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Selective Oxidation of Ethanol to Acetaldehyde on $V_2O_5/TiO_2/SiO_2$ Catalysts

Effect of TiO_2-Coating of the Silica Support

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The effect of coating the SiO_2 support of a V_2O_5 oxidation catalyst with different amounts of TiO_2 has been studied. X-ray photoelectron spectroscopy of the resulting $V_2O_5/TiO_2/SiO_2$ showed that the highest dispersion was reached for the low TiO_2 coverages. The catalysts were prepared by depositing vanadia in a quantity equivalent to one monolayer onto SiO_2, TiO_2, or TiO_2-coated SiO_2 samples, by impregnation with a vanadyl acetylacetonate solution in ethanol, drying at 348 K, and calcining at 773 K in air. This procedure decreased the surface area by up to 30%. TPR profiles of binary and ternary samples were similar, showing only a single peak, suggesting the presence of just one vanadium species. Electron spin resonance spectra of partially reduced TiO_2-coated silica carriers showed that, at very low titania content, titanium ions were present in the silica surface in small clusters. In the high content sample, TiO_2 covered the silica surface, as in a crystalline TiO_2 phase. The characteristics of supported vanadium oxide were affected by the TiO_2 distribution. These V/*x*TiSi catalysts were found to be active for the selective oxidation of ethanol. The titania coating of the support increased the activity of the supported vanadia as compared to that of the oxide supported on silica, but maintained a similar product distribution. This increase of activity depended on the number of titania monolayers (x), being maximum for $x \geq 1$. The selectivity to acetaldehyde also increased with x, being maximum for the same composition. The combination of the two factors allowed the attainment of acetaldehyde yields of 74% per pass at temperatures as low as 473 K. The modifications in the catalytic behavior are discussed in terms of the changes of the support surface and its interaction with the supported vanadia caused by the presence of the titania coating.

INTRODUCTION

The interaction between catalytically active metal oxide particles and oxide carriers greatly influences their structure and size. This makes the deposition of monolayer(s) of an active phase on a carrier an attractive technique for the tailoring of catalytic properties. It offers the advantage of an increased exposure of the active phase and allows one to modify its structural and catalytic properties by interaction with the carrier.

Vanadia catalysts constitute a relevant example of the influence of this interaction. Several authors (1–3) have compared the properties of vanadia supported on different carriers (SiO_2, Al_2O_3, TiO_2, MgO, ZrO_2) and have concluded that the nature of the dispersed surface metal oxide phase enables the vanadia, depending on which support is used, to become an effective catalyst for selective oxidation of aromatics (4–7), olefins (8), and alcohols (9–11), as well as for selective catalytic reduction (SCR) of NO_x by NH_3 (12).

Titania (anatase) interacts strongly with an immobilized vanadia layer, generating a molecular dispersion of V_2O_5 (13, 14), but the system suffers from limited specific surface area and low resistance to sintering. Conversely to TiO_2, interaction of V_2O_5 with SiO_2 is weak and, therefore, the properties of VO_x species over SiO_2 are modified to a lesser extent, showing a higher tendency for thermally induced aggregation, leading to a low dispersion of the active phase (15, 16). However, the use of SiO_2 as a support of vanadia has the advantage of presenting a higher specific surface area for coating by vanadia and a bigger resistance to sintering than can be provided by TiO_2. A way to obtain a titania surface with high, thermostable surface area and good mechanical properties is to apply TiO_2 onto silica (17). Vanadia supported on the mixed oxide TiO_2/SiO_2, either coprecipitated (18) or having the TiO_2 directly applied to the silica (19–24), has been developed because of its selectivity as a catalyst for SCR of nitrogen oxides. Moreover, vanadia-based systems such as V_2O_5/TiO_2 (10) and V_2O_5/SiO_2 (11) catalysts have been studied for selective oxidation of alcohols. In particular, V_2O_5 (25) and V_2O_5/SiO_2 (26) are very active and selective for oxidation of ethanol to acetaldehyde. By a proper selection of the catalytic oxide system and reaction conditions, ethanol can be converted oxidatively

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to acetaldehyde, acetic acid, or ethyl acetate, all of which can be used either as final products or as intermediates in synthetic routes.

In a previous paper (27), we studied the oxidation of ethanol on supported monolayer vanadia catalysts, prepared by impregnation of the acetylacetonate complex from an ethanolic solution, and compared the catalytic performance of a $V_2O_5/TiO_2/SiO_2$ catalyst with those of V_2O_5/TiO_2 and V_2O_5/SiO_2 catalysts. It was found that the coating of the silica carrier with a monolayer of TiO_2 increased substantially the activity of the catalyst, approaching that of the one supported on pure TiO_2, while it increased the selectivity to acetaldehyde as compared with the latter. Accordingly, it was decided to study the effect of varying the amount of the TiO_2 in the coating of the silica support with the aim of understanding the interrelations between TiO_2 and SiO_2 which can be important at low titanium content, and their influence on the catalytic properties of supported V_2O_5, as a way to improve its performance for the selective oxidation of ethanol.

EXPERIMENTAL

Preparation of the TiO_2/SiO_2 Supports

Titania-coated silica supports were prepared by homogeneous precipitation, as described by Geus (28). Nonporous silica (Aerosil MOX 80 from Degussa, specific surface area 86 m^2/g) was suspended in deionized water, and acidified with HCl to $pH < 1$. An appropriate amount (see below) of $TiCl_3$ (Merck, 15% solution in HCl) was added to the suspension with vigorous stirring to ensure a good homogeneity during the precipitation. Then, the suspension was neutralized up to a pH ca 8 by slow addition of a solution of ammonium hydroxide (Merck, 20% in NH_3) at a neutralization rate of 0.002 mol OH^-/min. The precipitate so obtained was thoroughly washed twice with deionized water and dried in air at 373 K for 48 h. The solid was finally calcined at 823 K in air for 2 h. This procedure allowed one to deposit hydrated Ti(III) oxide and, after the thermal treatment, to obtain TiO_2 dispersed on the silica surface. Four supports were prepared using the amounts of $TiCl_3$ necessary to obtain TiO_2 contents equivalent to 0.6, 1.0, 1.5, and 2.0 monolayers (ML) on the silica (denoted hereafter as 0.6TiSi, 1.0TiSi, 1.5TiSi, and 2.0TiSi, respectively). The ML of TiO_2 was considered as the complete covering of the silica surface by a film of TiO_2 0.38 nm thick (28), which corresponds to the longest axis of the rutile cell.

A commercial TiO_2 sample (Degussa P25) with BET area of 50 m^2/g and consisting of 82% anatase and 18% rutile was used as support reference.

Preparation of Catalysts

Catalysts were prepared by depositing vanadium on the supports by wet impregnation, by using the specific reaction of the surface hydroxyls with the vanadyl groups of the vanadium (IV) acetylacetonate complex (29). The impregnation was made by adding an ethanolic solution of the vanadyl acetylacetonate to the support particles. The suspension was evaporated at 348 K under continuous stirring. The impregnates were washed repeatedly with pure ethanol, dried again, and finally calcined at 773 K in air for 2 h to convert vanadium to vanadium oxide. The added amount of vanadium was that calculated for a complete monolayer, taking into account the specific surface areas. In the case of TiO_2 and TiSi supports a value of 0.166 nm^2 per center was considered, assuming that one vanadium oxide species is deposited on each center (28). In the case of SiO_2 the needed amount was calculated for a monolayer thickness of 0.234 nm (4) taking the density of V_2O_5 as 3.357 g/cm^3. The catalysts will be denoted henceforth by their component elements (V/Ti, V/Si, and V/xTiSi, where x denotes the number of ML of titania).

Characterization of Catalysts and Supports

Specific surface areas. Specific surface areas were determined by the BET method from the adsorption isotherms of nitrogen at 77 K, taking a value of 0.164 nm^2 for the cross-sectional area of the adsorbed nitrogen molecule at that temperature.

X-ray photoelectron spectroscopy (XPS). XP spectra were obtained with a Leybold LHS 10 spectrometer provided with a hemispherical electron analyzer and a Mg anode X-ray exciting source (Mg $K\alpha = 1253.6$ eV, $1\ eV = 1.602 \times 10^{-19}$ J). Samples were pumped to 10^{-5} Torr ($1\ Torr = 133.33$ Pa) before moving them into the analysis chamber. Pressure in this turbo-pumped main vacuum chamber was maintained below 7×10^{-9} Torr during data acquisition. Each spectral region was signal averaged for a number of scans to obtain good signal-to-noise ratios. Accurate binding energies (BE) were determined by reference to the C 1s and Si 2p lines to which BE values of 284.6 and 103.4 eV were respectively assigned (30).

Temperature programmed reduction (TPR). The TPR profiles were obtained with a Cahn 2000 microbalance ($sensitivity = 1\ \mu g$). Prior to the experiment, the samples were heated in a He flow (100 cm^3/min) at 4 K/min up to 773 K in order to clean the surface. After cooling in He flow down to 373 K, He was switched to H_2 (300 cm^3/min) and the experiment was begun; the sample was heated at 4 K/min up to 900 K, while continuously recording the weight changes.

Chemical analysis. Quantitative analysis of vanadium in catalyst samples was made by atomic absorption spectrometry. Prior to analysis, samples weighing ca 0.1 g were dissolved in 10 ml of HF, heated on a sand bath until complete solution, and then diluted to 100 ml with deionized water.

Electron spin resonance spectroscopy (ESR). ESR spectra were obtained with a Bruker ER 200D spectrometer operated in the X band. All the spectra were recorded at 77 K. DPPH was used as a reference ($g = 2.0036$) to calibrate the magnetic field. Samples were introduced in a quartz cell provided with greaseless stopcocks and were outgassed in high vacuum at 293 K, 573 K, and 773 K. Then they were reduced under a continuous flow of hydrogen at 573 K and 773 K.

Catalytic Activity

Catalytic activity tests were made in a tubular, fixed bed flow reactor at nearly atmospheric pressure in the temperature range 400–700 K, with a residence time W/F = 45 g cat · h/mol of ethanol and feeding reacting mixtures ethanol–oxygen–helium having the following composition (in mol%): ethanol 1.4, oxygen 27.5, and helium balance. Ethanol (Prolabo p.a., 99.85 vol.%), oxygen (SEO, 99.99%) and helium (SEO, 99.99%) were used as reactants and diluent, respectively. Catalyst samples (ca 250 mg, particle size 30–40 mesh) were diluted with SiC tips up to a bed volume of 5 ml. Reactants and products were analyzed on-line by GC using two columns: 13X molecular sieve for O_2 and CO, and Porapak Q for the rest of products. C and O mass balances of 100 ± 5% were obtained. Conversion and selectivity to products were calculated on a carbon atom basis, expressed as mol% ratio of ethanol transformed to ethanol fed, and ratio of ethanol transformed to each product to total ethanol transformed, respectively. All measurements were made after stabilizing the catalytic system for 1 h under reaction conditions. Preliminary tests showed that in the reaction conditions used, homogeneous reaction (in the absence of catalyst) started around 480 K with a conversion of 0.2 mol%, reaching 5.7 mol% at 593 K (28). As these values are around 15 to 20 times lower than those measured in the catalyzed reaction tests, the influence of homogeneous reaction can be considered to be negligible.

RESULTS

Chemical Analysis

The chemical analysis of the V/xTiSi catalysts (Table 1) showed that the titanium amount retained on the silica corresponded to that calculated to deposit 0.6, 1.0, or 1.5 ML on supports 0.6TiSi, 1.0TiSi, and 1.5TiSi, respectively, but in the 2.0TiSi preparation only 78% of the theoretical amount was retained, which corresponded to 1.6 ML. These results indicate that the hydrated Ti(III) oxide in direct contact with the silica surface is retained during the two washings with deionized water, but only hydrated Ti(III) oxide not interacting with the silica surface can be easily removed. When vanadia was deposited onto the mixed supports, the data in Table 1 show that there is not a direct relation between the titanium content and the vanadium retained after two washings with ethanol. Thus, while the incorporation of a small amount of titanium produced a marked decrease of the vanadium retained (40%), when the titanium content is equivalent to or a little higher than that corresponding to the monolayer the vanadium retained (81%) was higher than for V/Si (74%). For V/2.0TiSi only 70% of the vanadium was retained.

TABLE 1

Chemical Analysis and Microgravimetric Data for Vanadia-Containing Catalysts

	Content[a]				TPR	
	Theoretical		Analysis			
Sample	V	Ti	V	Ti	Weight loss (%)	T_r[b] (K)
V-Si	3.39	—	2.53	—	0.62	688
V-0.6TiSi	4.89	5.17	1.97	5.74	0.61	663
V-1.0TiSi	5.17	8.94	4.19	8.75	1.61	663
V-1.5TiSi	5.57	13.35	4.56	12.92	1.41	663
V-2.0TiSi	6.88	17.60	4.80	13.67	1.57	663
V-Ti	2.56	57.27	2.41	n.d.[c]	0.77	665

[a] Atomic percentages.

[b] T_r: temperature of maximum reduction rate.

[c] n.d. = not determined.

Using impregnation with vanadyl acetylacetonate in ethanol, films of vanadia having thicknesses of the order of 2–3 ML can be obtained, but vanadium not chemically bound to the surface is removed by the further washings with ethanol. This differs from the impregnation in toluene solution, where crystalline V_2O_5 can be obtained after consecutive impregnation and calcination steps. The low retention degree for vanadium of the V/0.6TiSi sample (40%), lower than on V/Si, indicates that titanium incorporated at the silica surface is hindering the vanadium retention, probably because at low titanium content both vanadium and titanium are bound at similar sites of the silica surface.

Surface Areas

Specific surface areas of supports and catalysts are shown in Fig. 1. The titania coating of silica produced an almost linear increase of the BET areas as titania content increased up to 1.5 ML (13.4 wt% Ti). The subsequent coating with vanadia decreased the surface areas by a 30% or more, producing very similar surface areas (85–92 m^2/g) for the ternary catalysts, always higher than that of V/Si (75 m^2/g). These effects were similar to those reported by Vogt *et al.* (17). As the silica support is constituted of nonporous microspherical particles, the increase of specific surface areas with titania content and the observed decrease after vanadium impregnation could be due to the deposition of porous titanium oxide, but it could indicate that a small fraction of the silica substrate was solubilized under the very low pH

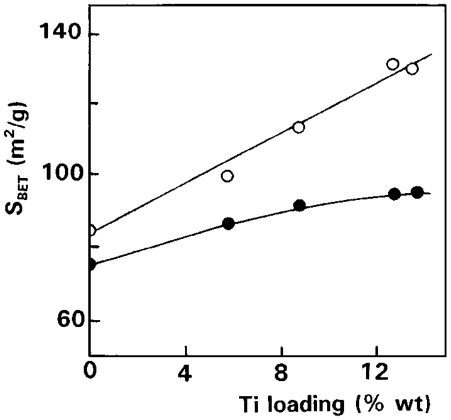

FIG. 1. Specific surface areas as a function of the nominal titania content. Symbols: open, *x*TiSi supports; full, V/*x*TiSi catalysts.

(below 1) employed at the beginning of the precipitation of Ti hydroxide from $TiCl_3$ solution and the subsequent precipitation of an extra and porous SiO_2 phase. Finally, some of this porosity is lost during incorporation of vanadium oxide.

TGA and TPR

The differential thermogravimetric (DTGA) profiles obtained from the dried supports before calcination at 823 K show two peaks, one between 323 and 373 K and the other between 508 and 513 K. They were assigned to water retained from the preparation and to desorption of NH_4Cl formed during the neutralization step, respectively. This assignment was possible by monitoring with XPS the N 1s and Cl 2p core levels (spectra not shown here) of the solid precursor at different stages of thermal decomposition.

The TPR profiles of each catalyst sample showed a single reduction peak (Fig. 2). Profiles corresponding to bulk V_2O_5, VTi, and VSi samples are also included for comparative purposes. A clear influence of titania and silica supports on the maximum reduction rate temperature (T_r) was observed, as reported by other authors (18). Ternary catalysts showed a close similarity to the V/Ti sample ($T_r = 665$ K), the only noticeable difference among them being that peaks widened as Ti content increased. Weight losses observed in the reduction step of every V/*x*TiSi catalyst corresponded to 1.00 ± 0.04 oxygen atoms per vanadium atom, equivalent to the complete reduction of all the V_2O_5 in the sample to V_2O_3, as in the V/Ti sample (Table 1). The only exception was V/1.0TiSi whose reduction went further at high temperatures, possibly due to the reduction of surface titanium in patches of TiO_2 not covered by vanadia. Conversely, weight loss for the VSi sample was intermediate between those corresponding to reduction to the lower oxides V_2O_3 and V_2O_4. These findings agree well with those reported by Baiker *et al.* (18) and Rajadhyaksha *et al.* (21) who reported a higher reduction degree of vanadia when supported on TiO_2/SiO_2 than on SiO_2.

The TPR results accordingly indicate that vanadia interacted mostly with titania. The presence of a single TPR peak suggests the presence of only one vanadium species, but having different reducibility, depending on the support. The peak widening when titania content increased can be due to a higher heterogeneity of the interaction between vanadium and the support surface. This means, in other words, that by varying the content of titanium which covers the silica surface one can modify the active phase-support interaction.

X-Ray Photoelectron Spectroscopy (XPS)

Prior to the incorporation of vanadia, the TiO_2-coated silica carriers were examined by XPS. The binding energy (BE) of the Ti $2p_{3/2}$ peak at 458.5 eV was unchanged for all the samples. The O 1s signal showed two components: a major one at ca 532.9 eV associated with the lattice oxygen of SiO_2 and a minor one, whose intensity increased with TiO_2 content, at ca 530.8 eV due to Ti–O bonds. The titanium-to-silicon intensity ratios (I_{Ti}/I_{Si}) calculated from

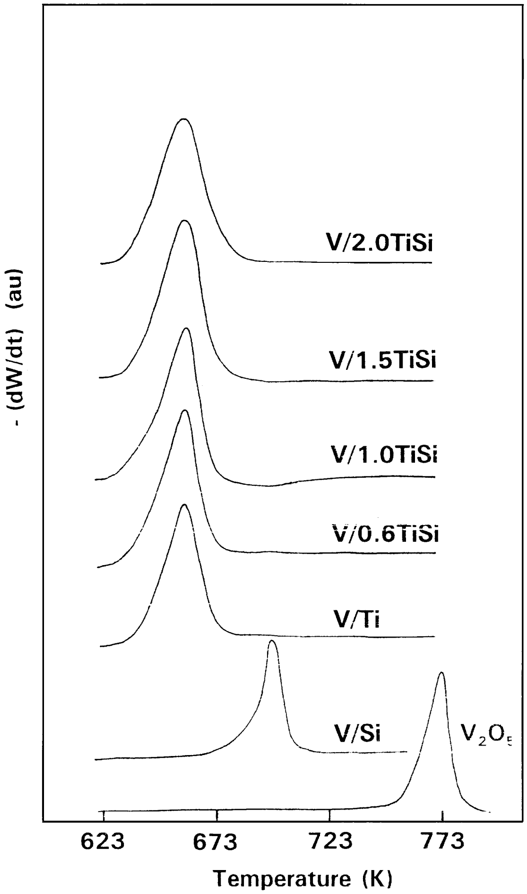

FIG. 2. TPR profiles obtained microgravimetrically for supported vanadia catalysts. Labelling is included in figure.

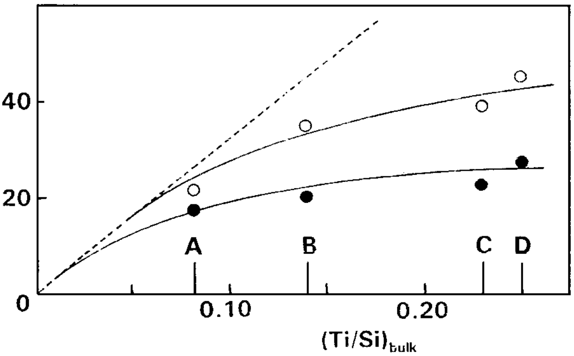

FIG. 3. XPS titanium-to-silicon intensities surface ratio of TiO_2-coated silica supports vs bulk composition (the dashed line corresponds to the intensity ratios expected for monolayer catalysts). Symbols: open, xTiSi samples; full, V/xTiSi catalysts. Samples A, B, C, and D refer to $X = 0.6$, 1.0, 1.5, and 2.0, respectively.

XP spectra increased progressively with increasing titania loading. In order to have an idea of the dispersion degree of TiO_2 on the silica surface, a model consisting of a TiO_2 layer on the silica surface with 100% dispersion has been assumed and the theoretical I_{Ti}/I_{Si} ratio has been calculated (31). The theoretical I_{Ti}/I_{Si} ratio as a function of the Ti/Si atomic ratio in the bulk is given by a dashed line in Fig. 3. As can be seen in Fig. 3, the titanium dispersion was indeed very high for 0.6TiSi, fitting well with that expected for the theoretical monolayer; the dispersion was a little lower for 1.0TiSi and decreased for samples 1.5TiSi and 2.0TiSi.

The ternary catalyst samples were also examined by XPS, and the respective BE of V $2p_{3/2}$, Ti $2p_{3/2}$, and/or Si 2p peaks are compiled in Table 2 for comparative purposes. Regarding the V $2p_{3/2}$ BE values, the decrease of 0.8 eV of the V/1.0TiSi catalyst with respect to that of the V/Si counterpart agrees well with literature findings (32, 33). V/xTiSi and V/Ti samples (the exception is V/1.0TiSi) showed an additional shift of 1.0 eV toward lower BE, which is typical of V^{4+} ions. Such a decrease can be explained in terms of a larger extent of reduction of surface V^{5+} ions upon exposure to X-ray radiation, since the V/Ti catalyst after XPS analysis showed a strong grey-bluish color which contrasts with the yellow and pale yellow color of V/Si and V/1.0TiSi samples, respectively. A higher hydroxylation of the sample surface can diminish the effect of the X-ray photoreduction of V_2O_5. In order to obtain an idea of the dispersion of vanadia on the carriers, the V/(Ti + Si) atomic ratios have been calculated from the intensities of the XP spectra and corrected by atomic sensitivity factors. Table 2 also shows that the V/(Ti + Si) atomic ratio for V/xTiSi catalysts increased with the titanium content, and for V/Ti it was the highest of all.

TABLE 2

Binding Energy (BE) of Core Electrons and XPS Intensity and Atomic Ratios for Fresh Vanadia-Containing Catalysts

	BE (eV)				XPS atomic ratios
Sample	V $2p_{3/2}$	Ti $2p_{3/2}$	I_V/I_{Ti}	I_V/I_{Si}	V/(Ti + Si)
V-Si	518.4	—	—	0.333	0.046
V-0.6TiSi	516.7	458.5	1.345	0.241	0.032
V-1.0TiSi	517.6	458.5	1.721	0.354	0.047
V-1.5TiSi	516.7	458.5	1.658	0.381	0.051
V-2.0TiSi	516.7	458.5	1.933	0.543	0.072
V-Ti	516.9	458.5	0.197	—	0.182

XPS experiments with mixed supports and catalysts indicate that incorporation of the active phase did not modify the interaction between the initially deposited Ti and the main support, SiO_2, as the same tendency of titania dispersion was observed before and after impregnation with vanadium (Fig. 3).

Electron Spin Resonance (ESR)

(a) xTiSi supports. In order to obtain information on the TiO_2 component in the support, the xTiSi samples were treated under vacuum and H_2 at 573 K and 773 K and then studied by ESR. The Ti^{3+} ions generated by these treatments were used as labels to obtain information on the distribution and redox properties of the titanium located on the silica surface.

Outgassing treatments at $T_v = 573$ K were necessary to generate Ti^{3+} cations in the supports, except in the case of 0.6TiSi which needed a higher T_v, indicating that the Ti^{4+} in the sample is less reducible. For $T_v = 773$ K, all the spectra showed a broad Ti^{3+} signal (Fig. 4) with higher intensity than for $T_v = 573$ K; a narrow signal with $g = 2.002$ due to some carbon impurities or to electrons trapped at oxygen vacancies was also observed. The lineshape of the Ti^{3+} signal, which appears with $g < 2$, can give some indications on the Ti^{3+} environments. In the case of sample 0.6TiSi, the relatively broad and not well-defined axial Ti^{3+} signal (Fig. 4a) indicates very heterogeneous environments of the paramagnetic centers. These titanium cations present at low titanium content and less reducible than titanium in TiO_2 clusters should be due to dispersed Ti^{3+} cations on the SiO_2 surface. For sample 1.0TiSi, the Ti^{3+} signal shows a slightly narrower lineshape and reducibility at lower outgassing treatments probably because in this sample a part of the titanium is well dispersed and another is forming TiO_2 clusters. The ESR spectrum of sample 1.5TiSi (Fig. 4c), shows a narrower axial Ti^{3+} signal with an intensity lower than that of the previous one, although the Ti content is higher. Both facts indicate that the Ti^{3+} ions are located in larger TiO_2 clusters with more homogeneous environments than in the previous samples. In these clusters TiO_2 reduction is probably more difficult and the formation of diamagnetic Ti^{3+} pairs more likely. For sample 2TiSi (Fig. 4d) the spectrum

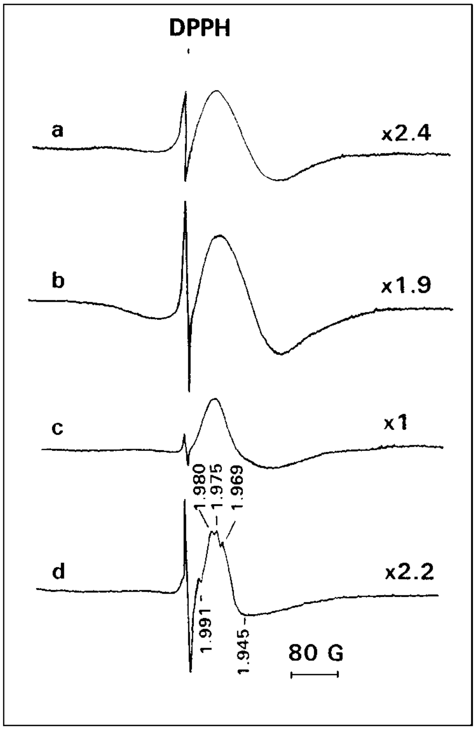

FIG. 4. ESR spectra at 77 K of mixed supports after outgassing at 773 K: (a) 0.6TiSi; (b) 1TiSi; (c) 1.5TiSi; (d) 2TiSi.

is formed by the overlapping of at least four narrow Ti^{3+} signals, with $g_{\perp} \approx 1.991$, 1.950, 1.975, and 1.969 and $g_{\parallel}$ close to 1.945. The relative narrow signals and lower intensity indicate an improved crystallinity of the TiO_2 clusters. The signal with $g_{\perp} = 1.991$ is indicative of Ti^{3+} in anatase, while the other titanium signals can be assigned to Ti^{3+} in rutile.

Thermal treatments under H_2 produced a broadening of the Ti^{3+} signal and a marked intensity increase, except for 2.0TiSi which showed a small increase, probably because of the formation of diamagnetic Ti^{3+} pairs. This is the usual mechanism of TiO_2 crystals to accommodate the oxygen vacancies produced by reduction treatments, and it can be taken as further evidence of an improved crystallinity of the titanium oxide.

(b) V/xTiSi catalysts. The ESR study on V/*x*TiSi catalysts provides information mainly on V^{4+} (or VO^{2+}), an oxidation state present in a small part of the vanadium cations because of its low stability. Therefore, the observed cations should be considered mainly as labels and not from a quantitative point of view.

In the catalyst V/Si only a very small amount of vanadium cations are stabilized as dispersed VO^{2+} species after calcination; most of the vanadium should be present as diamagnetic V^{5+}. These cations are not reduced by outgassing treatments even at 773 K, but treatments under H_2 at 573 K can reduce V^{5+} to V^{3+} with little stabilization as VO^{2+}. Reduction at 773 K followed by contacting the sample with O_2 at 77 K yields some dispersed VO^{2+} species formed by reoxidation of V^{3+} cations, with $g_{\parallel} = 2.005$, $g_{\perp} = 2.000$, $A_{\parallel} = 200$ G, and $A_{\perp} = 50$ G, signal A, and in some cases, O_2^{-}–V^{5+} species are also formed, with $g_1 = 2.023$, $g_2 = 2.009$, $g_3 = 2.003$, $A_1 = 10$ G, $A_2 = 7$ G, and $A_3 = 6$ G. At 295 K the VO^{2+} signal increases and the O_2^{-} signal disappears.

The spectra of V/0.6TiSi after thermal treatments under vacuum and H_2 show, in general, effects similar to those observed for sample V/Si. The reduction of V^{5+} to V^{3+} takes place at $T_v = 573$ K under H_2, with some formation of VO^{2+} cations which are reduced at $T_r = 773$ K; a subsequent O_2 adsorption produced VO^{2+} and some O_2^{-}–V^{5+} species. However, a small VO^{2+} signal is formed by outgassing at 573 K, indicating that some V^{5+} are reduced, and hyperfine constants of the VO^{2+} signal detected after O_2 adsorption on the sample reduced at 773 K show parameters slightly different from those of signal A; both modifications should be due to the interaction of vanadium and titanium cations dispersed in silica. As in the case of V/Si, most of the vanadium is not forming vanadium oxide clusters.

A first difference shown by the spectrum of V/1.0TiSi after calcination is the presence of a broad signal B with $g = 1.95$ that can be assigned to V^{4+} cations in vanadium oxide clusters. The signal of dispersed vanadium is also present (Fig. 5b), showing its largest intensity after reduction at 573 K, as in the previous cases. The broad signal B presents its maximum intensity after outgassing at $T_v = 573$ K, indicating that the clustered vanadium requires

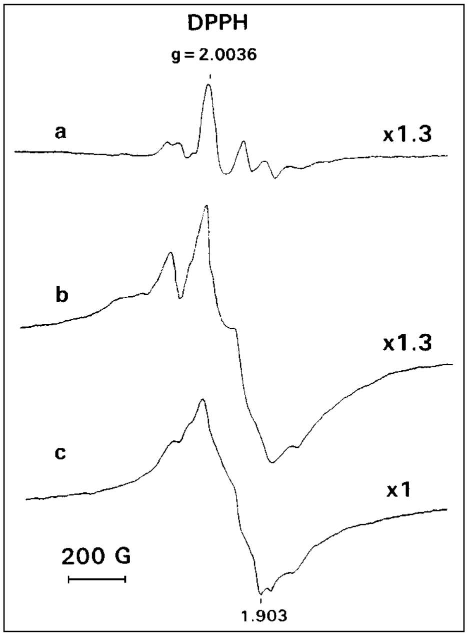

FIG. 5. ESR spectra of catalysts: (a) V/0.6TiSi; (b) V/1.0TiSi; (c) V/2.0TiSi.

milder reduction conditions than the vanadium dispersed on silica. Both signals disappear after reduction at $T_r = 773$ K; a subsequent contact with oxygen produces again the signal of vanadium dispersed on silica, and a very small one of $O_2^- - V^{5+}$, but not the signal of clustered vanadium.

The spectra obtained for V/1.5TiSi are relatively similar to those obtained for sample V/1.0TiSi, indicating that vanadium is present in the form of vanadium oxide aggregates and of vanadium dispersed on silica; however, the contact with O_2 of the sample reduced at 773 K did not lead to the generation of VO^{2+} signals, as was the case for the samples with lower titanium content. This difference, which originated when the Ti content is higher than that corresponding to the theoretical monolayer, is probably due to the interaction of the vanadium dispersed on silica with TiO_2 clusters which are covering most of the silica surface. After the reduction at 773 K, the interaction of V^{3+} and reduced titanium oxide clusters probably affect the vanadium reoxidation mechanism, favoring the reoxidation of V^{3+} to V^{5+} when oxygen is adsorbed as O^{2-} or O_2^{2-} not observable by ESR.

The spectra obtained for V/2.0TiSi are similar to those obtained for V/1.5TiSi, except that the contribution of signal A is lower and reduction at 573 K eliminates completely the VO^{2+} signal from vanadium oxide clusters. This second difference indicates that the vanadium oxide clusters formed on better crystallized titanium oxide are more easily reduced, probably because there is a more important interaction between the two oxides. The samples containing titanium oxide clusters showed small Ti^{3+} signals after reduction at 773 K, being smallest in the case of V/2.0TiSi, probably because in crystalline TiO_2 part of the Ti^{3+} cations form diamagnetic Ti^{3+} pairs. These Ti^{3+} signals disappeared on contact with O_2 without the formation of VO^{2+} or O_2^- signals, indicating as in the previous case that the formation of diamagnetic oxygen species such as O^{2-} or O_2^{2-} is favored.

Effect of TiO$_2$ Content on the Catalytic Activity

The activity of the V/*x*TiSi catalysts became measurable already around 380 K. The variation of activity of the catalysts with reaction temperature is shown in Fig. 6. As the oxidation reaction is exothermic, a slight increase in the temperature of the catalyst bed (approximately 15 K for the highest conversion levels) is produced. Therefore temperatures reported in Fig. 6 are adiabatic temperatures. The results obtained with the catalysts supported on bare silica (V/Si) and pure titania (V/Ti) supports are also included for comparative purposes. Ethanol conversion increased with increasing temperature. As can be seen, the activities of V/Si and V/0.6TiSi were relatively similar, but the activity of the catalysts with higher titanium content was superior to that of V/Si. In general, the activity of the catalysts containing clustered titania approached that of the vanadium supported on pure titania; however, V/2.0TiSi showed a rather exceptional behavior, its activity exceeding that of the V/Ti sample. Considering the V/*x*TiSi catalysts, this surprising behavior cannot be explained in terms of surface area, because the specific surface area was very similar for all of them; however, the differences in surface area could contribute to the conversion differences between V/2.0TiSi and V/Ti. Within the 95% confidence interval, the values of apparent activation energy calculated for the low conversion range were similar for all V/*x*TiSi catalysts (54 ± 21, 46 ± 5, 59 ± 10, and 56 ± 5 kJ/mol for $x = 0.6$, 1.0, 1.5, and 2.0, respectively), and similar to that for V/Si (54 ± 7 kJ/mol).

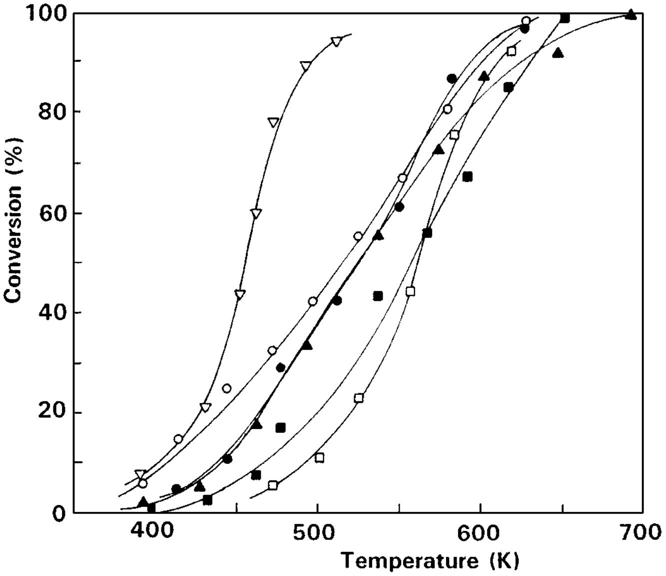

FIG. 6. Effect of catalyst support on the catalytic oxidation of ethanol on vanadia catalysts supported on: □, SiO$_2$; ■, 0.6TiSi; ▲, 1.0TiSi; ●, 1.5TiSi; ▽, 2.0TiSi; and ○, TiO$_2$. Experimental conditions are in the text.

Reaction Products and Their Distribution

In the conditions used, acetaldehyde (AcH) was the main product of ethanol oxidation on every catalyst. As no H_2 was detected among the products, the formation of AcH seems to proceed via the oxidative dehydrogenation of ethanol. Figure 7 shows the variation of selectivity to AcH as a function of the total conversion. The selectivity to AcH of V/*x*TiSi catalysts at a constant conversion level was affected by the titania content in a rather complex way, with V/0.6TiSi showing a higher selectivity than V/1.0TiSi. V/2.0TiSi showed an extremely high selectivity to AcH up to high conversion levels, thus giving rise to yields of AcH up to 72 mol%. The selectivity of V/Ti was high at low conversion levels, but decreased markedly above 20% conversion.

Additional information on the catalytic behavior can be obtained by analyzing the nature and distribution of the minor products: carbon oxides, acetic acid, ethene, and ethyl

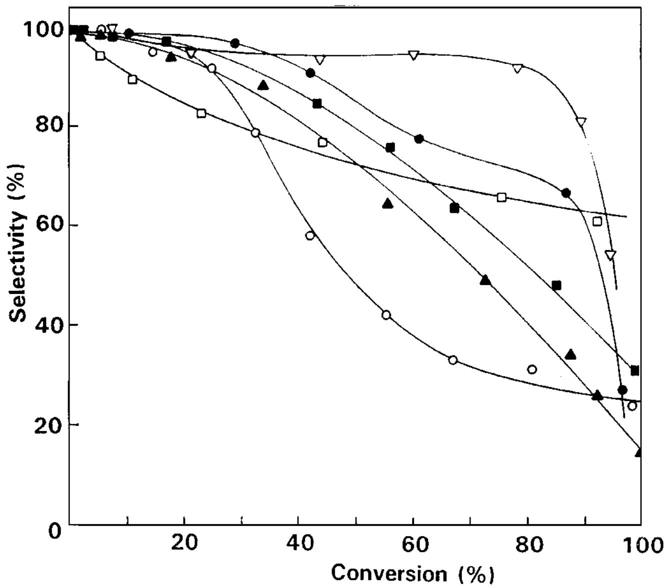

FIG. 7. Influence of catalyst support composition and total conversion on the selectivity to AcH. Symbols as in Fig. 6.

acetate. Diethyl ether and formic acid were also formed in some experiments (especially on V/Si), but as their yield never exceeded 1% nor their selectivity 2–3%, they will not be taken into account. In Fig. 8, the distribution of minor products over four representative catalysts (V/Si, V/Ti, V/1.0TiSi, and V/2.0TiSi) are shown as a function of ethanol conversion. The patterns with samples V/0.6TiSi and V/1.5TiSi were qualitatively similar to that of V/1.0TiSi.

Both carbon oxides were produced on every catalyst with their yields increasing with the conversion (and temperature). Carbon dioxide was usually detected at lower conversions but its yield increased with the temperature at a much lower rate than that of CO, which became detectable at higher conversions. Significant amounts of acetic acid were formed only on Ti-containing samples, especially on V/Ti (up to a 10 mol% yield; Fig. 8c). This indicates that, besides the higher activity, VTi showed another substantial difference with the VSi sample in the ability to oxidize the initially formed AcH to acetic acid. Besides, it may explain the lower selectivity to AcH in the medium conversion range observed with these catalysts, as compared to that of the V/Si counterpart. At variance with the Ti-containing catalysts, ethene was the main by-product on VSi at low conversions, indicating the presence of active centers for dehydration. Ethene was also detected among the products on V/*x*TiSi catalysts, but in much lower yields and at much higher conversions (the highest yield, less than 4%, was obtained at ca 90% conversion). Ethyl acetate was also detected among the products on every catalyst, but in much lower yields. Interestingly, it was detected even at

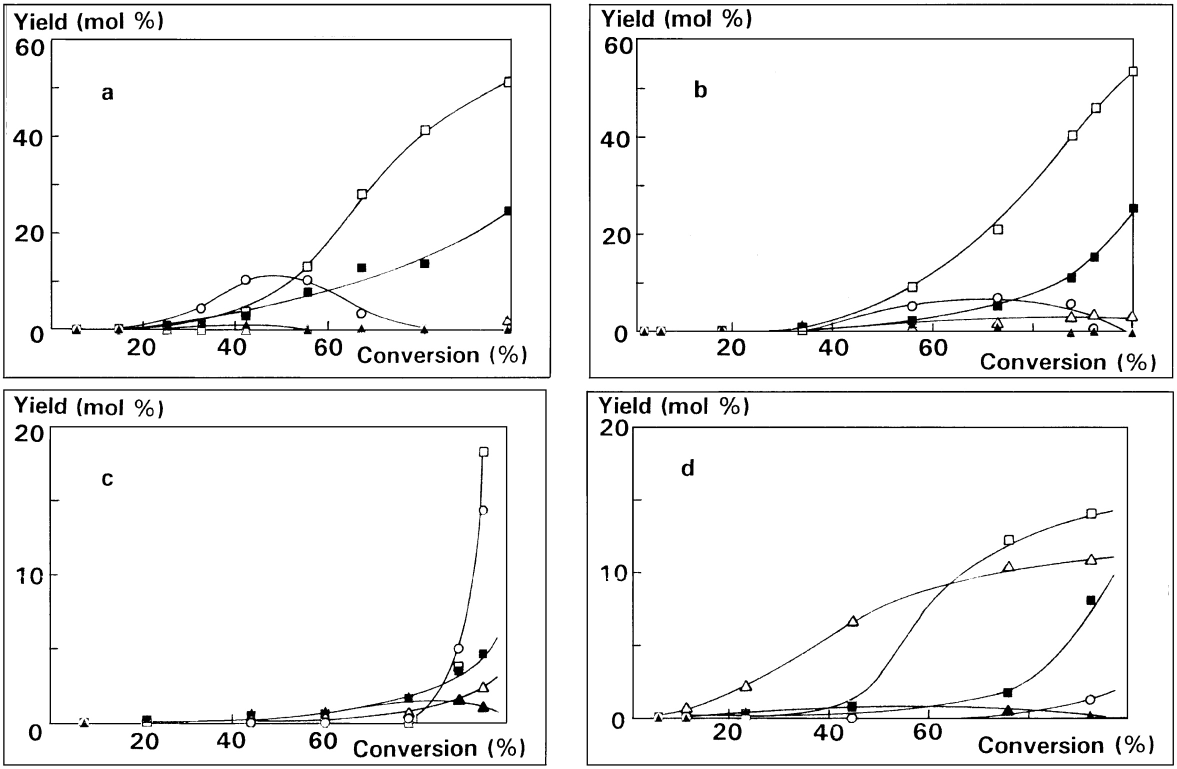

FIG. 8. Dependence of yields to minor products on ethanol conversion in the selective oxidation of ethanol on V/Ti (a), V/1.0TiSi (b), V/2.0TiSi (c), and V/Si (d). Symbols: □, CO; ■, CO_2; ○, acetic acid; ▲, ethyl acetate; and △, ethene.

temperatures and conversion levels where no acetic acid was detected among the products.

DISCUSSION

Surface Model

The results presented here show that the deposition of titania monolayers onto silica as a way to modify its properties as a catalyst support is a complex phenomenon in which the amount of added titanium plays an important role. Based on these results, a simplified model of the way increasing amounts of titania are deposited onto silica and how the nature of this deposit influences the later deposition of vanadia onto it may be proposed.

When small amounts of $TiCl_3$ are added to the stirred suspension of silica, titanium ions become bonded to the oxygen of silanol surface groups that hydrolyze the chloride. Consequently, titanium is highly dispersed at the silica surface (Fig. 9a), as already confirmed by quantitative XPS data (Fig. 3) and the ESR spectrum of sample 0.6TiSi (Fig. 4a). As the Ti content increases, the probability of Ti ions to be linked in small TiO_2 clusters on the silica surface (Fig. 9b) increases. This picture is supported by the monolayer-like dispersion found by XPS, as well as by the highly heterogeneous environment of Ti ions shown by ESR. ESR spectra of 1.0TiSi indicate that even in sample 1.0TiSi a substantial fraction of the silica surface remains uncovered. As a consequence, an increase of the surface area is produced by increasing its "roughness." At higher Ti content, the number and size of these clusters increases, partially covering the support surface as patches of defective TiO_2. The result is a decrease of the XPS-dispersion of titanium and the appearance of TiO_2 particles (Ti^{3+} signals in ESR spectra) in sample 1.5TiSi (Fig. 9c). This interpretation is in good agreement with the Raman results reported by Jehng and Wachs (34), who found that only surface TiO_2 species are formed on 3% TiO_2/SiO_2 samples, prepared from alkoxide precursors, while both dispersed TiO_2 and TiO_2 (anatase) particles were found in a sample with a much higher TiO_2 content (40%). Once enough titanium is used to reach a situation in which most of the silica surface is covered by three-dimensional arrangements of TiO_2, a further increase of added titanium to the silica suspension should lead to the completion of the hydrated Ti(III) oxide covering the silica surface and the formation after calcination of better crystallized TiO_2 (Figs. 9d and 9e), although those deposits will not be much thicker than the more defective deposits (see the small difference in titanium content between 1.5TiSi and 2.0TiSi).

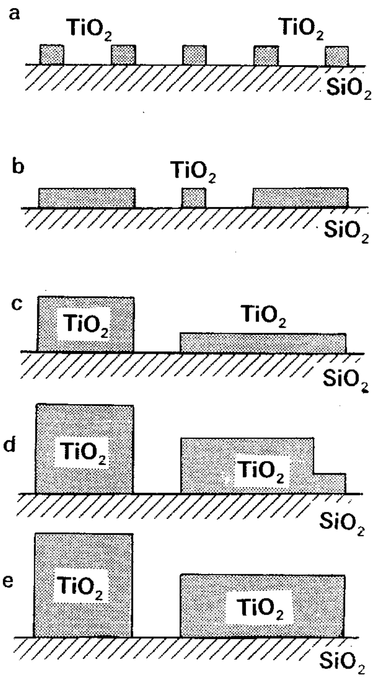

FIG. 9. Schematic model of the surface of supports as a function of Ti content: (a) 0.6TiSi; (b) 1.0TiSi; (c) 1.5TiSi; (d) 2.0TiSi precursor before washing; and (e) final state of 2.0TiSi support.

Reaction Pathway

Acetaldehyde formation over V/*x*TiSi catalysts proceeds through the oxidative dehydrogenation of ethanol. The formation of acetic acid should occur as a consecutive reaction by oxidation of the initially formed acetaldehyde. We found that the yield of acetic acid depended on the nature of the catalyst support. This means that the support may influence not only the dispersion of the supported vanadia but also its oxidizing power.

In our experimental conditions, little acetic acid was formed on the V/Si catalyst. Oyama *et al.* (11) reported a selectivity to acetic acid of ca 23% at ca 23% conversion during the oxidation of ethanol on a 9.8% V_2O_5/SiO_2 catalyst. The difference is probably due to the high vanadia loading of their sample, which will hinder the effects of vanadia–silica interactions, as well as to the use of water in their feed. In our case, the V/Ti catalyst produced a high amount of acetic acid, and it was also produced in significant amount on other Ti-containing catalysts. The surprising effect of the near absence of acetic acid among the products on the V/2.0TiSi catalyst until very high conversions can be explained by considering the reaction temperatures. In Fig. 10 the yields of acetic acid on VTi, V/1.0TiSi, and V/2.0TiSi catalysts as a function of reaction temperature are compared. As can be seen, acetic acid began to be detected in the products on both V/*x*TiSi catalysts at temperatures around 480 K and disappeared above 600 K, as can be observed also in the results of Oyama *et al.* (11). A similar effect when studying the oxidative dehydrogenation of ethanol on MoO_3/Al_2O_3 (35) and V_2O_5/Al_2O_3 catalysts (36) has been reported. In the latter case, it was found that the temperature at which acetic acid formation starts

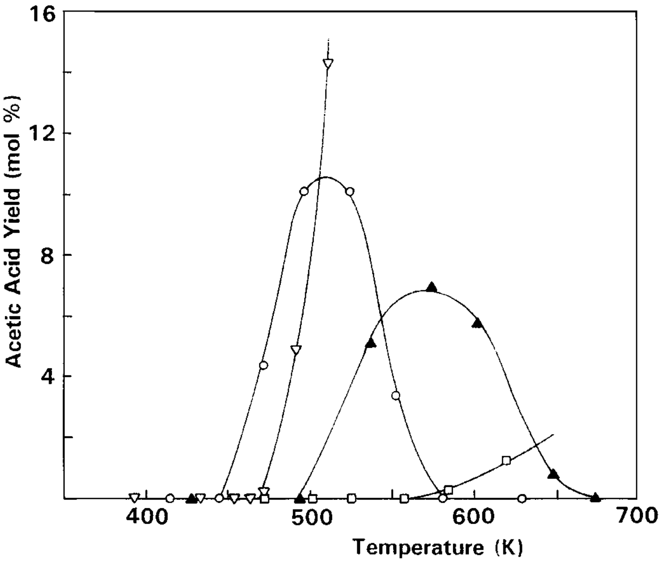

FIG. 10. Dependence of the yield of acetic acid on the reaction temperature. Experimental conditions are in the text.

is independent of space velocity. Thus, this seems to be a general phenomenon and can be related to the adsorption of the acetic acid. A possible interpretation is that, even if it is formed on the catalyst surface at lower temperatures, acetic acid is so strongly adsorbed that it cannot desorb at temperatures below 480 K.

At temperatures above 600 K, acetic acid probably either decomposes by decarboxylation or decarbonylation (as CO is the main combustion product) or it reacts further to form ethyl acetate. However, we did not observe an increase of ethyl acetate selectivity as the yield of acetic acid decreased, which points to its decomposition to carbon oxides. Furthermore, the ester was found among the products at conditions (reaction temperature and conversions), where no acetic acid was detected, which could indicate that the formation of ester proceeds by a way different from esterification of ethanol with the acid. Ethyl acetate can also be formed by condensation of acetaldehyde in the presence of aluminum ethoxide catalyst (Tischtschenko reaction) (37), or by oxidative condensation of acetaldehyde and the remaining alcohol, as has been reported over metallic palladium on active charcoal catalyst (Pd/C) (38) and over several transition metal oxides (39). As both *x*TiSi supports and V/*x*TiSi catalysts show rather strong Lewis acid sites in their surfaces (23, 24), the condensation of acetaldehyde seems to be the more probable route.

The formation of ethene on V/Si catalyst, even at low conversions, and the pattern of its yield with total conversion indicate that it was formed through a parallel route on this catalyst. Dehydration of alcohols is a characteristic reaction on acidic sites of transition metal oxides (40). Thus, ethene formation indicates the presence of acidic sites on the V/Si catalyst, which is corroborated by the formation of the highest quantities of diethyl ether observed on this sample. In contrast with Ti-containing samples, the very high BE value of the V $2p_{3/2}$ peak observed on fresh V/Si (see above) could be interpreted as due to V^{5+} cations coordinated to hydroxyl groups. These groups could be responsible for the higher acidity of this sample revealed by the dehydration of ethanol.

The much lower amounts of ethene found among the products on Ti-containing catalysts agree well with the results of Bond and Flamerz (10) on isopropanol decomposition on titania-supported vanadia. They found that, although both V_2O_5 and TiO_2 act principally as dehydration catalysts at 473 K, the latter is much more active than the former; V_2O_5/TiO_2 catalysts exhibit faster rates for dehydrogenation than for dehydration. Nakagawa *et al.* (41) reported that the rates of oxidation of isopropanol or ethanol in the absence or presence of gaseous oxygen over V_2O_5/TiO_2 catalysts containing below 11 wt% of V_2O_5 are similar to each other. As our V/*x*TiSi catalysts contain around 4–5 wt% of vanadia, one would expect to find a similar catalytic behavior, provided the vanadia phase is interacting mostly with the titania. This difference in the formation of ethene constitutes an additional proof of the preferential interaction TiO_2–V_2O_5 in V/*x*TiSi catalysts.

Summarizing, the oxidation of ethanol over V*x*TiSi catalysts proceeds through an initial oxidative dehydrogenation to acetaldehyde, followed by three consecutive parallel reactions: degradation by total oxidation to carbon oxides, acetaldehyde condensation to give ethyl acetate, and, depending on the temperature, oxidation to acetic acid.

Effect of TiO_2 Coating

An increase of *x* in the binary *x*TiSi supports prior to the deposit of vanadium oxide leads to a pronounced increase of the activity of the resulting catalysts, especially at low temperatures, and to changes in the distribution of the products. There is a general agreement in the literature that the active sites for ethanol oxidation on vanadia catalysts supported either on TiO_2 (41) or on SiO_2 (11) are surface V=O species and that the promoting effect of titania as a support comes from the effective dispersal of V_2O_5 on the titania surface, as well as the effect on the strength of these V=O bonds. Thus, the differences observed in the activity of the various V/*x*TiSi catalysts and with those of V/Ti and V/Si counterparts should be explained in terms of the variation of the interaction of the vanadia with the underlying support surface.

As stated above, surface areas of V/*x*TiSi catalysts are very close each other and they cannot account for the observed variation of activity. Moreover, the activity of the V/Ti sample, having a much lower surface area, was higher than most of the catalysts on mixed supports. A second factor to consider is vanadium dispersion. Quantitative XPS analysis of fresh samples showed that the V/(Ti + Si) atomic ratios of V/*x*TiSi catalysts increased with *x* in the range $x = 0.6$–2.0, but not in the same proportion as the vanadium content. The vanadium dispersion is not too different for V/Si, V/0.6TiSi, and V/2.0TiSi, but it is lower for V/1.0TiSi and V/1.5TiSi. V/Ti presented the highest value of the V/(Ti + Si) ratio, indicative of a high vanadium dispersion, despite showing the lowest surface area. Considering that vanadium cations are forming part of the active sites for ethanol conversion, different vanadium dispersion could explain differences in conversion, as is the case for V/1.0TiSi, V/1.5TiSi, and V/2.0TiSi catalysts. The only exception to this tendency is sample V/0.6TiSi, in which the vanadium dispersion is higher than on V/1.0TiSi, although its activity is lower. These observations and the increase of conversion with increasing titanium content suggest that differences in the nature and properties of the vanadium species induced by the nature of the support are also important in explaining catalyst performance.

Nakagawa *et al.* (30) reported that the rates of oxidation of ethanol in the presence of O_2 and of reduction by ethanol in its absence were similar over V_2O_5/TiO_2 catalysts, showing a direct correspondence between catalyst reducibility and activity for the oxidation of the alcohol. Thus, changes in the reduction properties may explain the increase of activity caused by the coating of silica with TiO_2. TPR results showed that the maximum reduction rate occurred at the same temperature for every V/*x*TiSi catalyst, practically equal to that for V/Ti and 25 K lower than for V/Si. Although these results cannot be directly related to catalytic activity because the measurements are carried out at higher temperatures, they indicate that interaction with TiO_2 causes a higher reducibility of vanadium than its interaction with silica.

This reducibility effect is corroborated by ESR results and may be explained by the nature of the titania and vanadia species in the catalysts as revealed by this technique. Vanadium in V/0.6TiSi is dispersed on the silica surface, where also titanium is present as very dispersed entities, as also indicated by XPS (Fig. 3), where the I_{Ti}/I_{Si} ratio measured for this sample is close to that corresponding to 100% dispersion. The vanadium dispersion in this sample is similar to that on V/Si and the reduction and reoxidation mechanisms (formation of $O_2^-{-}V^{5+}$ and stabilization of VO^{2+}) are also similar; the titanium incorporation does not affect the temperature needed to obtain 50% conversion, but favors the conversion at lower temperatures. In V/1.0TiSi there are patches of silica not covered by TiO_2, but very little of the silica surface remained uncovered for samples V/1.5TiSi and V/2.0TiSi, where V is mainly concentrated as vanadium oxide clusters on the TiO_2 aggregates and their surroundings.

The similar activity of V/1.0TiSi and V/1.5TiSi catalysts can be explained now, considering that both samples have most of the vanadium forming vanadium oxide clusters on poorly crystallized titania particles. This type of vanadium is reduced more easily than the vanadium dispersed on silica, as indicated by ESR. The better selectivity to acetaldehyde on V/1.5TiSi could be related to the absence of vanadium on silica that can give rise to O_2^- radicals that favor total oxidation. The main difference between 1.5TiSi and 2.0TiSi is the improved crystallinity of the latter, as shown by ESR. The better crystallinity of TiO_2 in V/2.0TiSi will favor titania–vanadia interactions able to facilitate the formation of vanadia layers that are more active for ethanol oxidation than the vanadium on less crystalline TiO_2, probably because of an easy vanadia reduction, in addition to the higher vanadium dispersion in V/2.0TiSi. Accordingly, the much higher activity of V/2.0TiSi, compared to that of V/1.5TiSi, seems to be due to the presence of these TiO_2 crystallites causing a higher V dispersion and a better V reducibility.

At low temperatures ethanol conversion on V/2.0TiSi was equivalent to that on V/Ti, as one should expect, taking into account the presence of crystalline TiO_2 in both samples. However, V/2.0TiSi became much more active above ca 450 K. This difference of activity seems to indicate that the nature of these small crystalline aggregates of TiO_2 is different from that of bulk titania. These differences should come from the genesis of these aggregates, different from that of bulk titania. They were formed by the deposition of a much higher amount of TiO_2 onto the silica surface, followed by removal of the outermost (and, hence, less influenced by silica) layers. Thus, silica probably acts as a template that directs the crystal habits of these aggregates, which may lead either to a preferential growth of some crystal planes or to a different proportion between the

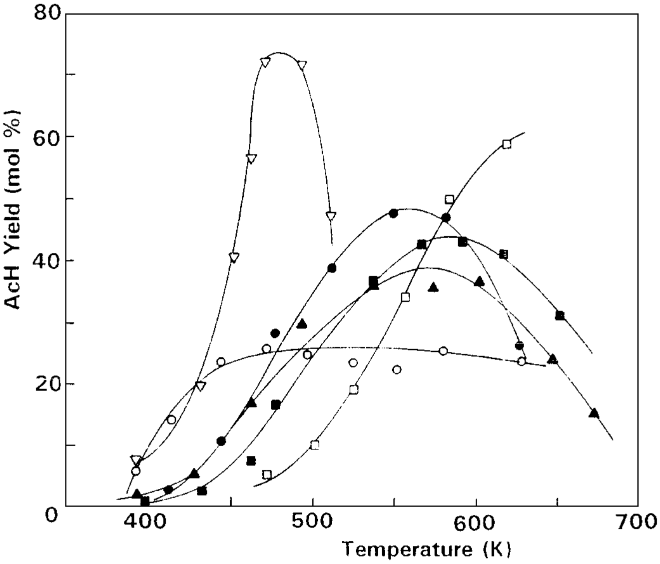

FIG. 11. Influence of catalyst composition and reaction temperature on the yield of acetaldehyde. Symbols as in Fig. 8.

rutile and anatase phases, or which affects the Ti–O bonds, thus influencing the interactions of these aggregates with the supported vanadia.

As a consequence, the use of a titanium content (ca 13 wt%) that is close to 1.5 ML, but prepared with an excess of titania precursor, allows the formation of crystalline TiO_2 particles with specific characteristics which through interactions with supported vanadium oxide modify the surface properties of the catalyst. This different interaction increases the catalyst activity and selectivity to AcH. The combination of these factors brings about a substantial increase of the acetaldehyde yield, compared to that on catalysts supported either on silica or titania, as can be observed in Fig. 11, reaching a value of 72 mol% at 473 K. To our knowledge this value is one of the highest reported in the open literature.

CONCLUSION

Nonporous SiO_2 microspheres have been coated by a thin layer of TiO_2 by using the homogeneous precipitation method from $TiCl_3$ (28). The resulting xTiSi supports, with x ranging between 0.6 and 2.0 ML, displayed different titanium distributions. At low content, titanium was deposited as a very dispersed TiO_2 species on the silica surface. As the content increased, it formed TiO_2 clusters, starting to cover the silica surface; for $x = 1.5$ ML the silica surface is covered by these clusters. The use of larger amounts of titanium in the suspensions did not lead to a significant increase of the titanium content, although it increased titania crystallinity after calcination. The incorporation of vanadium oxide onto xTiSi and the parent TiO_2 and SiO_2 carriers leads also to a different vanadium distribution. A high vanadium dispersion is observed for V/Si and V/0.6TiSi; in both cases vanadia is deposited with little clustering on the silica surface, affected by not too strong interactions with the dispersed titanium in 0.6TiSi. As titania content increased, vanadium was mainly concentrated on the TiO_2 particles forming vanadium oxide clusters, and the dispersion increased with the TiO_2 crystallinity.

The results confirm that incorporation of V_2O_5 onto xTiSi supports allows one to improve the catalyst performance, which makes vanadia supported on TiO_2-coated SiO_2 especially suited for selective oxydehydrogenation of ethanol to acetaldehyde. The use of a titanium content (13 wt%) close to 1.6 ML, but prepared with an excess of titania precursor, allows one to form crystalline particles of TiO_2 whose interaction with vanadium oxide increases substantially the catalyst activity and the selectivity to AcH. The combination of these factors brings about an important increase of the acetaldehyde yield, as well as a marked reduction of the reaction temperature, thereby permitting a molar yield of 72% per pass to be obtained at only 473 K in the experimental conditions used here. Further work is in progress in our laboratory in order to optimize these conditions for a better acetaldehyde yield.

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