

## AlNbO Oxides as New Supports for Hydrocarbon Oxidation

### II. Catalytic Properties of VO<sub>x</sub>-Grafted AlNbO Oxides

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Received January 3, 1992; revised April 16, 1992

Vanadium oxides were immobilized by grafting VOCl<sub>3</sub> on AlNbO oxides calcined between 500 and 750°C. Chemical analysis, XPS, and STEM measurements suggest an incomplete but homogeneous stoichiometric reaction between superficial hydroxyl groups and vanadyl oxychloride. By FTIR studies, it is observed that the interaction involves preferentially basic hydroxyl groups bonded to aluminium cations. UV-visible spectra show that mainly V<sup>5+</sup> is present at the solid surface. Corresponding spectra are compatible with tetrahedral symmetry, in agreement with a previous <sup>51</sup>V NMR investigation. The acido-basic properties of the catalyst were tested by isopropanol decomposition and compared with the corresponding supports. It has been observed that basicity is higher for VO<sub>x</sub> grafted on AlNbO oxide calcined at high temperature and corresponding to the AlNbO<sub>4</sub> structure. VO<sub>x</sub> grafted on AlNbO oxides calcined at intermediate temperatures and corresponding to a AlNbO disorganized structure present a good selectivity for the oxidative dehydrogenation of propane into propene. It has been observed that, for both reactions, the turnover number increases with the temperature of calcination of the catalysts. The reactivity of the superficial VO<sub>x</sub> species is discussed in relation to the structure and chemical composition of the aluminium niobate support. © 1992 Academic Press, Inc.

#### INTRODUCTION

Grafting methods have been extensively used to prepare well-dispersed vanadia layers on alumina or titania (1–9). Although there is not a general agreement on the resultant structure, the principle of a chemical reaction between superficial hydroxyl groups and vanadium complexes to form a M–O–V bond (M = Ti, Al) is well accepted. This interaction is highly dependent on the acido-basic properties which are different from one oxide to another (10). Combined Raman spectroscopy and <sup>51</sup>V NMR experiments have allowed the determination of the molecular structures of the surface vanadia species on alumina and titania (11–14). Some discrepancies exist between the authors due to limitations of both techniques, particularly on the oxidation state of vanadium, on its coordination, and on the influ-

ence of hydration (15, 16) and surface impurities (17). All these studies were focused on the possibility of changing the structure of the dispersed vanadia as a function of the nature of the support.

In a previous paper (18), we have described the preparation and the characterization of AlNbO oxides and the conditions of synthesis of pure AlNbO<sub>4</sub>. The absence of redox properties for these solids and the possibility of preparing them with a high surface area without microporosity led us to consider these oxides potential supports for hydrocarbon oxidation. Our interest was based on the structural similarity between aluminium niobate and TiO<sub>2</sub> (B) (19). Both structural and acido-basic properties of the support are commonly considered to determine the characteristics of the active site of the underlying catalyst (20). Specifically, we have observed on AlNbO oxides several

types of superficial hydroxyl groups, bonded to Al and Nb, with varying acidobasic properties (18).

The preparation of vanadia monolayers immobilized by grafting  $\text{VOCl}_3$  onto the different  $\text{AlNbO}$  oxides, according to the temperature of calcination and a  $^{27}\text{Al}$  and  $^{51}\text{V}$  solid state NMR study, have been reported elsewhere (21). This work deals with a physico-chemical study of the  $\text{VO}_x/\text{AlNbO}$  catalysts. Isopropanol decomposition and propane oxidative dehydrogenation were used to investigate the catalytic properties of these solids. A correlation between the catalytic properties of these oxides and the nature of the superficial vanadium sites is attempted. The influence of the chemical nature and of the crystallographic structure of the underlying support upon the structural properties of vanadia monolayers is discussed.

#### EXPERIMENTAL

$\text{AlNbO}$  oxides were prepared from aluminium nitrate and oxalatonioabate complex as described in a first issue (18). Aluminium nitrate and oxalatonioabate complex were dissolved in an oxalic medium and the pH was adjusted to a value of 3.0 with ammonia. The solution was evaporated and the resultant hygroscopic mass was calcined under air flow. Four oxides were thus obtained by calcination at 500°C (A), 600°C (B), 650°C (C), and 750°C (D), respectively. Solids A, B, and C were poorly crystallized and corresponded to a mixture of amorphous alumina and niobium oxide, while solid D corresponded to the structure of the aluminium niobate  $\text{AlNbO}_4$ . Vanadyl oxychloride was grafted on these oxides using the exchange capability of the surface hydroxyl groups of the four materials. The procedure has been described elsewhere (21). Let us recall that the  $\text{AlNbO}$  supports were contacted with a tetrahydrofuran (THF) solution of  $\text{VOCl}_3$  after outgassing at 200°C *in vacuo* ( $<10^{-2}$  Torr). All the operations were conducted under dry argon. After filtration and washing with dry THF, solids were calcined 3 h

under wet air flow ( $p_{\text{H}_2\text{O}} = 23.3$  Torr) at 300°C, then 3 h more at 500°C (21). The catalysts are referred to as A', B', C', and D' for V grafted on A, B, C, and D, respectively.

For chemical analysis, solids were primarily solubilized in a HF/HCl solution. V, Ti, Al, and Nb contents were determined by atomic absorption using a Perkin-Elmer 1100 spectrophotometer. Microanalysis of the elemental composition of the solids was performed using a STEM (scanning transmission electron microscope) HB5 from Vacuum Generator.

For XPS measurements, samples were introduced into a Hewlett-Packard HP 5950 A spectrometer and outgassed at room temperature to a pressure of  $10^{-9}$  Torr. The spectrometer was monitored by a computer and the different spectra were accumulated from 5 min to 2 h, depending on their intensity. The experimental spectra were treated by computer software for smoothing, subtraction of the background, and determination of the peak areas. Binding energy values were referred to  $\text{C}_{1s}$  peak (pollution carbon) at 284.5 eV.

The study of the surface hydroxyl groups was performed using a Fourier transform spectrometer (IFS 110 from Bruker) and signal accumulation in the 4000–1000  $\text{cm}^{-1}$  range. Mass samples ranging from 8 to 30 mg were pressed into a thin wafer. They were pretreated in the IR cell under  $\text{O}_2$  for 3 h at 500°C and then outgassed at 150°C under final pressure of  $10^{-5}$  Torr to eliminate physisorbed water before IR examination at room temperature. Five hundred spectra were accumulated for each sample examination.

UV-visible diffuse reflectance spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer equipped with an integration sphere. Pure corresponding  $\text{AlNbO}$  oxides A, B, C, and D were used as references.

Catalysts were compared for isopropanol transformation in a flow system. The solids (200 mg) were deposited on a fixed bed in a

Pyrex microreactor (U tube, 13 mm diameter) operating under atmospheric pressure. The catalytic zone was isothermal. Reaction temperature was varied from 150 to 200°C. The isopropanol vapor pressure ( $p = 28$  Torr) was controlled by a saturator condenser system with three vessels. Nitrogen was used as a carrier gas. Analysis of reactants and reaction products was performed by on-line chromatography. For the permanent gases, a Delsi/IGC 120 MB gas chromatograph equipped with a flame ionization detector was used. Nitrogen was the carrier gas. Propene and acetone were separated on a 1-m,  $\frac{1}{8}$ -in. Porapak Q column.

Propane oxidative dehydrogenation (ODH) was performed in a flow system. The catalyst ( $m = 100$ – $350$  mg) was deposited on a fixed bed in a quartz microreactor (U tube, 13 mm diameter) operating under atmospheric pressure. The catalytic zone was isothermal (6 mm height,  $0.8$  cm<sup>3</sup> volume) with a postcatalytic zone ( $0.4$  cm<sup>3</sup>). Analysis of the reactants and reaction products was performed by on-line chromatography. For the permanent gases and H<sub>2</sub>O, a Delsi/IGC 120 MB gas chromatograph equipped with a thermal conductivity detector was used. Two columns were operated in parallel, a 3-m,  $\frac{1}{4}$ -in. molecular sieve column to separate O<sub>2</sub> and CO and a 2-m,  $\frac{1}{4}$ -in. Porapak Q to separate CO<sub>2</sub> and H<sub>2</sub>O. Hydrogen was the carrier gas. For the organic products, a Delsi/IGC 120 FB gas chromatograph equipped with a flame ionization detector was used. The carrier gas was nitrogen. Three columns were operated in parallel: a 4-m,  $\frac{1}{8}$ -in. Durapak column to separate light hydrocarbons (methane, ethane, ethene, propane, propene), a 3-m  $\frac{1}{8}$ -in. Carbowax column to separate oxygenates (ethanal, propanal, acetone, acrylaldehyde), and a 2-m  $\frac{1}{8}$ -in. AT column to separate acids (acetic, propionic, and acrylic acids). The last column was situated in a hot box together with the four injection valves which were monitored by a Spectra Physics computer. The reactor was directly connected to the hot box to prevent any condensation of the reac-

TABLE 1  
Chemical Analysis of AlNbO Catalysts

Catalysts	Al (wt%)	Nb (wt%)	Al/Nb (at.%)	V (wt%)
A' <sup>a</sup>	12.8	40.5	1.08	1.20
B'	13.5	43.0	1.08	0.61
C'	13.0	45.0	1.00	0.51
D' <sup>b</sup>	13.6	45.0	1.04	0.41

<sup>a</sup> For support A: Al(12.9 wt%); Nb(41.0 wt%), Al/Nb(1.09 atom%)

<sup>b</sup> For support D: Al(14.4 wt%); Nb(48.7 wt%), Al/Nb(1.02 atom%)

For AlNbO<sub>4</sub>: Al(14.7 wt%); Nb(50.5 wt%), Al/Nb(1.00 atom%)

tion products. Catalytic runs were automatically monitored by the computer. The gas mixture containing propane (2% vol), O<sub>2</sub> (19.6% vol), and N<sub>2</sub> (78.4% vol) was fed at a flow rate of 50 ml/min and the temperature was 500°C.

## RESULTS

### Solids Characterization

Table 1 shows the results of chemical analysis of the catalysts. For Al and Nb, the composition of the V supported catalysts is very similar to that of the corresponding supports, as can be seen on catalysts A' and D'. Though the atomic Al/Nb ratio is very near the expected ratio of 1.00, there is some depletion with the optimal AlNbO<sub>4</sub> composition. The V yield decreases from catalyst A' to catalyst D'.

A strong decrease of the BET area has been observed after grafting, as can be seen in Table 2. However, no modification of the

TABLE 2  
Some Features of V/AlNbO<sub>4</sub> Grafted Catalysts

Supports	BET area (m <sup>2</sup> /g)	OH/nm <sup>2</sup>	Catalysts	BET area (m <sup>2</sup> /g)	V/nm <sup>2</sup>
A	168	2.1	A'	79	1.6
B	115	2.0	B'	73	1.4
C	95	1.5	C'	57	1.1
D	53	0.9	D'	39	1.5

external morphology of the solids grains was detected by STEM. In addition, X-ray diffraction patterns were unaltered. The same decrease of the BET area was observed on the supports calcined under the same conditions and it was postulated that this sintering effect of the materials was due to the wet calcining atmosphere. The  $\text{AlNbO}_4$  structure has been identified on catalyst D', while catalyst A', B', and C' were observed to be poorly crystallized, in agreement with the corresponding support, and appeared as a mixture of amorphous  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  (18). It should be noted here that an amorphous  $\text{AlNbO}_4$  oxide cannot be completely ruled out as a precursor to the crystalline oxide. However, the  $^{27}\text{Al}$  NMR spectra (21) of the amorphous oxides A, B, and C show the presence of five- and four- (tetrahedrally) coordinated Al, which is not compatible with the structure of  $\text{AlNbO}_4$  containing only octahedral aluminium. Moreover, the infrared spectra of the amorphous oxides in the  $3300\text{--}3800\text{ cm}^{-1}$  region (18) are rather well interpreted as the sum of the spectra of hydroxyl groups at the surface of alumina and niobium oxide, showing that the local superficial structure is similar to that of pure oxides. On the other hand, the band at  $3820\text{ cm}^{-1}$  has been attributed to Al bonded hydroxyl groups modified by the niobia structure. This might indicate a strong mixture of small amorphous regions of both oxides. This interpretation is corroborated by the fact that it has been impossible to obtain the  $\text{AlNbO}_4$  oxide by calcining at the same temperature ( $750^\circ\text{C}$ ) a mechanical mixture of the separate precursors  $\text{P}_{\text{Al}}$  and  $\text{P}_{\text{Nb}}$  (18).

An XPS examination of the catalysts showed no modification of the binding energy and the shape of Al  $2p$ , Nb  $3d_{3/2}$  and Nb  $3d_{5/2}$  photoemission peaks in comparison with the corresponding supports (18). As shown in Table 3, the Al/Nb ratio appeared to be higher (1.18–1.30) when measured by XPS as opposed to STEM (0.90–1.00), indicating an agreement with the expected ratio (1.00). The superficial Al enrichment observed for catalysts A' and D' was however

TABLE 3  
Atomic Ratios as Determined by XPS and STEM

Catalysts	XPS			STEM	
	Al/O	Al/V	Al/Nb	Al/V	Al/Nb
A	0.26	—	1.34	—	—
A'	0.23	16.80	1.30	10.0	0.90
D	0.25	—	1.18	—	0.95
D'	0.27	21.40	1.30	31.2	1.00

observed for supports A and D, indicating that it was not connected with V grafting. Figure 1 shows the O1s photoemission peak of catalyst A' compared to support A and of catalyst D' compared to support D. The shoulder observed at 532.1 eV for A, previously attributed to OH surface species (18), has disappeared for A', confirming the interaction of these species with  $\text{VOCl}_3$ . A slight displacement of the peak at 530.4 eV is observed up to 530.7 eV. The shoulder at 532.1 eV is difficult to observe both for D' and for D, which shows that the lower density of hydroxyls on this support (see Table

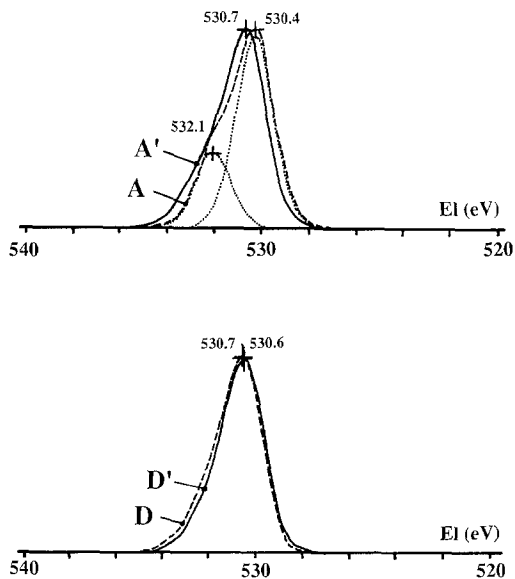


FIG. 1. O1s photoemission peaks of catalysts A' and D' compared to supports A and D.

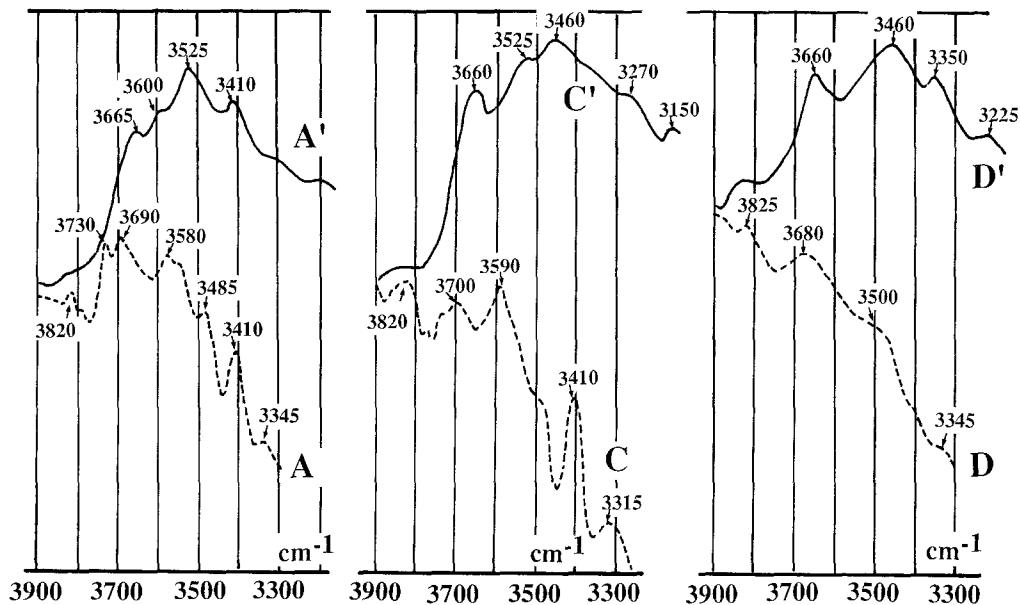


FIG. 2. Fourier transform infrared spectra of catalysts A', C', and D' compared to supports A, C, and D.

2) are in agreement with the IR study. Thus, in accordance with the postulated mechanism of reaction between vanadyl oxychloride and conventional oxide supports, the attack of AlNbO oxides by VOCl<sub>3</sub> appears to be essentially a superficial process.

Figure 2 shows the IR spectra of the catalysts in the 3300–3900 cm<sup>-1</sup> range compared to the corresponding supports. Characteristic bands of the OH groups are observed for catalyst A' at 3665, 3600, 3525, and 3410 cm<sup>-1</sup>, for catalyst C' at 3660, 3525, 3460, 3270, and 3150 cm<sup>-1</sup>, and for catalyst D' at 3830, 3660, 3460, 3350, and 3225 cm<sup>-1</sup>. It can be noted that the IR bands attributed to Al bonded hydroxyl groups at 3820 cm<sup>-1</sup> (18) have mainly disappeared and have been substituted by new ones at 3525 and 3660 cm<sup>-1</sup>. These new bands should thus correspond to vanadium bonded hydroxyls on octahedral Al sites. As expected, VOCl<sub>3</sub> reacts with the more basic OH groups. On the other hand, the 3410 cm<sup>-1</sup> band on spectra A and C and attributed to a niobium bonded OH group in the Nb<sub>2</sub>O<sub>5</sub> structure is slightly

affected by grafting for A' but completely disappears for C'. We postulate that the new bands observed at 3460, 3350, and 3270 cm<sup>-1</sup> should correspond to vanadium bonded hydroxyls on Nb sites. It is noticeable that the relative intensity of the band at 3660 cm<sup>-1</sup> and corresponding to the more basic vanadium-bonded hydroxyls increases from A' to C' while there are not very many modifications on the relative intensity of the less basic (or more acidic) vanadium bonded hydroxyls on Nb sites below 3500 cm<sup>-1</sup>. This point will be discussed later on.

UV-visible DRS spectra of the catalysts are shown on Fig. 3. The same characteristic band at around 400 nm is observed in the charge transfer region 300–500 nm, and has been attributed to V<sup>5+</sup> ion. No signal is observed in the 700–800 nm zone corresponding to the *d-d* transition of the V<sup>4+</sup> ion. However it is difficult, only on the basis of the UV experiments, to postulate any symmetry of the V<sup>5+</sup> grafted species.

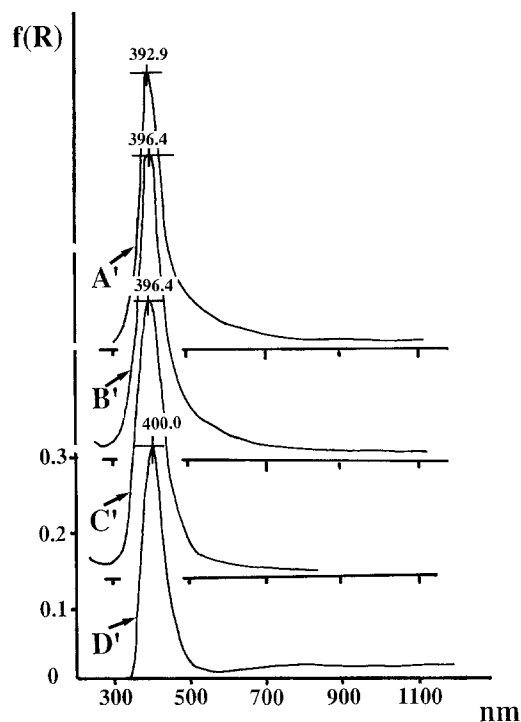


FIG. 3. UV-visible spectra of catalysts.

### Catalytic Study

The catalytic transformation of isopropanol has been used to compare the superficial properties of the  $\text{VO}_x/\text{AlNbO}$  catalysts with that of the corresponding supports. Propene and acetone yields are reported as a function of temperature in the 150–200°C range in Fig. 4 for catalysts A' and B' (and corresponding supports A and B) and in Fig. 5 for catalysts C' and D' (and corresponding supports C and D). The apparent activation energy for the four catalysts and the two reactions are very similar, 20–22 kcal · mol<sup>-1</sup>. While propene is only detected on the supports (18), it appears from Figs. 4 and 5 that selectivity into acetone increases regularly from A' to D', as can be observed in Table 4.

The results for the oxidative dehydrogenation of propane are shown in Table 5 compared to the AlNbO supports. A variable mass of catalyst was used in order to com-

pare the catalysts at equal conversions of approximately 10%. Carbon balance based on  $\text{C}_3\text{H}_6$ , CO, and  $\text{CO}_2$  was nearly 100%, except perhaps for D', for which the carbon balance is 87%. However, in this latter case, neither oxygenates like ethanal, propanal, acetone, and acrylaldehyde nor acids like acetic, propionic, and acrylic acid, were detected. We postulated the formation of polymers on this last catalyst. Selectivity for propene runs through a maximum for catalysts B' and C'.

### DISCUSSION

$\text{VO}_x/\text{AlNbO}$  catalysts obtained by grafting  $\text{VOCl}_3$  on AlNbO oxides have been studied by STEM, XRD, and XPS. From these techniques, it can be observed that the interaction of vanadyl oxychloride does not affect the bulk structure of the corresponding supports. This conclusion is also supported by our <sup>27</sup>Al NMR solid-state spectroscopy studies (21). Indeed the signal observed at 0–2 ppm and attributed to aluminium in an

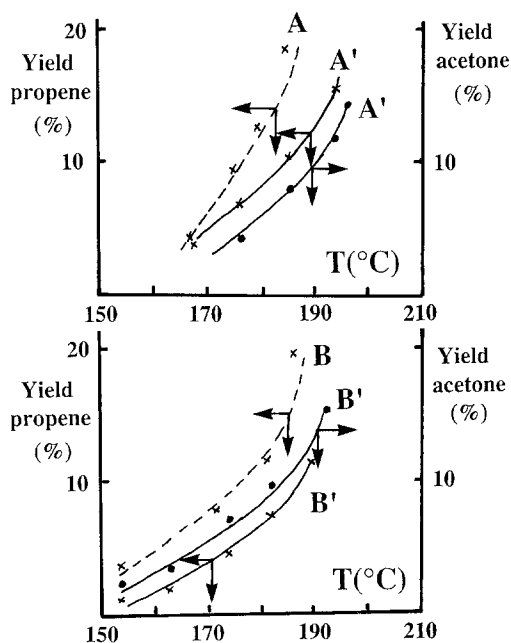


FIG. 4. Results for isopropanol dehydration on catalysts A' and B' compared to supports A and B.

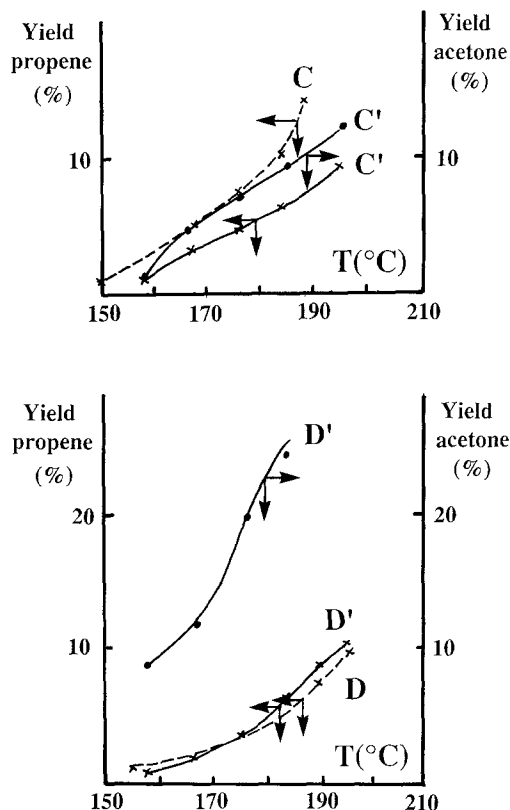


FIG. 5. Results for isopropanol dehydration on catalysts C' and D' compared to supports C and D.

octahedral environment in crystalline AlNbO<sub>4</sub> (support D) is still observed for catalyst D', as for the two peaks at 28–30 and 58–60 ppm and previously attributed to five-coordinated or tetrahedrally distorted Al co-

TABLE 4

Comparison of Propene and Acetone Selectivities for Isopropanol Dehydration at Low Conversion (<5%) Measured at 170°C Compared to the Corresponding Supports

Catalysts	Selectivity propene (%)	Selectivity acetone (%)
A'(A)	63 (100)	37(0)
B'(B)	43 (100)	57(0)
C'(C)	40 (100)	60(0)
D'(D)	16 (100)	84(0)

ordination and tetrahedrally Al coordination, respectively, also observed for catalysts A', B', and C' as for supports A, B, and C. (21).

XPS and FTIR spectra indicate a strong interaction between superficial hydroxyl groups and VOCl<sub>3</sub>. This is evident from the evolution of the O1s photoemission peak after grafting, especially for calcination of the AlNbO oxide at lower temperature for which the OH density is higher (see Table 2). This can be deduced also from the disappearance of the more basic hydroxyl groups at 3820 cm<sup>-1</sup> and the appearance of new ones at 3525 and 3660 cm<sup>-1</sup>. It has been proposed previously (18) that these hydroxyls should correspond to Al sites of alumina in octahedral symmetry and modified by the proximity of niobia. On the contrary, Nb sites giving a band at 3410 cm<sup>-1</sup> should correspond to less basic (or more acidic hydroxyls), which should be slightly affected by VOCl<sub>3</sub> grafting for AlNbO oxide calcined at low temperatures (the band is still present after vanadium grafting on support A) but totally involved for AlNbO oxide calcined at higher temperatures (like for support C). The situation is different for support D for which a new structure of the support is obtained with the crystallisation of AlNbO<sub>4</sub>. The same type of V bonded hydroxyls on the AlNbO supports appears to be generated as can be seen from the appearance, after grafting, of new bands in the 3700–3500 cm<sup>-1</sup> range. A linear correlation is observed, (Fig. 6) between the V density for catalysts A', B', C' corresponding to supports A, B, and C for which both structures of Al<sub>2</sub>O<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> are observed, and the OH density of the same supports. Solid D', which corresponds to support D with the structure of crystallized AlNbO<sub>4</sub> (18) is out of this correlation. This should correspond to a different type of dispersion of vanadium.

No signal of V<sup>4+</sup> was detected on the UV-visible DRS spectra of all catalysts. Previous <sup>51</sup>V NMR experiments showed the presence of two coordination states for grafted

TABLE 5  
Catalytic Results for Oxidative Dehydrogenation of Propane at 500°C Compared to the Corresponding Supports

Catalysts (Supports)	Conversion (%)	Catalysts mass (mg)	Selectivities (%)			
			C <sub>3</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	Σ
A'(A)	11.8(3.7)	200	12(10)	—(—)	87(88)	99(98)
B'(B)	9.2(3.1)	200	65(8)	33(7)	2(85)	100(100)
C'(C)	10.4(2.8)	350	62(6)	21(10)	16(83)	99(99)
D'(D)	11.5(1.8)	125	44(3)	25(18)	18(64)	87(85)

vanadium, the proportion of which depends on the calcination of the supports (21). The first state, which corresponds to a broad signal at  $-486$ ,  $-580$  ppm, is predominant on catalyst A' and is characteristic of vanadates species on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (22). We assigned this signal to vanadium in a very distorted octahedral or tetrahedral environment (22). From Eckert's study of vanadate reference compounds (12), it appears that the chemical shift and width of the spectral line are characteristics of condensed tetrahedral vanadate species. On the basis of EXAFS and XANES experiments, other authors showed the existence of condensed vanadates characterized by the presence of V—O—V bonds, and concluded for pyrovanadate V<sub>2</sub>O<sub>7</sub> structures on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (5). The

second state of vanadium characterized by a quite symmetric peak at  $-1900$  ppm appeared to be associated with the AlNbO<sub>4</sub> structure as the area of this peak was observed to increase with the temperature of calcination of the support, accompanying the crystallization of the AlNbO oxide (21). By considering the anisotropy of the NMR signal, it has been stated that the corresponding species is a tetrahedral isolated superficial vanadate. A tetrahedral environment is compatible with the UV-visible spectra. The statement of site isolation is quite straightforward from the low density of superficial hydroxyl groups of the Al NbO<sub>4</sub> support [ $0.9$  OH/nm<sup>2</sup> (see Table 2) in comparison with  $6.0$  OH/nm<sup>2</sup> which has been measured for TiO<sub>2</sub> anatase] (26).

The physicochemical results obtained on the different catalysts can explain the differences observed for the catalytic results. Methanol and ethanol dehydrogenation have recently been described as structure-insensitive reactions (23, 24). On the contrary, ethane and propane oxidative dehydrogenation are known to be structure sensitive reactions (24, 25). Thus it was of interest to compare catalytic results obtained from different vanadia layers both for such reactions.

As shown in Table 4 for isopropanol transformation, grafted vanadium is responsible for the oxidative properties of the catalysts. No changing of the activation energy was

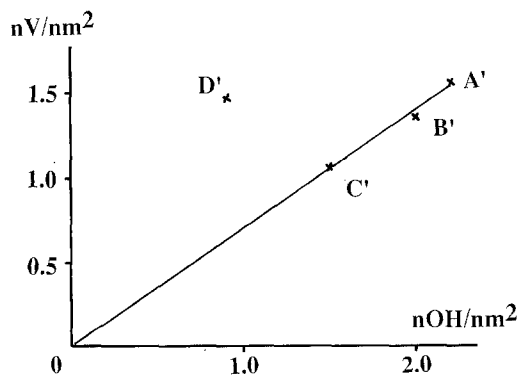


FIG. 6. Comparison of V and OH densities on the different catalysts.



TABLE 6  
Comparison of Turnover Number (TON) Values  
Depending on Catalysts and Reactions Considered

Catalysts	Reaction considered	Turnover number (s <sup>-1</sup> )
A	Isopropanol	1.5 × 10 <sup>-4</sup>
B'		5.0 × 10 <sup>-4</sup>
C'	↓	6.0 × 10 <sup>-4</sup>
D'	Acetone	20.0 × 10 <sup>-4</sup>
A'	Propane	1.7 × 10 <sup>-3</sup>
B'	↓	2.7 × 10 <sup>-3</sup>
D'	Propene	10.0 × 10 <sup>-3</sup>

*Note.* TON was defined as the number of acetone molecules produced per second and per V atom for the isopropanol transformation and as the number of propane molecules transformed per second and per V atom for ODH, using data from Tables 4 and 5.

observed from catalyst A' to D'. In order to obtain a quantitative comparison between the four catalysts, we have tentatively computed a turnover number (TON) related to oxidation paths, using the total vanadium content. The exact definition is formulated along with the results in Table 6. These figures will be discussed later.

In contrast, some difficulties appear in discussing the dehydration properties of the solids. It has not been possible to determine reliably the total number of hydroxyl groups after V grafting, as was done by thermogravimetric analysis for pure supports (18), because of the presence of residual ammonia and chlorides at the surface of the catalyst. We can only estimate from FTIR measurements that niobia and alumina bonded hydroxyl groups have been partially substituted by vanadia bonded OH. The loss of specific area is another misleading factor. However, we note that propene yields for catalysts A', B', and C' are approximately reduced by half in comparison with supports A, B, and C. The two curves are curiously fitting for solids D and D'. We should thus conclude that vanadia bonded hydroxyl groups are highly effective sites (i.e., may be more acidic than niobia bonded OH) for

isopropanol dehydration. The molecular ratio (V-OH)/(V) is certainly an important parameter which depends on the aggregation state of vanadium. Bridged vanadates could bear one or two hydroxyl groups per grafted vanadium. However, our data do not allow for such a discussion.

We turn now to discuss oxidative properties. Table 6 shows an increase of the turnover number for acetone from catalysts A' to D'. As discussed in Ref. (24), a variation of a factor of 10 should not be incompatible with the definition of structure insensitivity.

On the other hand, V grafted AlNbO<sub>4</sub> catalysts appear to be good catalysts for propane oxidative dehydrogenation, even better than VMgO catalysts known to be good catalysts for this reaction (25). Table 6 shows that the turnover number into propene increases with the temperature of calcination of the support. An abrupt discontinuity is observed for propene and CO/CO<sub>2</sub> selectivities between catalysts A' and B'. This might be associated with the structural modification of the superficial vanadates as evidenced by solid-state NMR spectroscopy (21). It is noteworthy that best selectivities for ODH are observed for V grafted on AlNbO oxides calcined at intermediate temperatures (catalysts B' and C'). These possess the V tetrahedral coordination which should be useful for this reaction and should interestingly correspond to condensed species as mentioned above. However, note that these catalysts are not the most basic as evidenced by the test of isopropanol decomposition. The decrease of selectivity into propene for catalyst D' can be explained by a different V condensation degree characterized by the presence of monovanadates with some Brønsted acidity, as has been previously postulated. Comparing turnover numbers, we see that the symmetric (isolated) tetrahedral species grafted onto AlNbO<sub>4</sub> is more active but less selective for ODH than distorted (condensed) species which are characteristic of γ-Al<sub>2</sub>O<sub>3</sub>.

In conclusion, the results obtained in this

work show that it is possible to control the structure and reactivity of vanadia monolayers by modifying the local structure of the oxide support. As expected, the acidobasic properties of superficial hydroxyl groups determine the reactivity toward the nucleophilic attack of the  $\text{VOCl}_3$  reagent. Our experiments suggest that the presence of amorphous alumina, as previously discussed, with dense basic OH groups leads to the formation of condensed tetrahedral vanadate (preferentially Al bonded) species. On the contrary,  $\text{AlNbO}_4$  with less concentrated and slightly more acidic superficial hydroxyl groups as observed by isopropanol transformation and FTIR measurements leads to monovanadate tetrahedral species (probably Al and Nb bonded) with some Bronsted acidity. In both cases, vanadates appear to fix on an aluminium cation in octahedral symmetry in the vicinity of niobium cations. Thus the dilution of these aluminium sites in the niobia matrix determines the aggregation state of vanadium and its reactivity.

#### ACKNOWLEDGMENTS

Synthesis of catalysts was developed at the Instituto Militar de Engenharia, Brazil. The experimental work was carried out at the Institut de Recherches sur la Catalyse, CNRS, France, within the French-Brazil cooperation program. We thank CNPq, Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil, for financial support. We thank Mr. J. Billy for the FTIR experiments and Dr. V. Soenen for the propane ODH measurements. We thank Dr. J. C. Védrine for fruitful discussion.

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