimetric curves as a function of the temperature: (vertical lined) V₂O₅ prereduced by H₂, (medium plane) V₂O₅ prereduced by C₂H₆, (dotted) V₂O₅ prereduced by ethylene.

gain. The catalyst was orange at the end of each oxidation. All the curves are given for an initial mass of 11.64 mg of catalyst. The results are summarized in Table I which reports the heats of reduction and reoxidation, the associated mass variations, and the temperatures of the maxima of the peaks.

These results lead to the conclusion that C₂H₄ is a better reducing agent than H₂ and C₂H₆, referred to the maxima peak temperatures, but the heats evolved are in the order

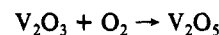
$$\Delta H(\text{H}_2) > \Delta H(\text{C}_2\text{H}_4) > \Delta H(\text{C}_2\text{H}_6)$$

It is known that the reduction of V₂O₅ by a stream of helium and hydrogen takes place according to the scheme



but only one exothermic effect is observed in the 773–823 K range. The thermodynamic characteristics of the reoxidation processes

of the samples completely differ from those of reduction. And in the case of reoxidation after hydrogen reduction three peaks can be seen corresponding probably to the three suboxides cited above. The calculated values of ΔH for the process



equals 884 kJ·mol⁻¹ O₂ and the reduction process corresponds to 220 kJ·mol⁻¹ O₂. The mass balance sheets in each case of the reduction–oxidation cycles with hydrogen, ethane, and ethylene are very good.

The results of this work lead to the conclusion that diffusion of oxygen from the bulk is predominant in the case of selective oxidation of ethane and that the redox process plays a more important role than the acidic sites in the case of unsupported vanadium pentoxide. Strong acid sites of V₂O₅ have not been detected at the steady state of the reaction of ethane oxidative dehydrogenation. That fact has to be related to the lability of lattice oxygen which can fill the initial superficial electronic vacancies. Pulse methods linked to microcalorimetry have well shown the different stages of the reaction mechanism in the absence of oxygen. A trend to a lower conversion and a better ethylene selectivity of bulk oxygen, i.e., of reduced catalyst, has been confirmed. However, ethylene yield was found to decrease with the degree of reduction of V₂O₅. Vanadium in its higher valence state is necessary to maintain a high ethylene yield. This can be realized by gaseous oxygen which recovers lattice oxygen vacancies. TG-DSC measurements have shown that the reducibility levels of V₂O₅ by ethane or hydrogen are similar, whereas ethylene is much more active than ethane over that oxide. Enhancement of the ethylene selectivity is expected if ethylene molecules can desorb rapidly from the surface and if a complete reoxidation state of the surface can occur. This last point might be obtained by an optimum regeneration of the surface acidic properties as, in most redox processes, acidity favors reoxidation.

Registry No. V₂O₅, 1314-62-1; C₂H₆, 74-84-0; H₂, 1333-74-0; C₂H₄, 74-85-1.